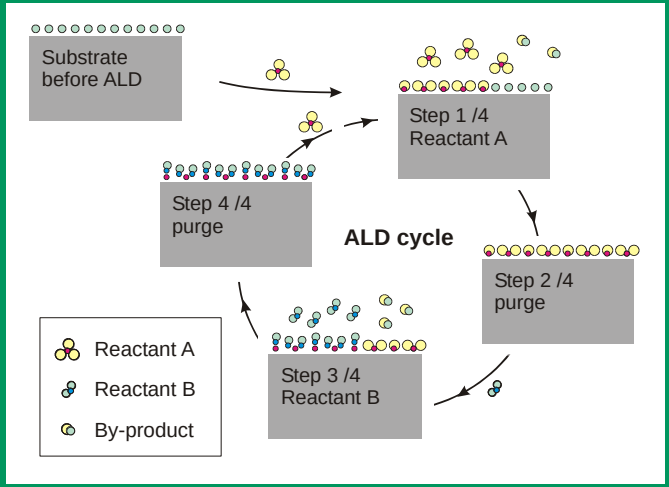


CHEM-E1130 Catalysis

Adsorption-controlled catalyst preparation by ALD

Aalto University
School of Chemical
Engineering

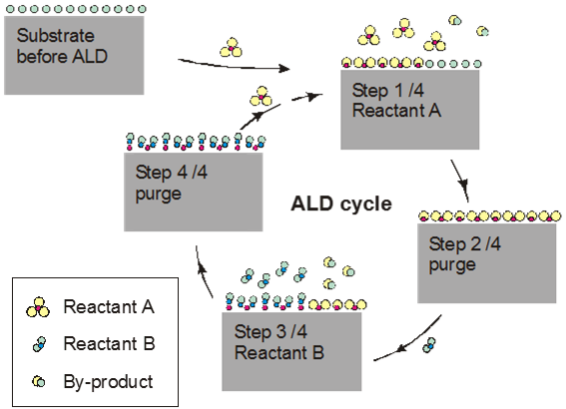
Prof. Riikka Puurunen

25.2.2019

Contents (+ 3 x Presemo)

1. **Introduction to atomic layer deposition (ALD)**
2. **Some words on the history of ALD**
3. **ALD for catalyst preparation**
   * 5 ways to control the metal loading
4. **Case: overcoats to slow down deactivation**
5. **Conclusion / Take-home message**

- **Bonus slides**



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Learning outcomes (modified)

After the course the students are able to:

1. give the definition of catalysis and describe concepts related to heterogeneous and homogeneous catalysts

2. explain steps and methods in catalyst preparation

3. describe and apply selected catalyst characterization methods

4. explain why and how catalysts deactivate and how catalyst deactivation can be postponed or prevented

5. give examples of where catalysts are applied

6. recognize challenges potentially solvable by catalytic reactions

Note, Prof. Puurunen, 7.1.2019: These learning outcomes have not yet been accepted for the course. Students are welcome to comment on these proposed learning outcomes. We will in practice follow these in the course in 2018-2019

Today's learning outcomes: After this lecture, you should…

- **Be able to describe the principles of atomic layer deposition (ALD)**
  - Principles same for catalyst and thin film preparation
- **Be aware of the (changing views on the) history of ALD**
- **Know five ways to control the loading of supported metal catalysts by ALD**
- **Be able to name some benefits and limitations of ALD for catalyst preparation**

Let’s go to Presemo

Go to:

http://presemo.aalto.fi/cheme1130lect5

http://presemo.aalto.fi/cheme1130lect5/screen

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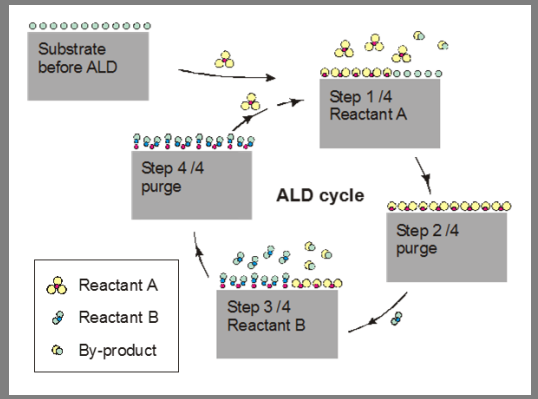
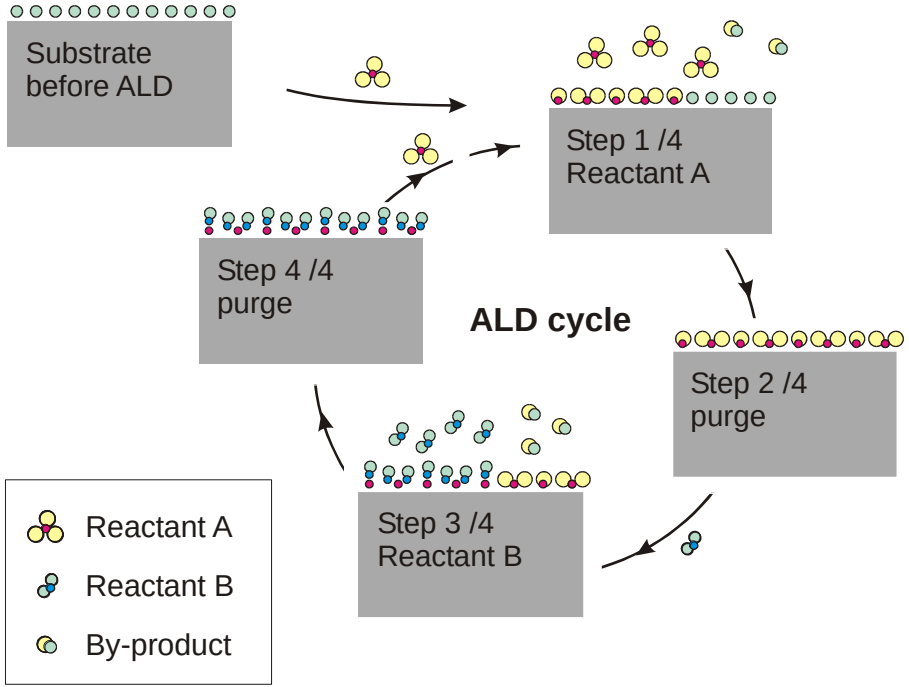


Introduction to ALD

ALD: chemical vapor deposition (CVD) method for (inorganic) thin films



"ALD can be defined as a film deposition technique that is based on the **sequential** use of **self-terminating gas–solid reactions**"*

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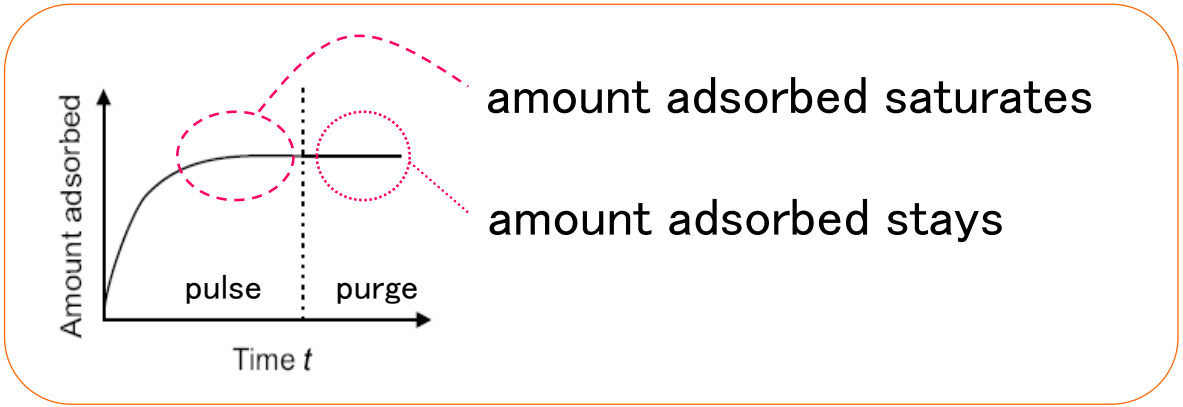
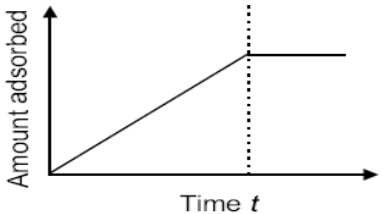
*R. L. Puurunen, " Surface chemistry of atomic layer deposition: a case study for the trimethylaluminum/water process", J. Appl. Phys. 97 (2005) 121301 1-52. http://dx.doi.org/10.1063/1.1940727
Open Access: http://www.vtt.fi/inf/julkaisut/muut/2010/Puurunen.pdf

Gas-solid reactions in ALD ideally self-terminating: saturating, irreversible*

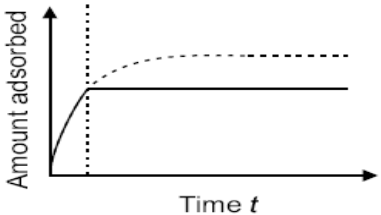


NO:

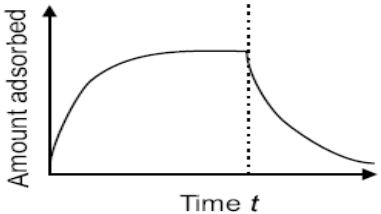
non−saturation



unsaturation



desorption

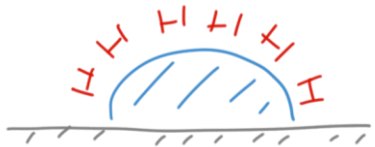


Puurunen, Appl. Phys. 97 (2005) 121301. https://doi.org/10.1063/1.1940727

*chemisorption

Chemisorption

- chemically specific
- changes in electronic state
- reversible/irreversible
- chemisorption energy as for a chemical reaction (exothermic/endothermic)
- may involve an activation energy
- for “large” activation energies (“activated adsorption”), true equilibrium may be achieved slowly
- **monolayer adsorption**



Physisorption

- non-specific
- minimal electronic interaction
- reversible
- adsorption energy exothermic and (higher or) similar to the energy of condensation
- non-activated
- equilibrium established
- chemical nature of the adsorbate & adsorbent ~not altered
- **multilayers may form**

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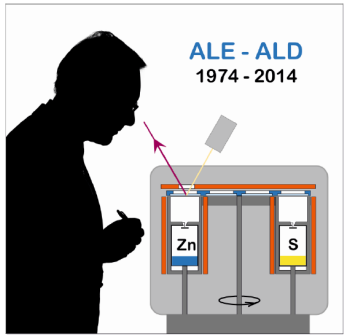
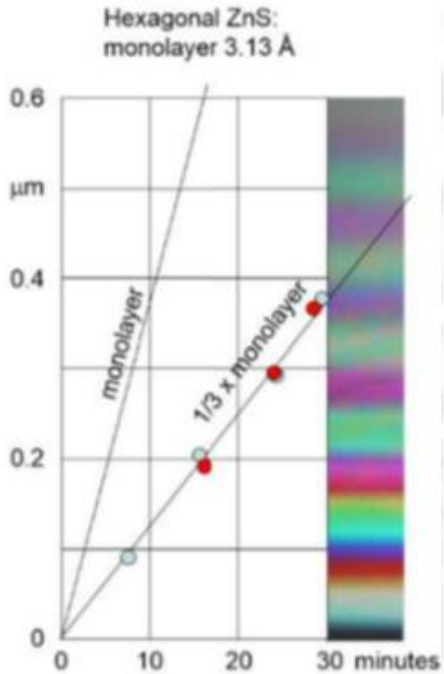
http://old.iupac.org/reports/2001/colloid_2001/manual_of_s_and_t/node16.html

Summary slide wording slightly updatedin 2019/Puurunen

Film grows ~linearily with cycles



FinALD40 exhibition



Growth Per Cycle can vary in the beginning

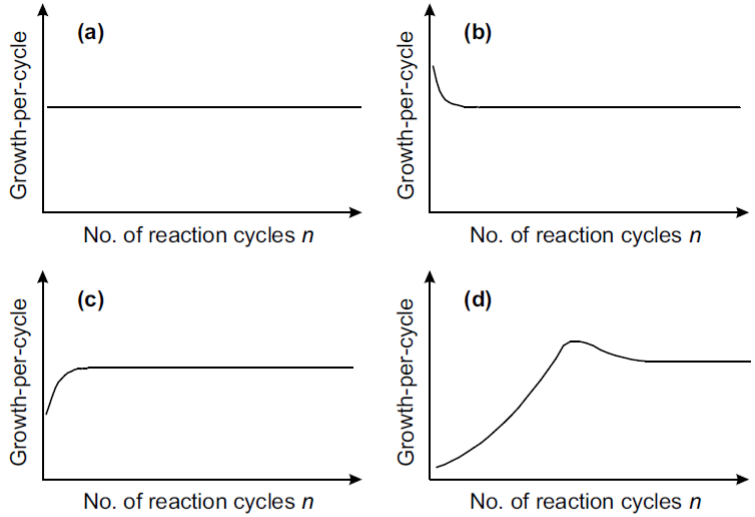
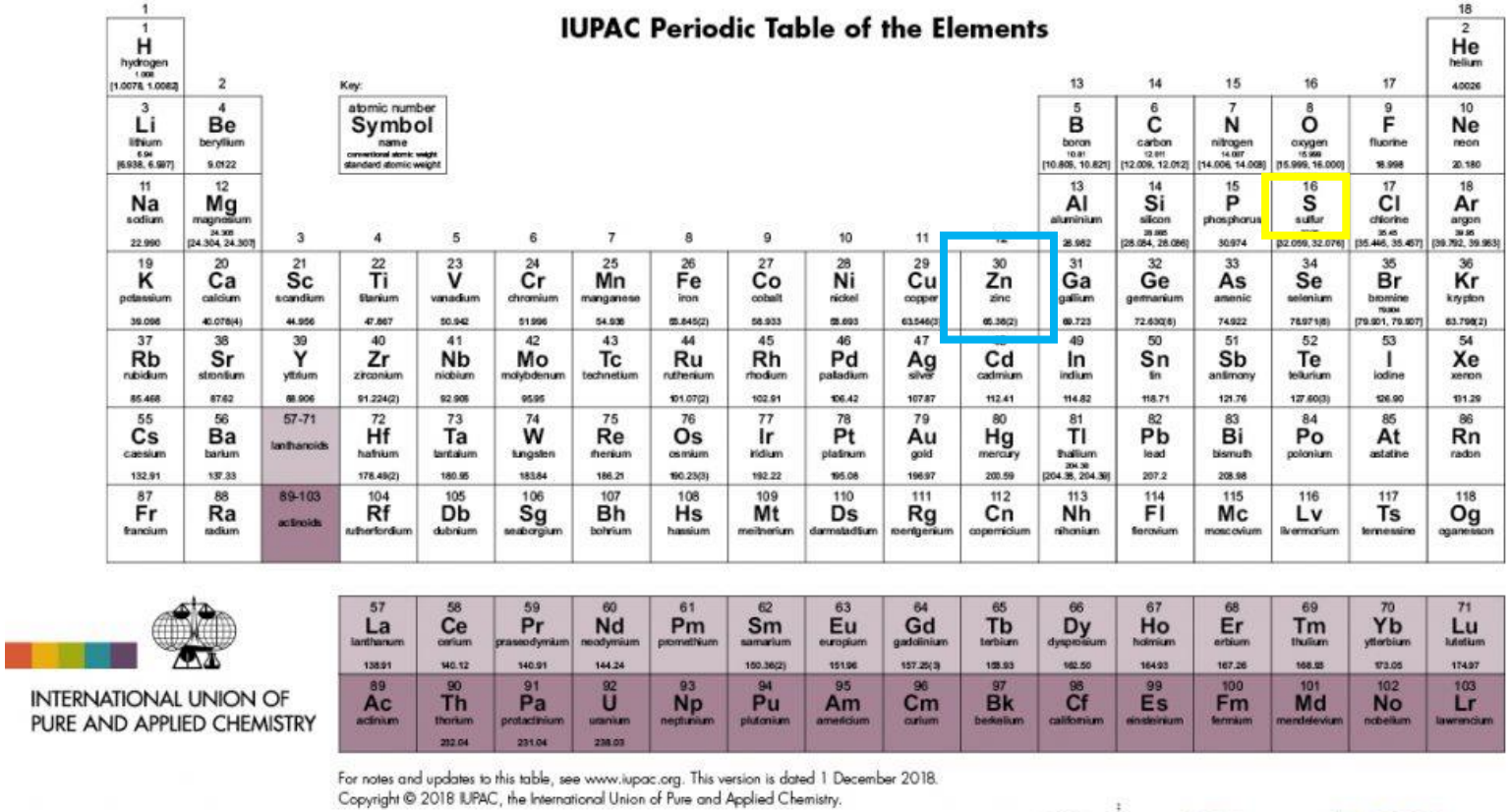


Figure 15: Dependency of the GPC on the number of reaction cycles in different types of ALD processes:[247] (a) linear growth, (b) substrate-enhanced growth, (c) substrate-inhibited growth of Type 1, and (d) substrate-inhibited growth of Type 2.

- Puurunen, " A Short History of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy", Chem. Vap. Deposition 20 (2014) 332-344. http://dx.doi.org/10.1002/cvde.201402012 (open access)
- Puurunen, J. Appl. Phys. 97 (2005) 121301. https://doi.org/10.1063/1.1940727

Tuomo Suntola in 1974 (except that the Periodic Table is from 2019)

R. L. Puurunen, ” A Short History of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy”, Chem. Vap. Deposition 20 (2014) 332-344. http://dx.doi.org/10.1002/cvde.201402012 (open access)



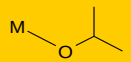
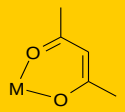
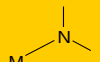
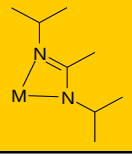
Source: https://iupac.org/what-we-do/periodic-table-of-elements/ , accessed 12.1.2019

United Nations Educational, Scientific and Cultural Organization

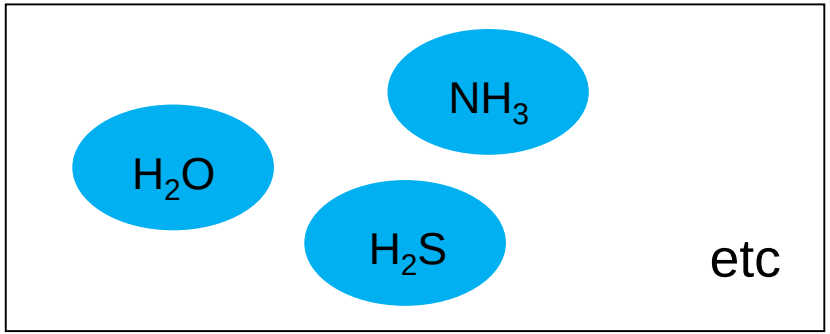
2019 IYPT International Year of the Periodic Table of Chemical Elements

IUPAC

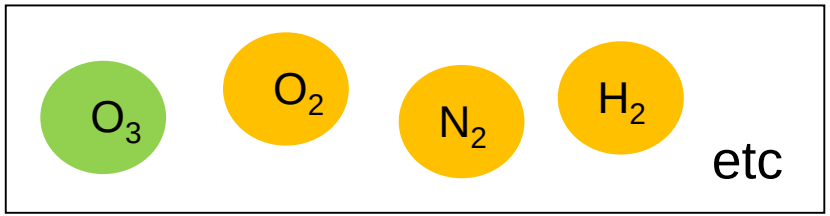
Overview of the different reactant/precursor classes

Class		Metal precursor type
Inorganic		Elements
		Halides
Metal-organic	Organo-metallic	Alkyls
		Cyclopentadienyls
		Alkoxides 
		β-diketonates 
		Alkylamides and silylamides 
		Amidinates 
		…

Non-metal precursors, “thermal” ALD



Energy-enhanced ALD



Puurunen, Appl. Phys. 97 (2005) 121301. https://doi.org/10.1063/1.1940727
Miikkulainen, Leskelä, Ritala, Puurunen, J. Appl. Phys. 113 (2013) 021301. http://dx.doi.org/10.1063/1.4757907.

Examples of ALD processes

Metal reactant	Non-metal reactant	Product	By-product

$Zn\ (g) + S\ (g) \rightarrow \mathbf{ZnS\ (s)}$ **Suntola 1974 →**

$2\ Me_3Al\ (g) + 3\ H_2O\ (g) \rightarrow \mathbf{Al_2O_3\ (s)} + 6\ CH_4\ (g)$ *

$3\ TiCl_4\ (g) + 4\ NH_3\ (g) \rightarrow \mathbf{3\ TiN\ (s)} + 12\ HCl\ (g) + 0.5\ N_2\ (g)$ (?)

$2\ Me_3Pt(CpMe)\ (g) + 26\ O_2\ (g) \rightarrow \mathbf{2\ Pt\ (s)} + 18\ CO_2\ (g)$ (?) $+ 16\ H_2O\ (g)$

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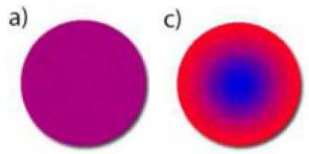
*** "prototypical ALD process"** → R. L. Puurunen, " Surface chemistry of atomic layer deposition: a case study for the trimethylaluminum/water process" J. Appl. Phys. 97 (2005) 121301. → http://dx.doi.org/10.1063/1.4757907 open access pdf → S. M. George, Chem. Rev. 2010 http://dx.doi.org/10.1021/cr900056b https://www.slideshare.net/RiikkaPuurunen/presentation-at-ald-2016-by-puurunen-comparison-of-al2o3-chemistry-interpretations-final-20160723

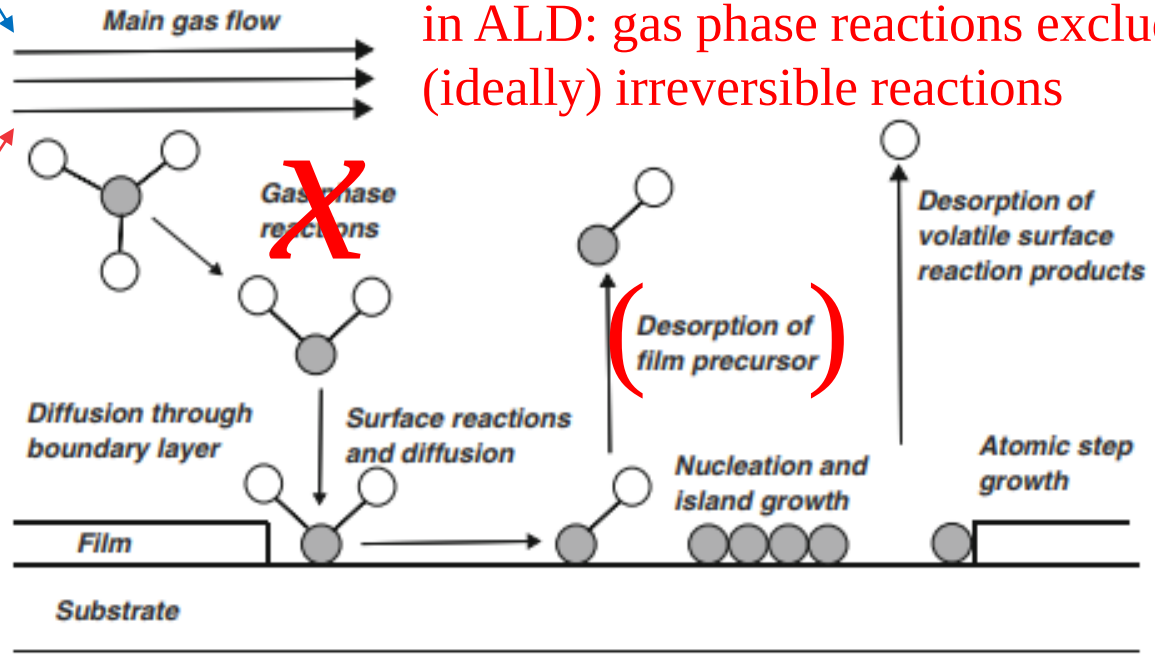
CVD, chemical vapor deposition



Expected metal distribution
a) homogeneous, ALD
c) egg-shell, CVD
https://dx.doi.org/10.1021/cr500486u

CVD: continuous flow

Fig. 1 Schematic summary of the most important chemical reactions involved in thin film synthesis by CVD, after [41]. It should be noted that not all types of chemical reactions are desired in all types of CVD processes



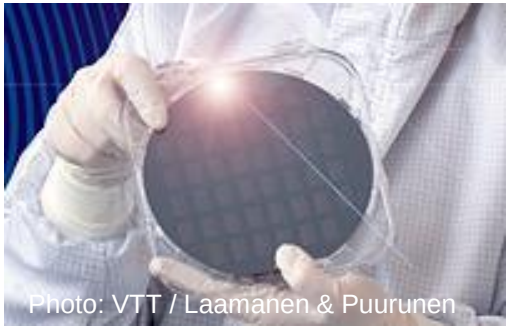
in ALD: gas phase reactions excluded, (ideally) irreversible reactions

ALD: separate pulsing of reactant vapors

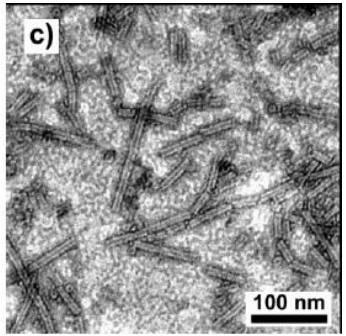
Image: Pedersen, H. & Elliott, S.D. Theor Chem Acc 133 (2014) 1476. https://doi.org/10.1007/s00214-014-1476-7

Any shape can in principle be coated…

Planar wafers; Si, Ge, glass, …



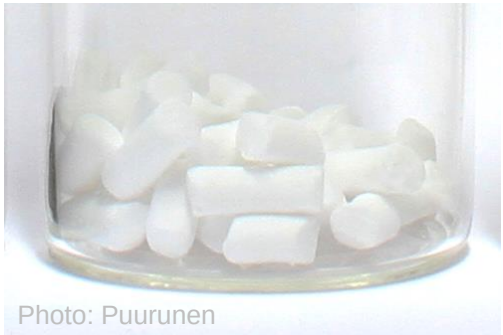
Biological macromolecules



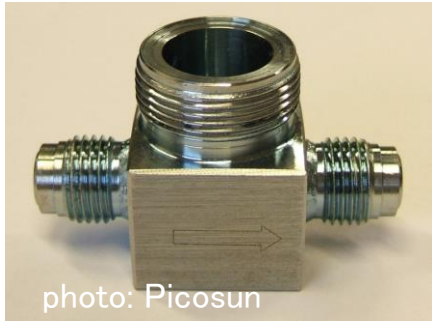
Tobacco mosaic virus→ double-walled nanotubes by ALD
Knez et al., Nano Lett. 6 (2006) 1172

etc.

High-area catalyst supports

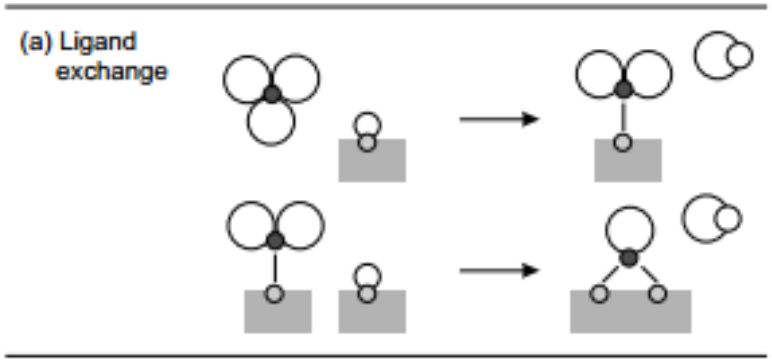


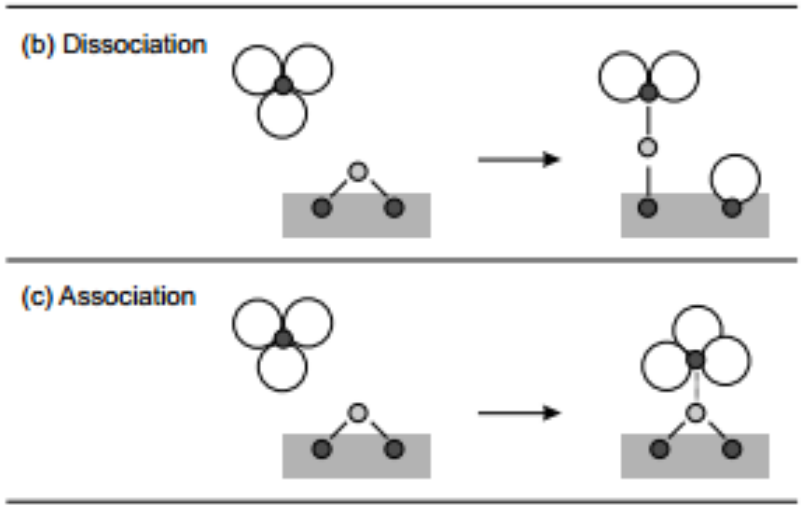
Macroscopic 3D objects



Dedicated test structures

… as long as the surface has suitable reactive sites





Typical for ligand exchange:

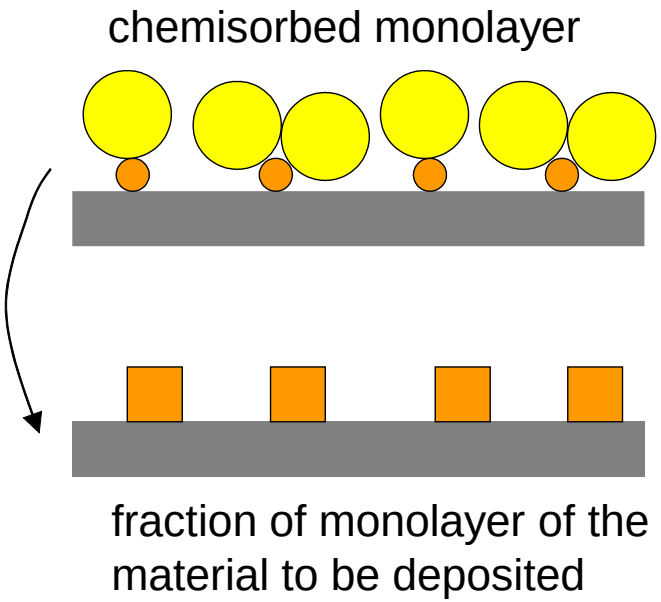
-OH -NH -SH

Also –O– and sometimes other groups

Puurunen, Appl. Phys. 97 (2005) 121301. https://doi.org/10.1063/1.1940727

Growth per cycle (GPC) in ALD typically small fraction of a monolayer (ML)

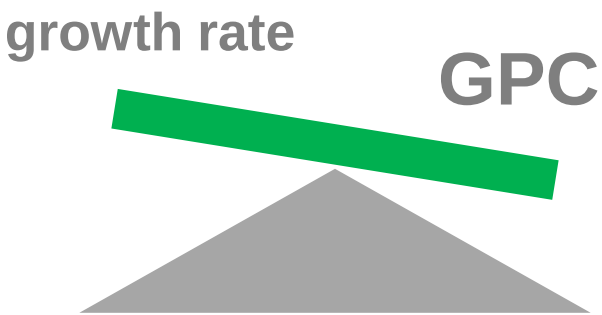
- **By definition (IUPAC, adsorption), a chemisorbed monolayer forms in an ALD reaction**
- **This converts to less than a monolayer of the material to be deposited, typically ~5-50% of ML**
- **Many ways to estimate a monolayer thickness (e.g. density)**



Puurunen, J. Appl. Phys. 97 (2005) 121301. https://doi.org/10.1063/1.1940727

Note: evolving nomenclature!
GPC (growth per cycle) vs growth rate

- Both terms can be encountered in scientific literature, >50% GPC
- More on the topic:
  - http://aldhistory.blogspot.fi/2016/10/term-growth-per-cycle-gpc-gaining-use.html
  - https://www.atomiclimits.com/2019/02/12/atomic-layer-deposition-process-development-10-steps-to-successfully-develop-optimize-and-characterize-ald-recipes/



No growth/island growth if no/little reactive sites

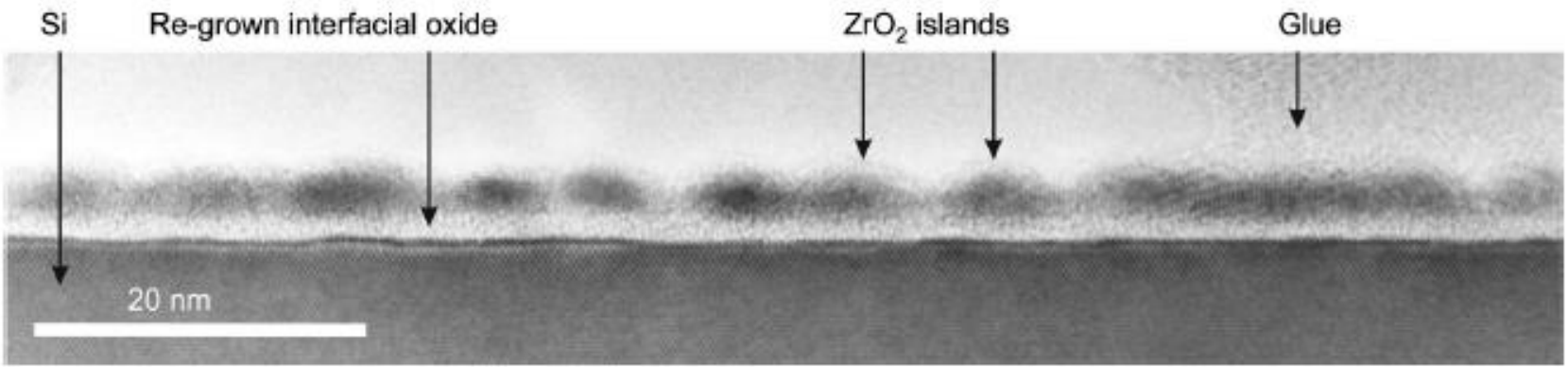


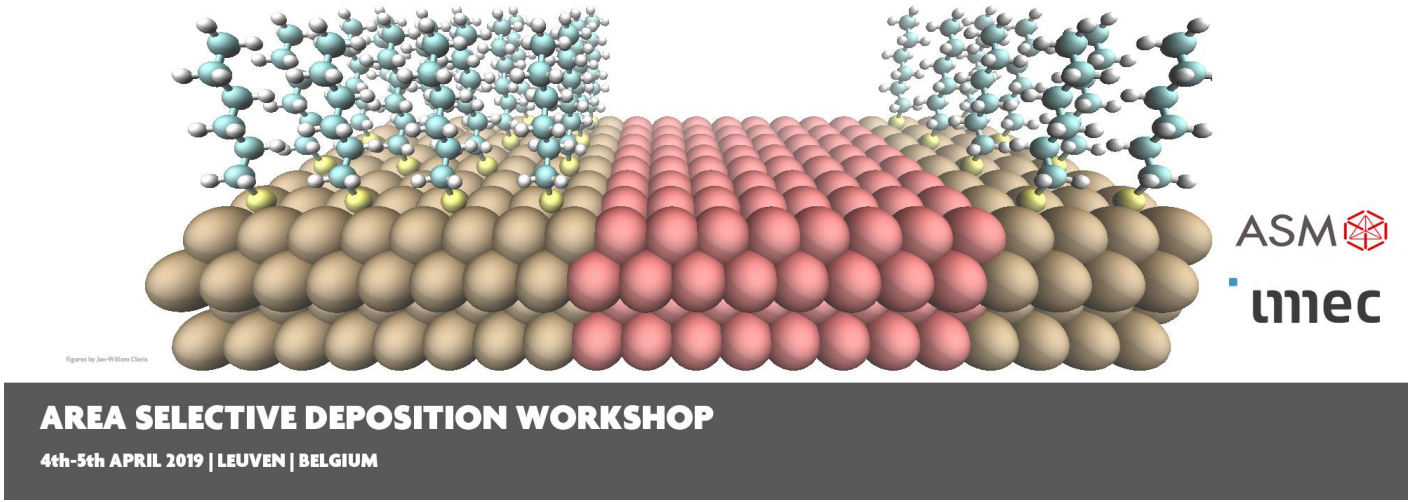
FIG. 8. Cross-sectional TEM image for ZrO_2 deposited in 60 $ZrCl_4/H_2O$ cycles at 300 °C on hydrogen-terminated silicon, pretreated with H_2O at 300 °C for 5 min. Reoxidation of the silicon substrate has taken place due to exposure to ambient air.

→ Possibility for area-selective ALD

Puurunen et al., J. Appl. Phys. 96 (2004) 4878. http://dx.doi.org/10.1063/1.1787624

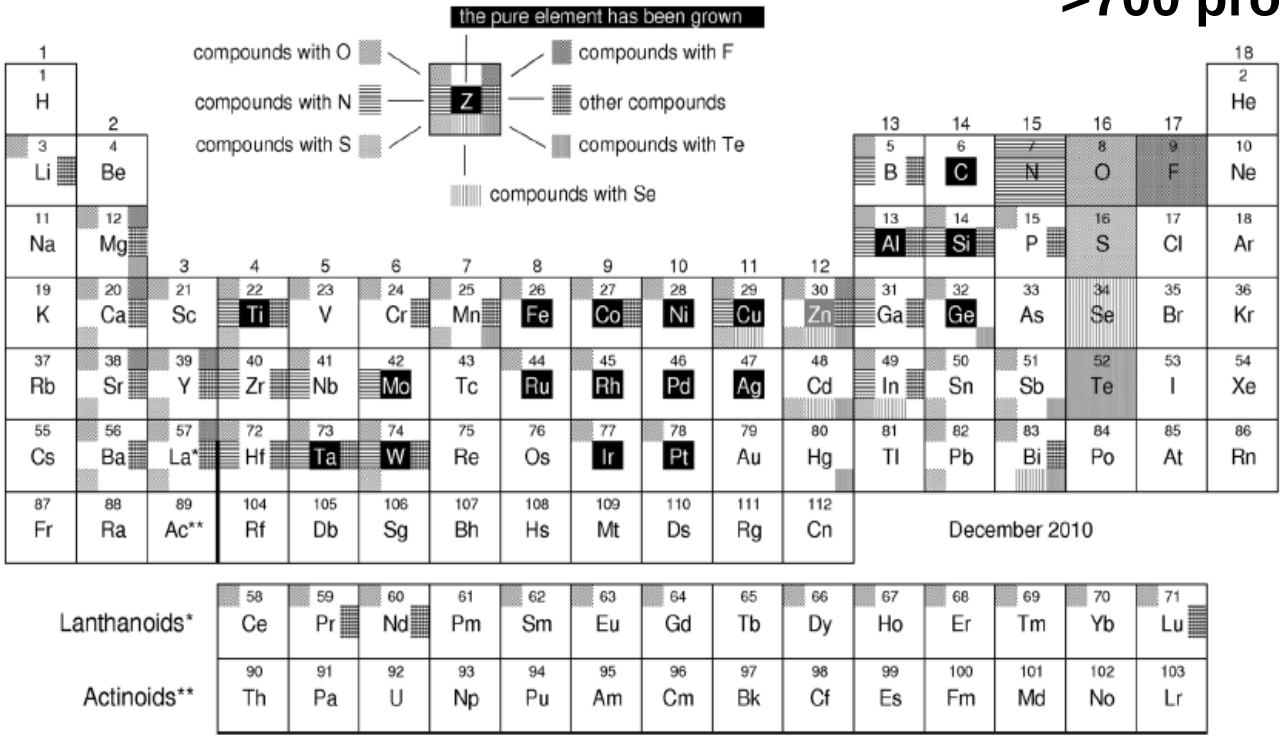
Area-selective ALD: a growing field

- https://www.asd2019-workshop.org/



Status of two-reactant ALD process research (end 2010)

>700 processes



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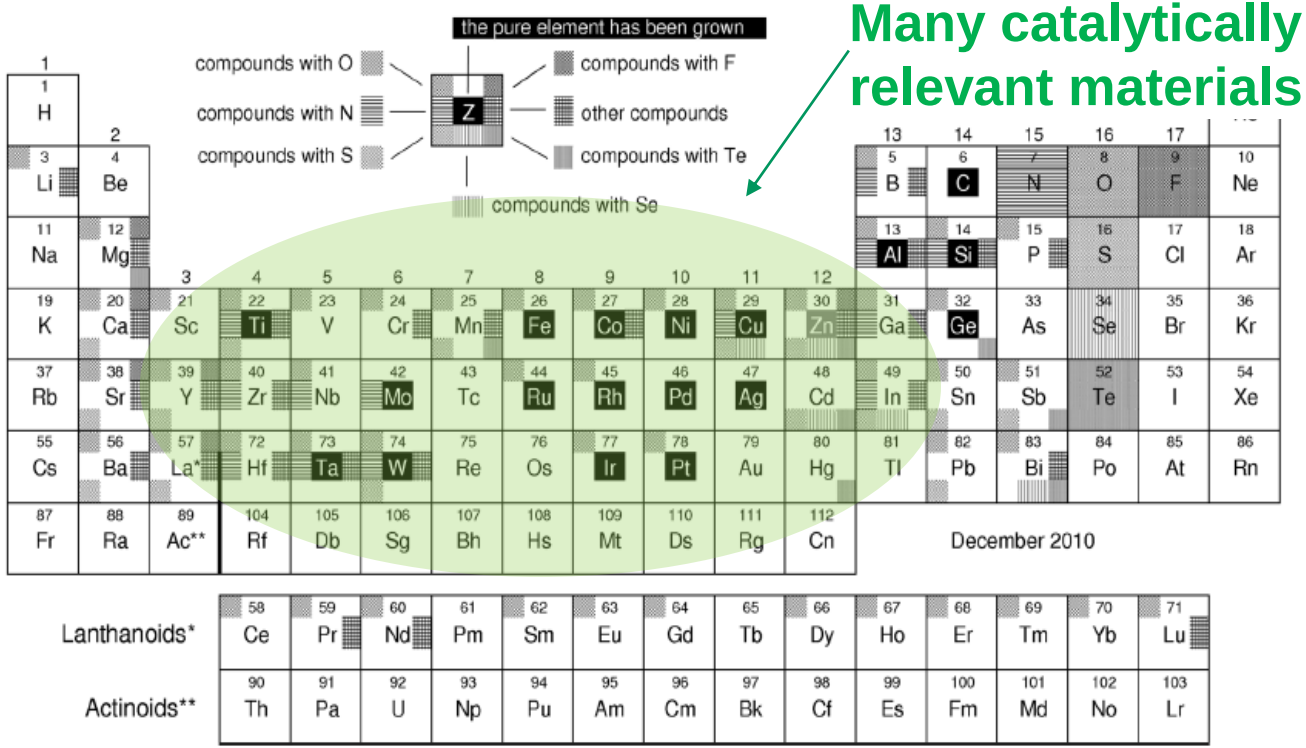
Miikkulainen, Leskelä, Ritala, Puurunen (review), J. Appl. Phys. 113 (2013) 021301.
http://dx.doi.org/10.1063/1.4757907. open access pdf. >2000 references

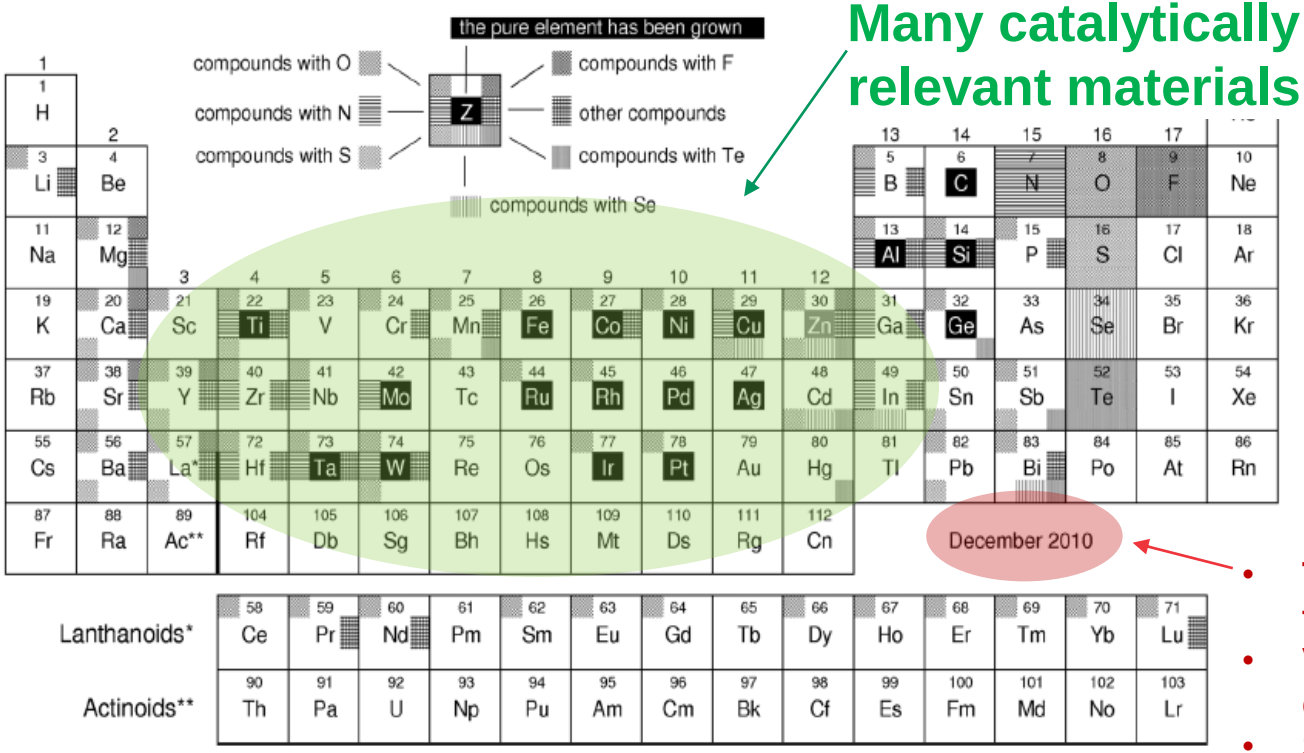
Status of two-reactant ALD process research (end 2010)

Many catalytically relevant materials made



Miikkulainen, Leskelä, Ritala, Puurunen (review), J. Appl. Phys. 113 (2013) 021301. http://dx.doi.org/10.1063/1.4757907. open access pdf. >2000 references

Status of two-reactant ALD process research (end 2010)



Many catalytically relevant materials made

- **Time to update the table?**
- **Voluntary-based collaboration?**
- **Some online system to develop?**

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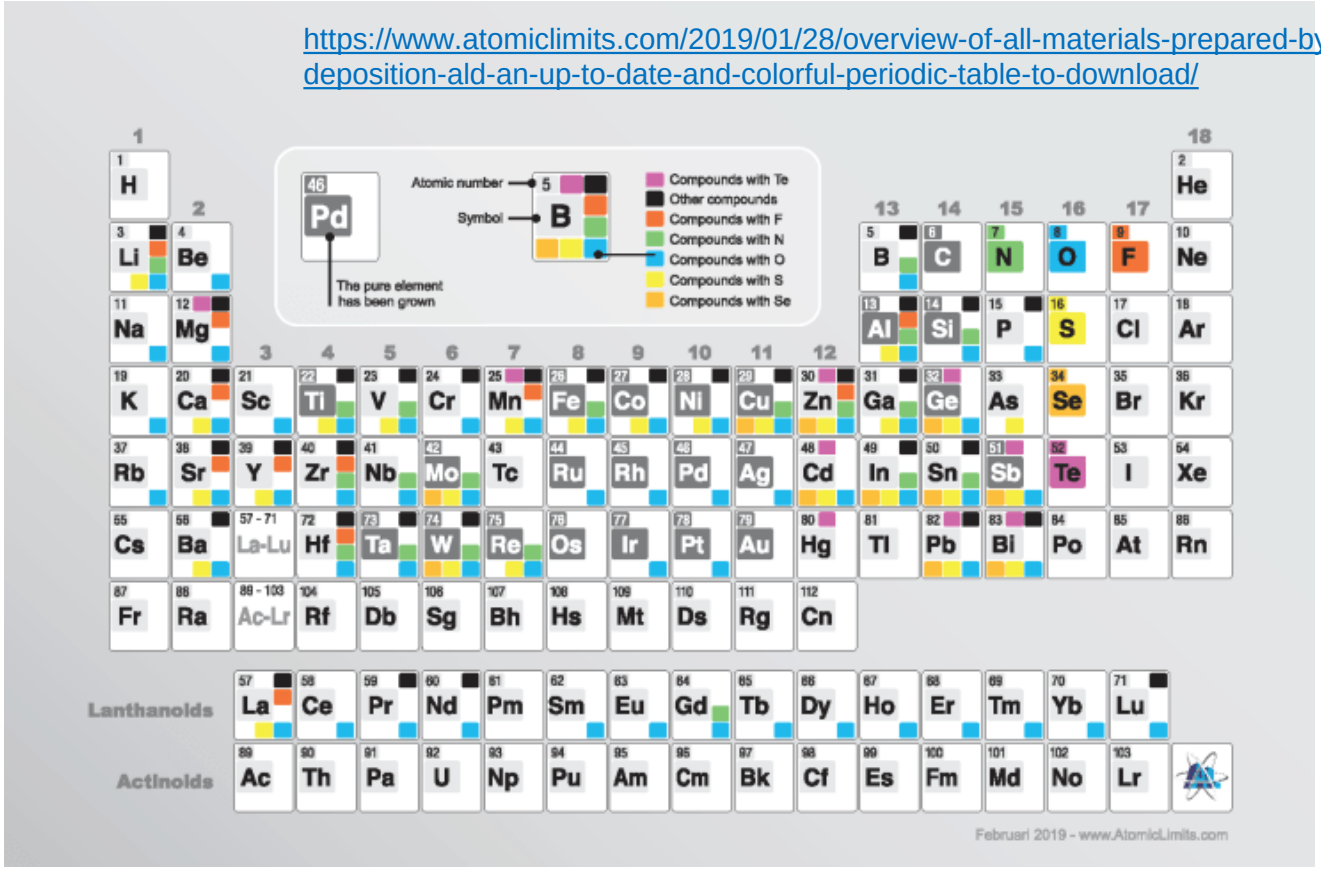
Miikkulainen, Leskelä, Ritala, Puurunen (review), J. Appl. Phys. 113 (2013) 021301. http://dx.doi.org/10.1063/1.4757907. open access pdf. >2000 references

Atomic Limits version

https://www.atomiclimits.com/2019/01/28/overview-of-all-materials-prepared-by-atomic-layer-deposition-ald-an-up-to-date-and-colorful-periodic-table-to-download/



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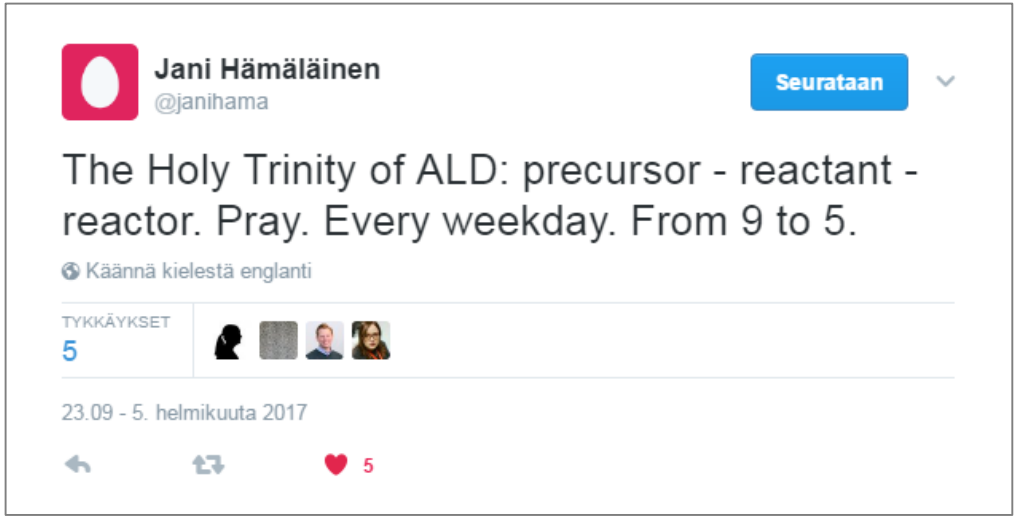
Updates info from published version with tabulated references (nicknamed ”mammoth table”):

- Puurunen, J. Appl. Phys. 97 (2005) 121301 1-52. http://dx.doi.org/10.1063/1.1940727,
- Miikkulainen, Leskelä, Ritala, Puurunen, J. Appl. Phys. 113 (2013) 021301. http://dx.doi.org/10.1063/1.4757907.

ALD process development active worldwide.

* One view related to developing new ALD processes ☺



- https://twitter.com/janihama/status/828500958745337856

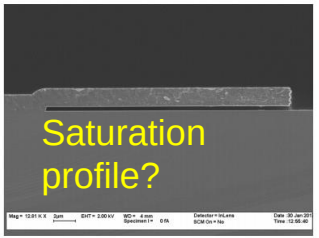
- **Nature often surprises**
- **… and that is why ALD keeps on being interesting**

ALD in Twitter: #ALDep

Caution! Not all processes reported as ALD actually fulfil requirements 100%

- **Many of the reported for planar films actually may contain a CVD contribution which will result in severe decomposition at long reaction times needed for catalyst preparation**
  → uniform distribution may not achievable

- **Challenge: we often cannot know without experiments the quality of a process published in a scientific article**
  → thin-film conformality investigations may help?



Miikkulainen, Leskelä, Ritala, Puurunen (review), J. Appl. Phys. 113 (2013) 021301. http://dx.doi.org/10.1063/1.4757907. open access pdf.

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Virtual Project on the History of ALD

VPHA, vph-ald.com: *Worldwide collaborative effort, in an atmosphere of openness, respect and trust*

Some words on the history of ALD

Conclusion: two independent roots of ALD

(Riikka's own current personal view)

Invited tutorial at ALD 2014

Atomic Layer Epitaxy (ALE)

- Initiated in industry,
  - originally for EL displays,
  - by people with semiconductor physics background
- Directed to industrial use of the ALD
- Very secret in the beginning, only patent publications
- Commercial reactors triggered worldwide ALD activity in 1990s

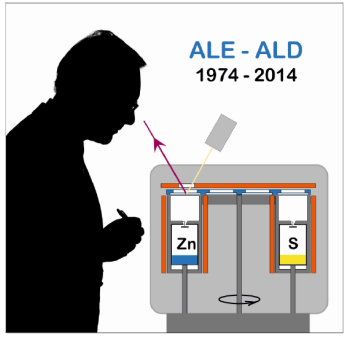
Molecular Layering (ML)

- Initiated in academia,
  - for broad goals,
  - by people with chemistry background
- Key: understanding ways of modifying solids
- Partly secret in the beginning, broad variety of publications
- Rich history in ALD, details being unraveled in VPHA

https://www.slideshare.net/RiikkaPuurunen/aldhistory-tutorial-in-kyoyo-al-dhistory-tutorialald2014riikkapuurunen20140615

Some history – ALD in Finland

- **Tuomo Suntola, 1974:**
  ALE-ALD for ZnS for electroluminescence
  → thin film display production since 1985 in Espoo, Finland
- **ALD for catalysis in Finland, Microchemistry since end 1980s**
- **…**



FinALD40 exhibition

”40 years of ALD in Finland: Photos, Stories”: http://www.aldcoe.fi/events/finald40.html
R. L. Puurunen, A Short History of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy, Chemical Vapor Deposition 20 (2014) 332-344. http://dx.doi.org/10.1002/cvde.201402012. Open Access.

ALD (ML) also created in the Soviet Union – already in the 1960s

Molecular Layering, sometimes other names

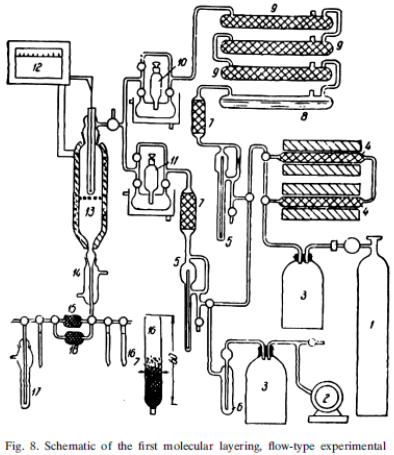
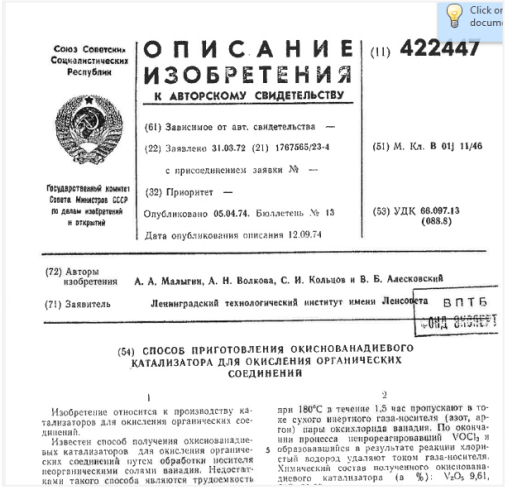


Fig. 8. Schematic of the first molecular layering, flow-type experimental setup by S. I. Kol'tsov. Where 1 is the nitrogen tank; 2 is the blower; 3 is the buffer vessel; 4 is the oven with absorber for separating nitrogen from oxygen impurities; 5 is the rheometer; 6 is the CO_2 absorber; 7,8,9 are H_2O absorbers (silica gel, concentrated sulfuric acid, phosphorus pentoxide); 10,11- are boats with CCl_4 and H_2O; 12 is the regulating potentiometer; 13 is the quartz reactor; 14 is the refrigerator; and 15 to 18 are absorbers (granulated zinc powder, alkali silica gel, solution of barium hydroxide, granulated antimony sulfide). Reproduced with permission.[43] Copyright 1971, LTI by Lensovet.



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Государственный комитет Совета Министров СССР по делам изобретений и открытий

ОПИСАНИЕ ИЗОБРЕТЕНИЯ К АВТОРСКОМУ СВИДЕТЕЛЬСТВУ

(11) 422447

(61) Зависимое от авт. свидетельства —

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ВПТБ

(54) СПОСОБ ПРИГОТОВЛЕНИЯ ОКИСНОВАНАДИЕВОГО КАТАЛИЗАТОРА ДЛЯ ОКИСЛЕНИЯ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ

1

Изобретение относится к производству катализаторов для окисления органических соединений.

Известен способ получения окисноваиадиевых катализаторов для окисления органических соединений путем обработки носителя неорганическими солями ванадия. Недостатками такого способа являются трудоемкость

2

при 180°С в течение 1,5 час пропускают в тоже сухого инертного газа-носителя (азот, аргон) пары оксихлорида ванадия. По окончании процесса непрореагировавший $VOCl_3$ и образовавшийся в результате реакции хлористый водород удаляют током газа-носителя. Химический состав полученного окисноваиадиевого катализатора (в %): V_2O_5 9,61,

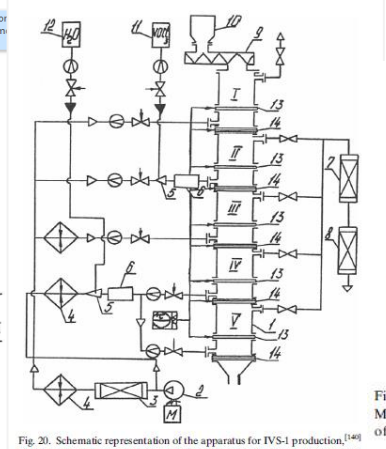


Fig. 20. Schematic representation of the apparatus for IVS-1 production.[140] 1) ML reactor; 2) blower; 3) dehumidifier; 4) heater; 5) spray gun; 6) mixer; 7, 8) absorbers; 9) feeder; 10,11,12) tanks with silica gel, vanadium oxochloride and water; 13) gas distribution device; 14) isolating assembly. Reproduced with permission.[140] Copyright 1987, LTI by Lensovet.

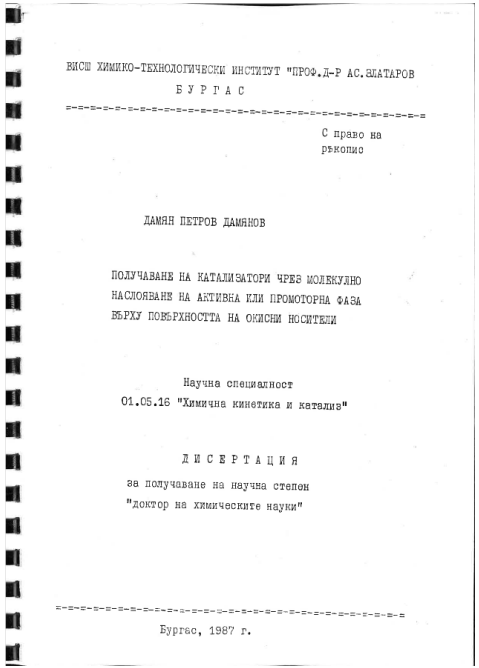
Fig. 22. The first experiments on the column flow unit (1982) (right – A. A. Malygin). Photograph from Malygin's collections; published with permission of Anatoly Malygin (private collection).

USSR author's invention for ALD catalysts: 1972

Aalto University School of Chemical Engineering

- Review article (62 authors): "Recommended reading list of early publications on atomic layer deposition—Outcome of the "Virtual Project on the History of ALD"", JVSTA 35 (2017) 010801 (13 pages). http://dx.doi.org/10.1116/1.4971389. Open access.
- Malygin et al., "From V. B. Aleskovskii's "Framework" Hypothesis to the Method of Molecular Layering/Atomic Layer Deposition" Chem. Vap. Deposition 21 (2015) 216-240. doi: 10.1002/cvde.201502013

Catalysis-ALD activity also in Bulgaria in the 1970s



ВИСШ ХИМИКО-ТЕХНОЛОГИЧЕСКИ ИНСТИТУТ "ПРОФ.Д-Р АС.ЗЛАТАРОВ
Б У Р Г А С

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ДАМЯН ПЕТРОВ ДАМЯНОВ

ПОЛУЧАВАНЕ НА КАТАЛИЗАТОРИ ЧРЕЗ МОЛЕКУЛНО
НАСЛОЯВАНЕ НА АКТИВНА ИЛИ ПРОМОТОРНА ФАЗА
ВЪРХУ ПОВЪРХНОСТТА НА ОКИСНИ НОСИТЕЛИ

Научна специалност
01.05.16 "Химична кинетика и катализ"

Д И С Е Р Т А Ц И Я
за получаване на научна степен
"доктор на химическите науки"

Бургас, 1987 г.

- Much of the early works from the USSR, Bulgaria etc. have been ignored in ALD publications (and patents!?) until the Virtual Project on the History of ALD, http://vph-ald.com, started in 2013

D. Damyanov, Growth by molecular layering of a catalytically active phase on the oxide surfaces, Doctor of Science thesis, 1987, Burgas Institute of Technology

The first major review in English discussing the two independent discoveries was:
Puurunen, J. Appl. Phys. 97 (2005) 121301. https://doi.org/10.1063/1.1940727

View on ALD's history is now changing → "Self-correcting mechanism of science"

- **Virtual Project on the History of ALD (VPHA), started by a group of scientists in 2013, still on-going**
- **Many presentations + four scientific articles produced**
  - Review article: "Recommended reading list of early publications on atomic layer deposition—Outcome of the "Virtual Project on the History of ALD"" (62 authors), Journal of Vacuum Science and Technology A 35 (2017) 010801 (13 pages). http://dx.doi.org/10.1116/1.4971389. Open access.
  - Essay by A. A. Malygin, V. E. Drozd, A. A. Malkov, V. M. Smirnov, "From V. B. Aleskovskii's "Framework" Hypothesis to the Method of Molecular Layering/Atomic Layer Deposition", Chemical Vapor Deposition 21 (2015) 216-240. http://dx.doi.org/10.1002/cvde.201502013.
  - Essay by R. L. Puurunen, "A short history of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy", Chemical Vapor Deposition 20 (2014) 332-344, http://dx.doi.org/10.1002/cvde.201402012. Open Access.
  - Proceedings article, R. L. Puurunen, "Learnings from an Open Science Effort: Virtual Project on the History of ALD", ECS Transactions 86(6) (2018) 3-17; doi: 10.1149/08606.0003ecst. Open access preprint doi: 10.1149/osf.io/exyv3.
- **Final review to be written in 2019, more volunteers still welcome**

Virtual Project on the History of ALD

VPHA, vph-ald.com: *Worldwide collaborative effort, in an atmosphere of openness, respect and trust*

ALD history

http://vph-ald.com
http://aldhistory.blogspot.fi

2018 Millennium Technology Prize (MTP) to Dr. Tuomo Suntola for ALD

- **MTP is Finland's tribute to innovations for a better life.**
- **The Prize is worth one million euros and it is awarded every second year.**
- **Dr. Suntola thanks the community for support and shares honor for the prize.**

President Sauli Niinistö, Dr. Tuomo Suntola

Photo: Technology Academy Finland 2018

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More: www.taf.fi
http://aldhistory.blogspot.com/search/label/MTP2018
https://issuu.com/aaltouniversity/docs/aum_23_en_pdf-150dpi/24

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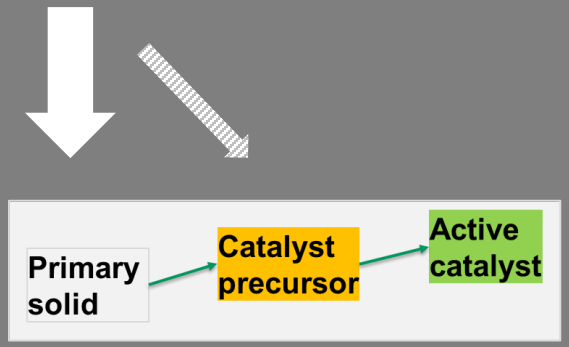


ALD for catalyst preparation

Four main routes to prepare the ”primary solid”

1 Deposition
2 Precipitation and co-precipitation
3 Gel formation
4 Selective removal

- Impregnation
- Ion exchange
- Gas phase depositions
- Solid-solid reactions
- Wash coat

ALD

(OED: Deposition: the action of putting down)

Manual of Methods and Procedures for Catalyst Characterization, Pure and Applied Chemistry 67 (1995) 1257-1306.
https://old.iupac.org/publications/pac/1995/pdf/6708x1257.pdf

Uniform metal distribution (should be) obtainable by ALD

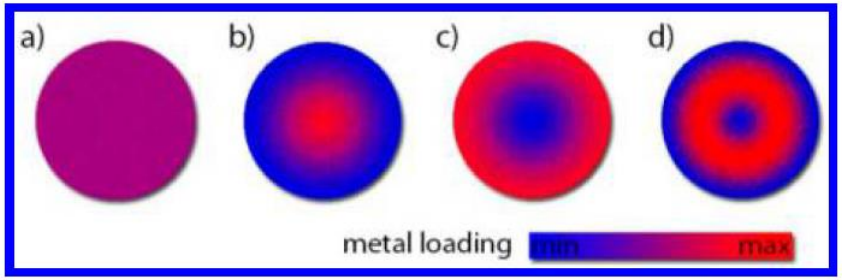
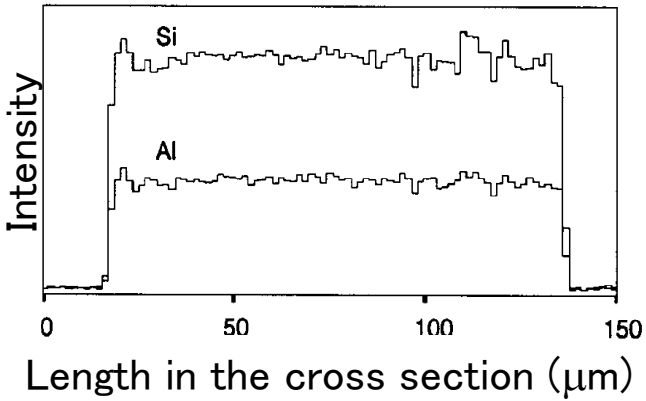


Figure 1. Different types of macroscopic metal distributions across a support body: (a) homogeneous distribution, (b) egg-yolk distribution, (c) eggshell distribution, (d) egg-white distribution (red, high concentration of metal; blue, low concentration of metal).

Munnik et al., Chem. Rev. 115 (2015) 6687.
Link: http://pubs.acs.org/doi/pdfplus/10.1021/cr500486u



- SEM-EDS line scan
- AlN deposited on silica from $AlMe_3/NH_3$
- Puurunen et al., Chem. Mater. 14 (2002) 720. http://dx.doi.org/10.1021/cm011176i

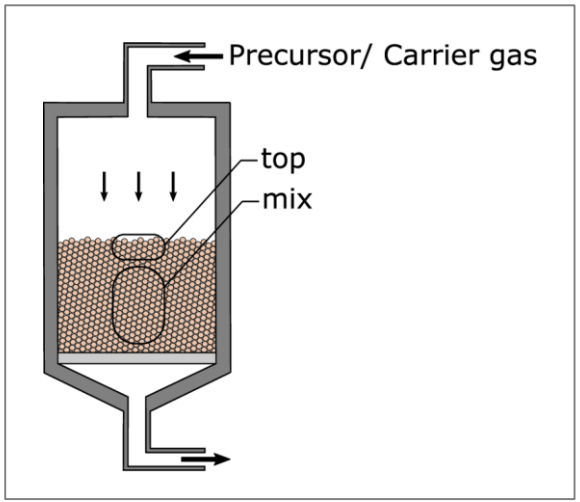
ALD needs specialized equipment

- Typically flow of inert gas in ”low” vacuum (mbar range)
- Heated lines and reaction space
- Growth typically at 100-500°C
- After-handling of the gases
  - Example: F-120 reactor, several at Aalto University
  - (Riikka would like to have with inert handling of samples)

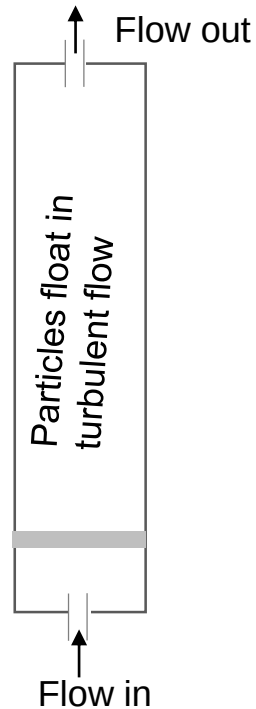
R. L. Puurunen, A Short History of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy, Chemical Vapor Deposition 20 (2014) 332-344. http://dx.doi.org/10.1002/cvde.201402012. Open Access.

Catalyst research in Finland made in fixed-bed ALD reactors

Fixed-bed reactor



Fluidized-bed reactor



Other options

- Rotary bed
- (Thin film ”flow-over” reactor with separate holder for powder)
- Delft ”riser” reactor
- …

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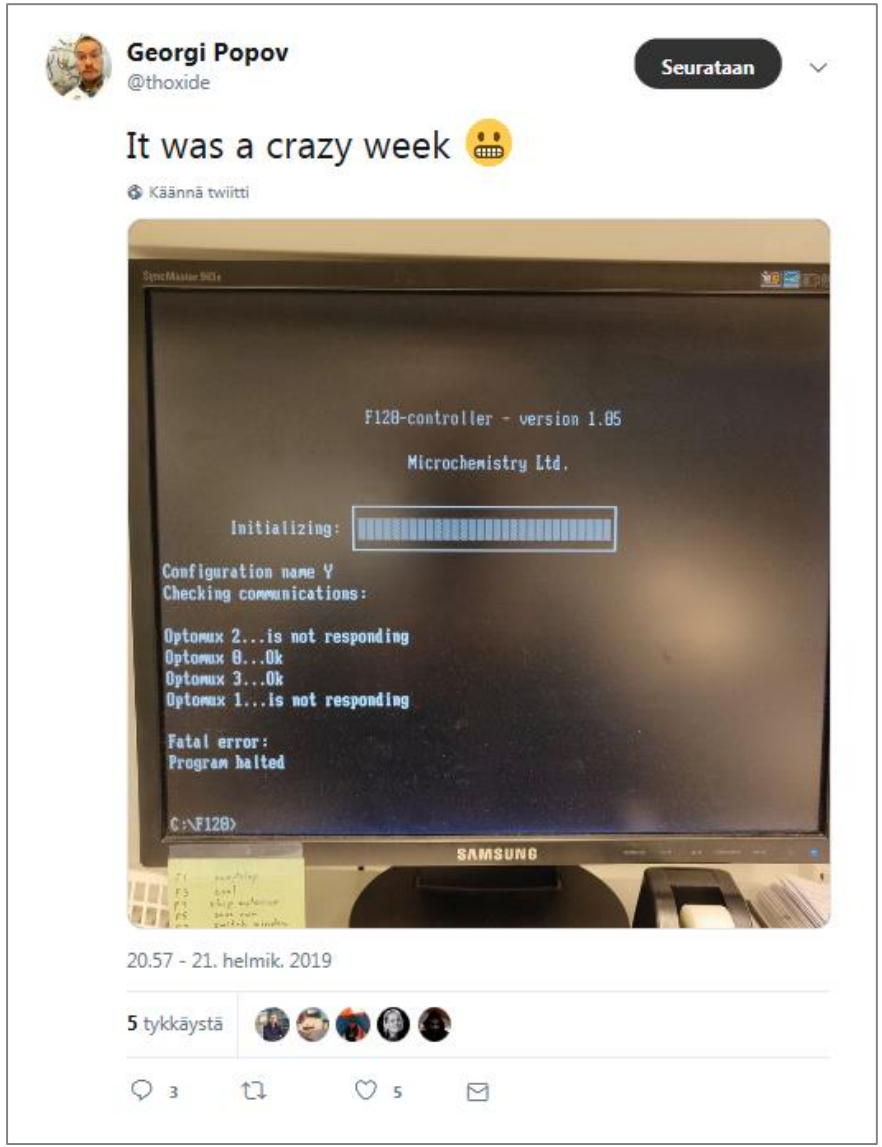
Puurunen, Chemical Vapor Deposition 20 (2014) 332-344, http://dx.doi.org/10.1002/cvde.201402012. Open Access.
S. Haukka, E.-L. Lakomaa and T. Suntola, Stud. Surf. Sci. Catal. 120 (1998) 715.
Voigt et al. Topics in Catalysis (2019), advance online article https://dx.doi.org/10.1007/s11244-019-01133-w © The Author(s) 2019 [CC BY 4.0]

- **The F-120's by Suntola & co are classical …**
  … and old…
- **Would be nice to get reactor upgrades (commercial or self-made particle ALD reactors)**
  at Aalto CHEM, too



https://twitter.com/thoxide/status/1098808950244294656?s=21

ALD catalysts typically have high dispersion

$$D = N_S/N_T$$

- D metal dispersion
- N_S number of metal atoms exposed at the **surface**
- N_T total number of metal atoms in a given amount of catalyst

”Small” particles: dispersion high
”Large” particles: dispersion low

Single atoms: dispersion = 1 (i.e. 100%)

Definition: Deutschmann et al., Ullmann's Encyclopedia of Industrial Chemistry., http://onlinelibrary.wiley.com/doi/10.1002/14356007.o05_o02/pdf (available via Aalto library)
Image: Puurunen, 2019

ALD catalysts typically have narrow particle size distribution

- **Impregnation: particle size distribution large**
  → control: concentration of impregnation liquid + temp

- **ALD: typically monotonous particle size distribution**
  → particle size controllable with number of cycles
  → monodisperse catalysts at best

Idealized schemes: Puurunen, 2019

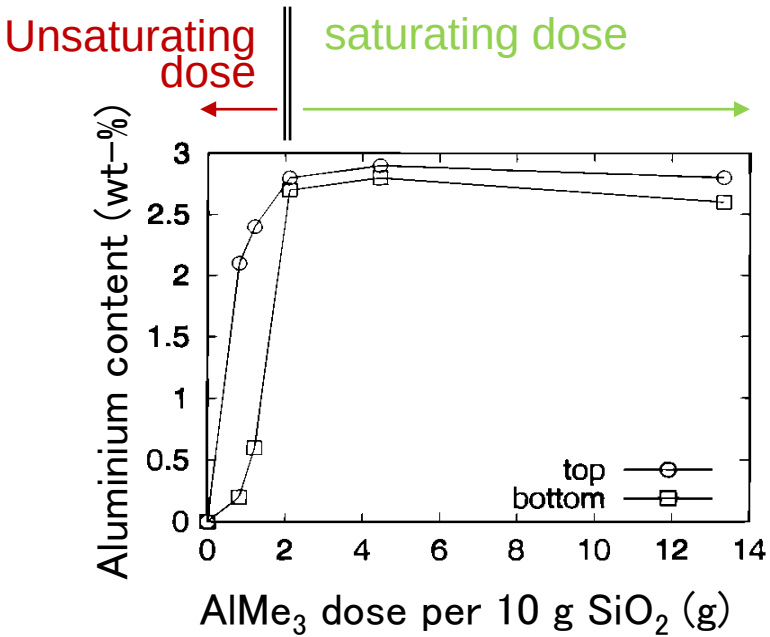
Examples of catalysts prepared in one ALD reaction

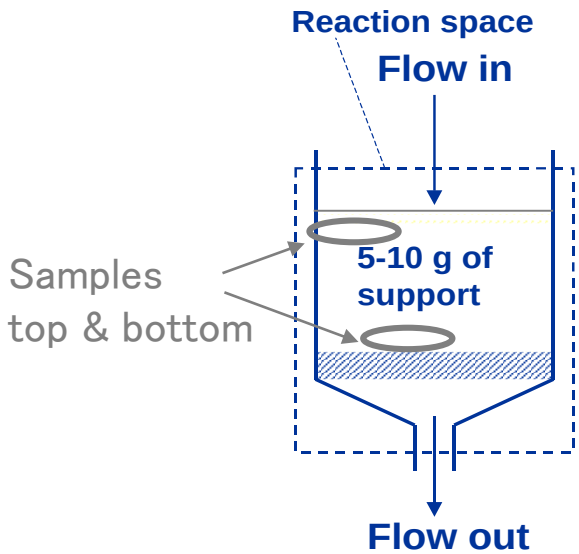
Support	Reaction	Wt-%	Groups or atoms per nm^2
Alumina 400°C	$Cr(acac)_3$	1.4 wt-% Cr	Cr: 0.64 nm^{-2}
Alumina 400°C	$Ir(acac)_3$	5.6 wt-% Ir	Ir: 0.68 nm^{-2}
Zirconia	$Cr(acac)_3$	0.4 wt-% Cr	Cr: 1.0 nm^{-2}
Alumina 400°C	-		OH: 6 nm^{-2}

Note: Monolayer typically contains on the order of 10^1 atoms per nm^2

Source: Krause, Vuori, EuropaCat-VII, Sofia, Bulgaria, Aug 28-Sept 1 2005, Keynote lecture.

Reaction saturated in the full catalyst bed? Time (dose) experiment





Puurunen et al., J. Phys. Chem. B, 104 (2000) 6599. http://dx.doi.org/10.1021/jp000454i

Springer Link

Topics in Catalysis
pp 1–10 | Cite as

Nickel Supported on Mesoporous Zirconium Oxide by Atomic Layer Deposition: Initial Fixed-Bed Reactor Study

Authors | Authors and affiliations

Pauline Voigt, Eero Haimi, Jouko Lahtinen, You Wayne Cheah, Eveliina Mäkelä, Tiia Viinikainen, Riikka L. Puurunen

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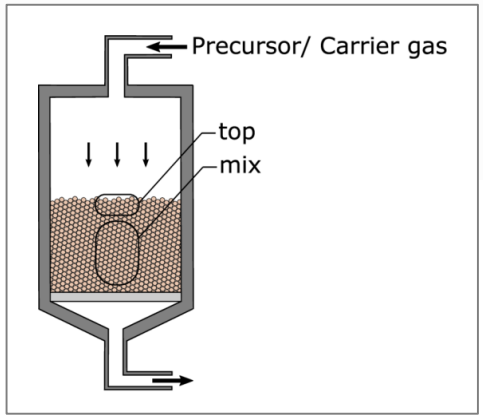
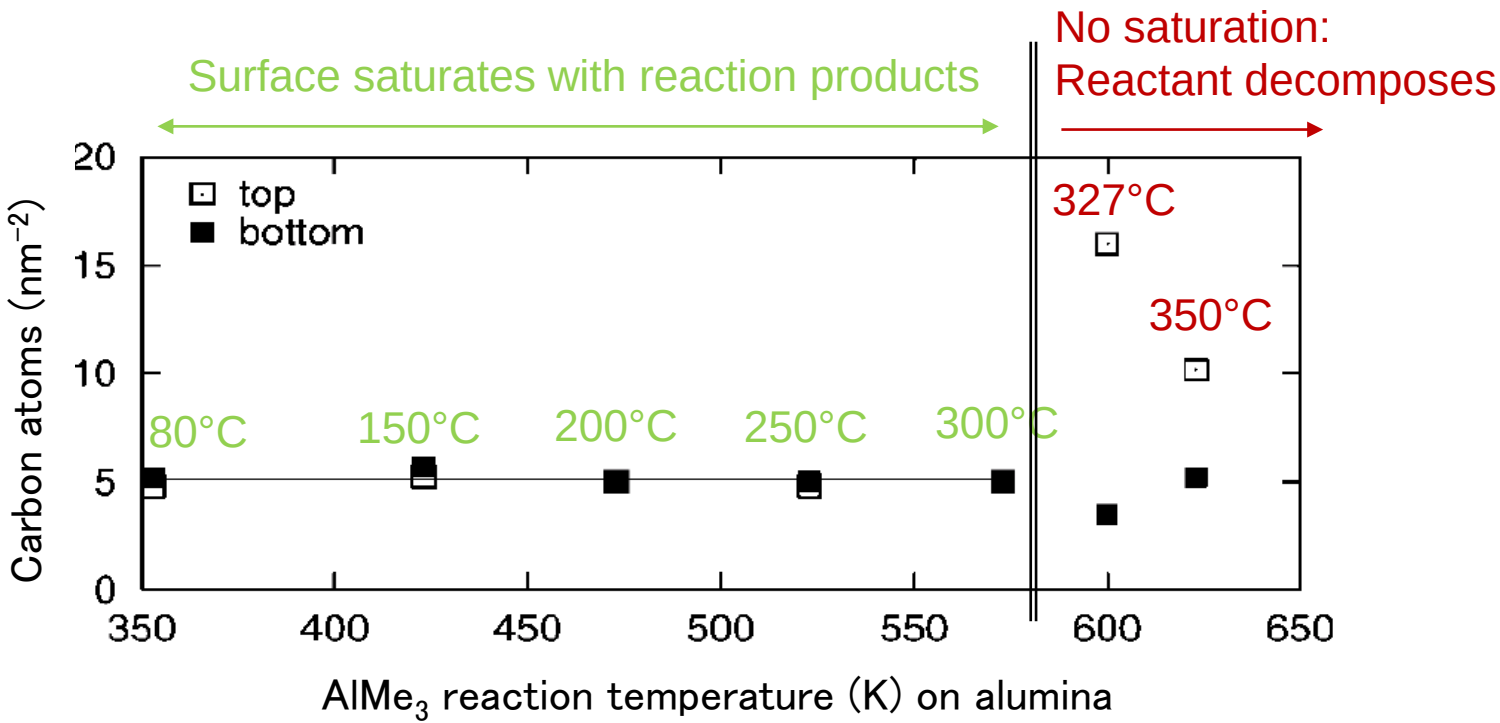


- Characterization: XRF, BET, BJH, XPS, TGA, SEM-EDS, DRIFTS
- Uniform distribution did not succeed (yet/again)
- Mix/top ratio ~60% (XRF)

Voigt et al. Topics in Catalysis (2019), advance online article https://dx.doi.org/10.1007/s11244-019-01133-w
© The Author(s) 2019 [CC BY 4.0]

Reaction saturated in the full particle bed? Sample uniformity experiment



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Puurunen et al., Phys. Chem. Chem. Phys. 3 (2001) 1093. http://dx.doi.org/10.1039/B007249O

Break + then let’s go to Presemo

- Go to:
- http://presemo.aalto.fi/cheme1130lect5

- http://presemo.aalto.fi/cheme1130lect5/screen

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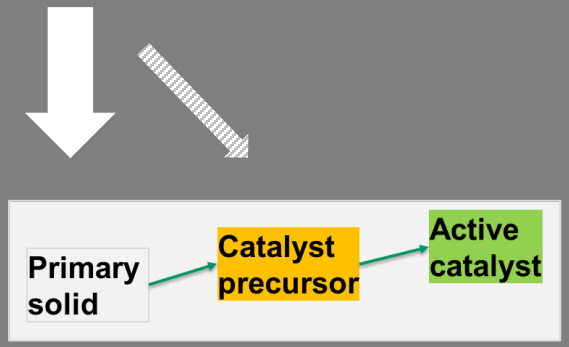


5 ways to control the metal loading by ALD

Means to control the metal loading (saturation density; GPC)

1. **Choise of support material and its pretreatment**
   - Choise of substrate & heat treatment → number of reactive sites (often OH)
2. **Choise of metal compound**
   - Reactant family (halides, β-diketonates, alkoxides, amides…)
   - Ligand size
   - Other factors (e.g. specific reactivity matters)
3. **Chemisorption temperature**
   - Trend with temperature specific to reactant-substrate pair
4. **Repeated reaction cycles for increased loading**
   - Conditions of the ligand removal step (reactant, temperature)
5. **Blocking of the reactive sites for decreased loading**
   - Selection of blocking agent

1

2

3

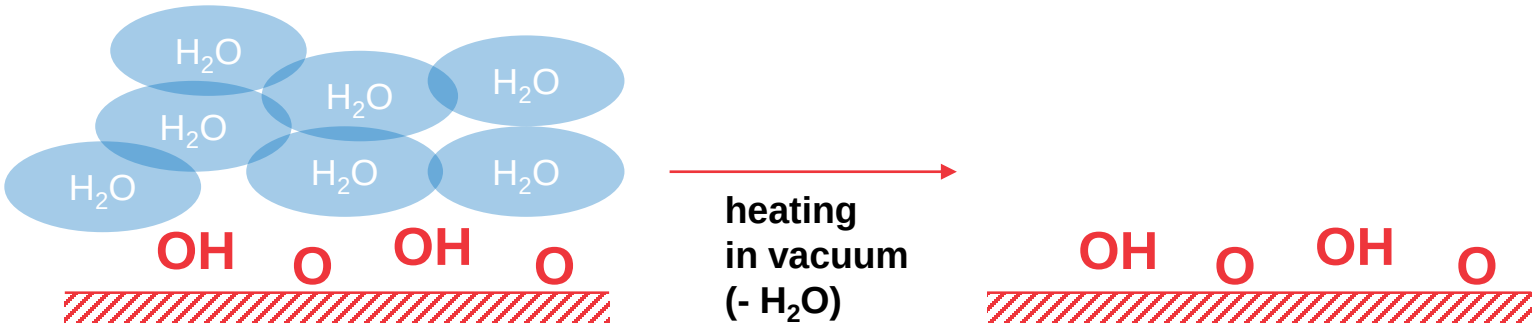
4

5

Lakomaa, " Atomic layer epitaxy (ALE) on porous substrates" Appl. Surf. Sci. 75 (1993) 185.
https://doi.org/10.1016/0169-4332(94)90158-9

Number and type of reactive sites on the surface define the growth

- **Physisorbed water removed before ALD by pre-heating at the same or higher temperature than the growth**

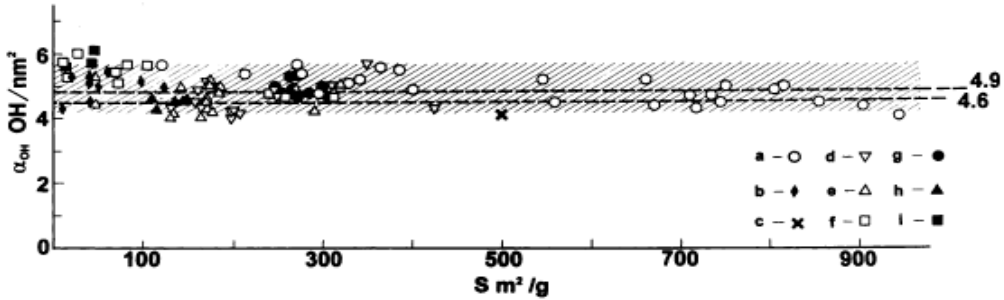


Phenomena:
- dehydration (shown)
- dehydroxylation (not shown)

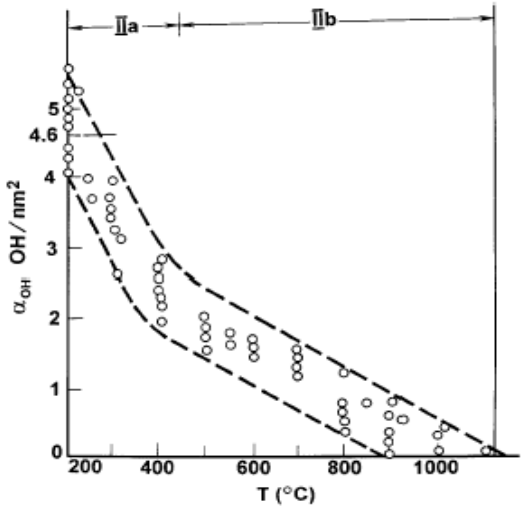
Controlling silica OH density through heat-treatment

- **OH density does not generally depend on the specific surface area (S)**
- **OH density function of the heat-treatment temperature**
- **Results similar to other oxides also**

Silica: same heat–treatment, different S



Silica:
different heat–treatment,
different S



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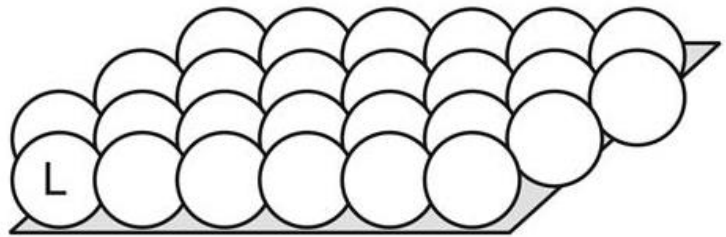
Zhuravlev, Colloids Surf., A 173 (2000) 1. https://doi.org/10.1016/S0927-7757(00)00556-2

Selection of metal reactant: Bulkier ligands → smaller saturation density

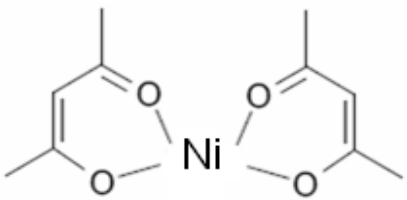
Reactant	Ni per nm2
$Ni(acac)_2$	2.3
$Ni(thd)_2$	0.92

Lakomaa, Appl. Surf. Sci. 75 (1993) 185.
https://doi.org/10.1016/0169-4332(94)90158-9

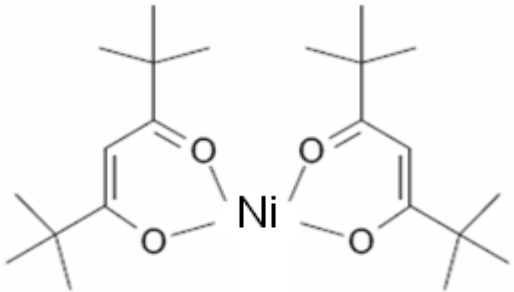


”Ball models” to estimate the maximum ligand density

→ Review: Puurunen, J. Appl. Phys. 97 (2005) 121301.
https://doi.org/10.1063/1.1940727



$Ni(acac)_2$

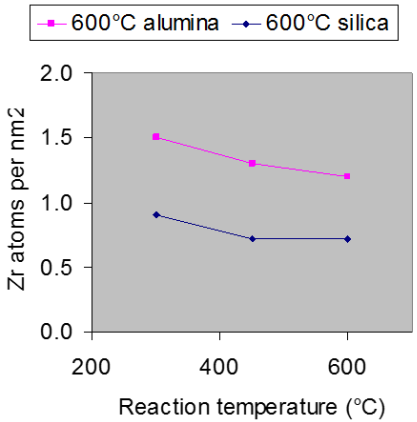


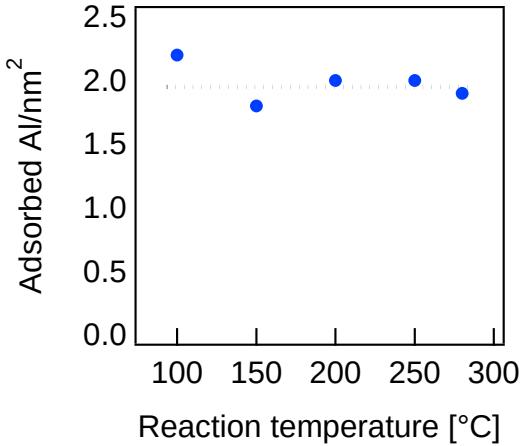
$Ni(thd)_2$

Acac: Acetylacetonato
Thd: 2,2,6,6-Tetramethyl- 3,5-heptanedionato

Effect of reaction temperature to saturation density

Data: Kytökivi et al., Langmuir 12 (1996) 4395. http://dx.doi.org/10.1021/la960198u





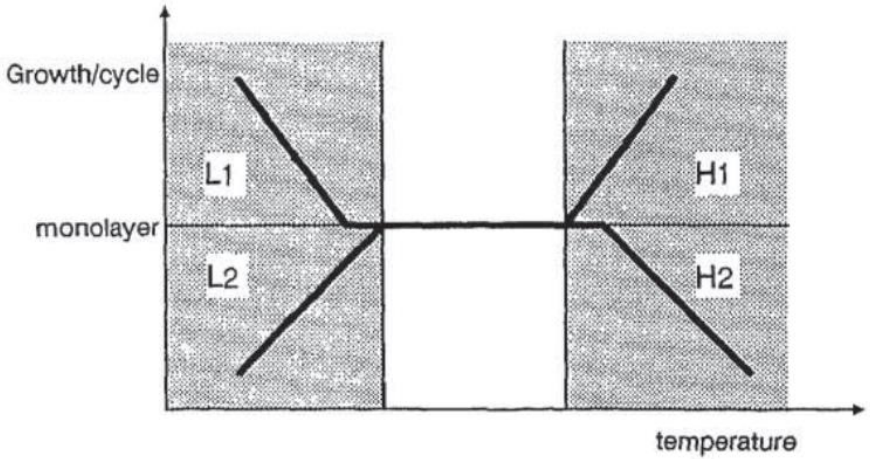
Data: Lakomaa et al., Appl. Surf. Sci. 107 (1996) 107. https://doi.org/10.1016/S0169-4332(96)00513-2

- **Effect of the reaction temperature on saturation density often weak**
- **Details depend on the reactant-substrate pair: saturation density can decrease, stay constant or increase**
- **Note: on planar substrates, decreasing trend with increasing temperature often observed, because of simultaneous dehydroxylation of the substrate**

(images: Puurunen)

Concept of ”ALD window”

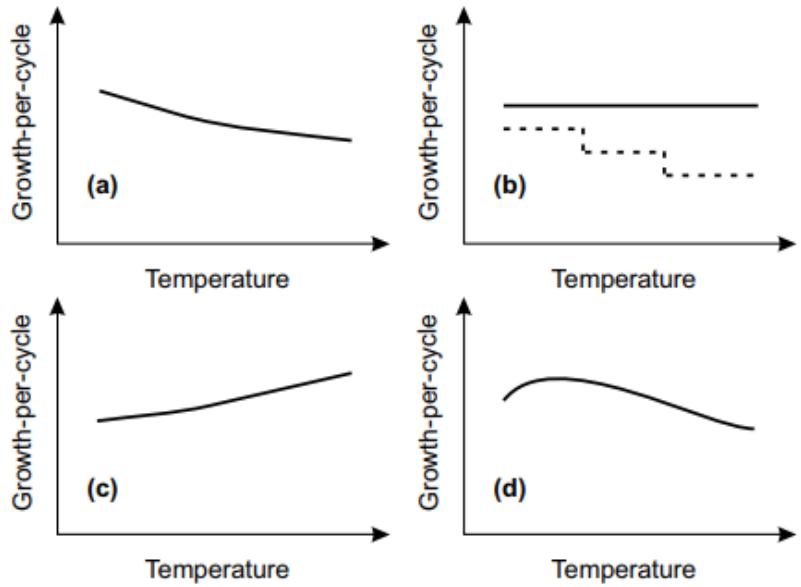
(original by Suntola)



Suntola, ”Atomic layer epitaxy” Mater. Sci. Rep. 4 (1989) 261-312.
DOI: 10.1016/S0920-2307(89)80006-4

Explanations (shortened by RLP)
L1: condensation to be prevented
L2: activation energy to exceed
H1: decomposition
H2: re-evaporation

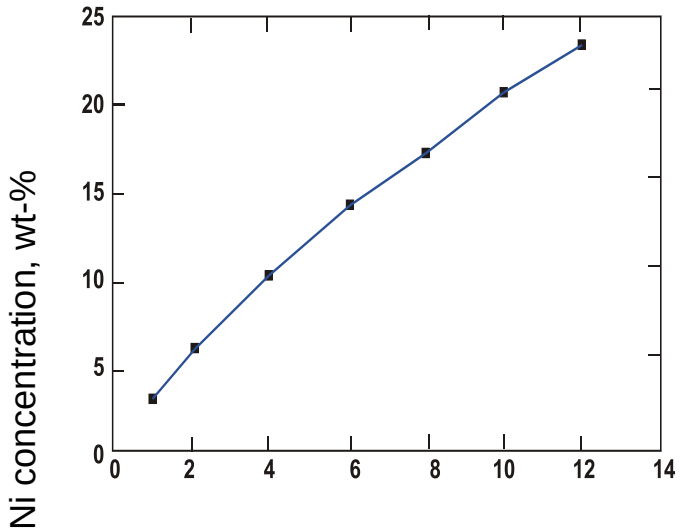
How GPC can vary within ALD window?



Puurunen, J. Appl. Phys. 97 (2005) 121301.
https://doi.org/10.1063/1.1940727 open access pdf

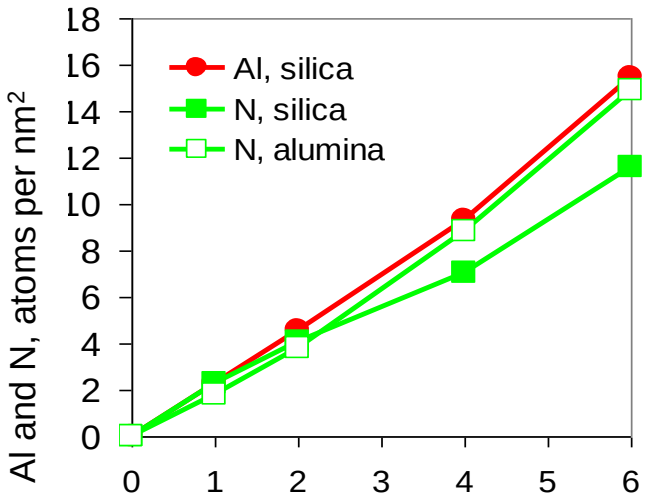
(Recent discussion on ”ALD window” in the scientific community e.g. here and the follow-up tweets)

Repeated reaction cycles for increased loading



Cycles of Ni $(acac)_2$ and air

Lindblad, Catal. Lett. 27 (1994) 323.
https://doi.org/10.1007/BF00813919

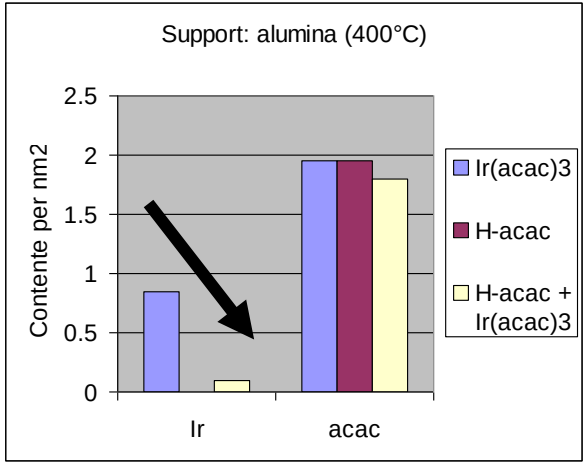


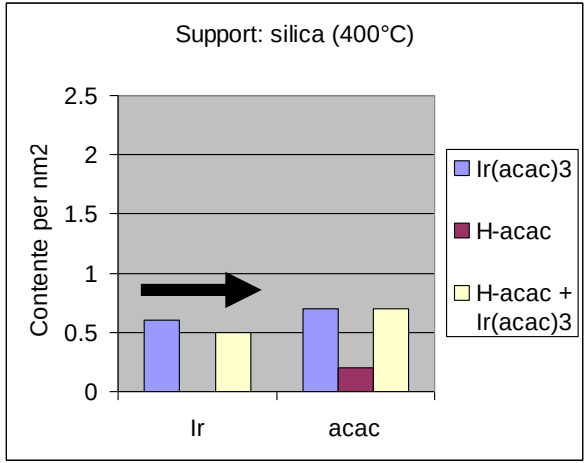
Cycles of $AlMe_3$ and NH_3

Puurunen, Doctoral thesis, HUT 2002,
http://lib.tkk.fi/Diss/2002/isbn9512261421/

(images: Puurunen)

Reducing the metal loading by blocking the reactive sites





Data: Silvennoinen et al., Appl. Surf. Sci. 253 (2007) 4103. http://dx.doi.org/0.1016/j.apsusc.2006.09.010

- Blocking of alumina and silica with H-acac (2,4-pentanedione)
- $Ir(acac)_3$ reaction at 250°C on alumina and silica
- Blocking reduces the Ir content on alumina (~90%) but not on silica
  → Success depends on the support, blocking agent and ALD reactant

(images: Puurunen)

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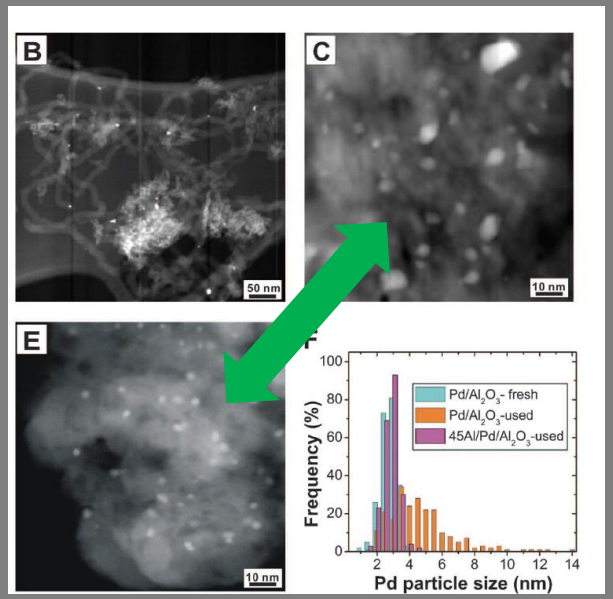
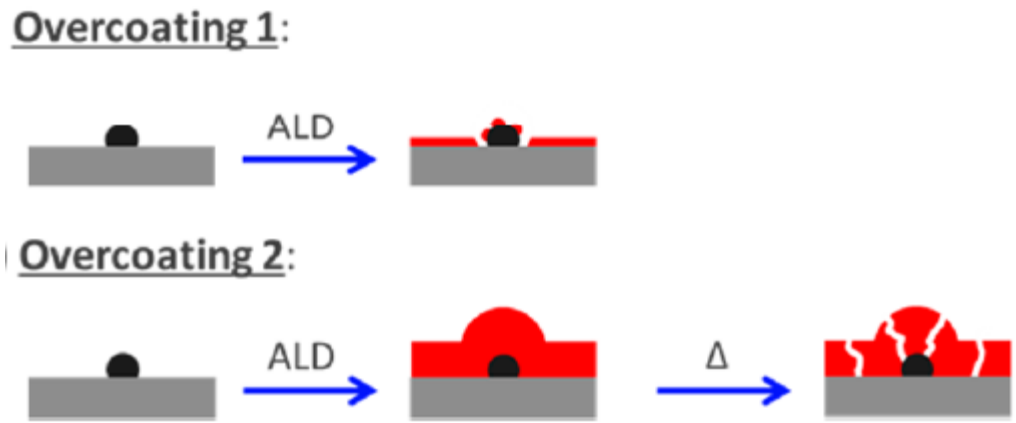
Case: Overcoats to slow down deactivation



Lu et al., Coking- and sintering-resistant palladium catalysts achieved through atomic layer deposition, Science 335 (2012) 1205-1208. doi: http://dx.doi.org/10.1126/science.1212906

Overcoats: a rather new area in ALD catalysis research



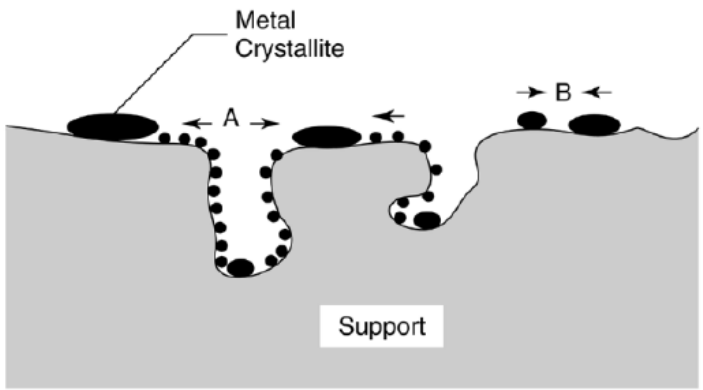
From Figure 10:
Overcoating 1: selective decoration of nanoparticles; and
Overcoating 2: complete overcoating, followed by heating to induce nanoscale porosity.
Gray represents the support material, black represents a metal nanoparticle, red represents the ALD overcoat

- **Postpone sintering**
- **Also: influence activity and selectivity**
- **Much space for new research**

O'Neill et al., Catalyst design with atomic layer deposition, ACS Catalysis 5 (2015) 1804. Open access. http://dx.doi.org/10.1021/cs501862h

Deactivation

Sintering



(Figure 17.) Two conceptual models for crystallite growth due to sintering by (**A**) atomic migration or (**B**) crystallite migration.

Fouling

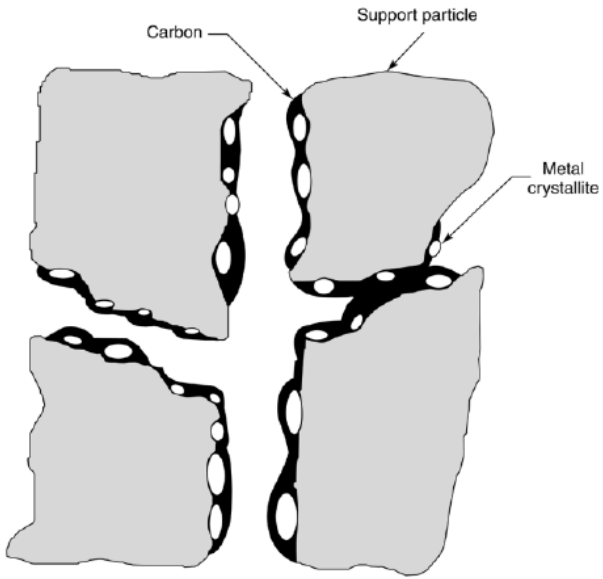


Figure 10. Conceptual model of fouling, crystallite encapsulation, and pore plugging of a supported metal catalyst owing to carbon deposition.

Morris D. Argyle and Calvin H. Bartholomew: Heterogeneous Catalyst Deactivation and Regeneration: A Review, Catalysts 5 (2015) 145-269; DOI:10.3390/catal5010145 (open access).

Case: ethane oxidative dehydrogenation with Pd/Al_2O_3 catalysts

Coking- and Sintering-Resistant Palladium Catalysts Achieved Through Atomic Layer Deposition

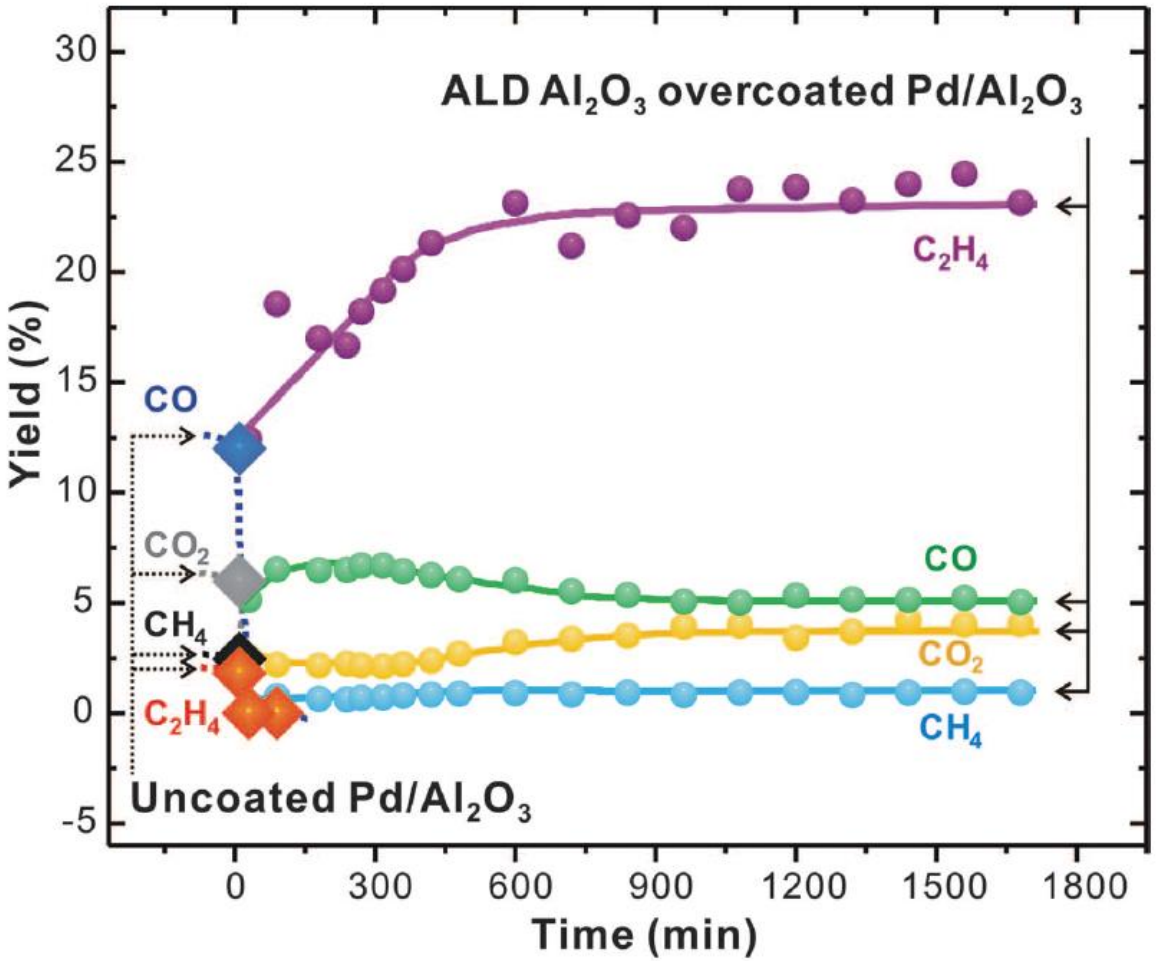
Junling Lu,[1] Baosong Fu,[2] Mayfair C. Kung,[3] Guomin Xiao,[2] Jeffrey W. Elam,[1] Harold H. Kung,[3] Peter C. Stair[4,5]*

We showed that alumina (Al_2O_3) overcoating of supported metal nanoparticles (NPs) effectively reduced deactivation by coking and sintering in high-temperature applications of heterogeneous catalysts. We overcoated palladium NPs with 45 layers of alumina through an atomic layer deposition (ALD) process that alternated exposures of the catalysts to trimethylaluminum and water at 200°C. When these catalysts were used for 1 hour in oxidative dehydrogenation of ethane to ethylene at 650°C, they were found by thermogravimetric analysis to contain less than 6% of the coke formed on the uncoated catalysts. Scanning transmission electron microscopy showed no visible morphology changes after reaction at 675°C for 28 hours. The yield of ethylene was improved on all ALD Al_2O_3 overcoated Pd catalysts.

2012, Lu et al., Coking- and sintering-resistant palladium catalysts achieved through atomic layer deposition, Science 335 (2012) 1205-1208. doi: http://dx.doi.org/10.1126/science.1212906

Case: ethane dehydrogenation with Pd/Al_2O_3 catalysts

Fig. 1. Products yield on the Pd/Al_2O_3 samples with and without ALD Al_2O_3 overcoat during ODHE reaction as a function of reaction time under identical reaction conditions. Diamonds with a dashed line, product yields on the uncoated Pd/Al_2O_3 sample; circles with solid lines, product yields on the $45Al/Pd/Al_2O_3$ sample.



2012, Lu et al., Coking- and sintering-resistant palladium catalysts achieved through atomic layer deposition, Science 335 (2012) 1205-1208. doi: http://dx.doi.org/10.1126/science.1212906

Case: ethane dehydrogenation with Pd/Al_2O_3 catalysts

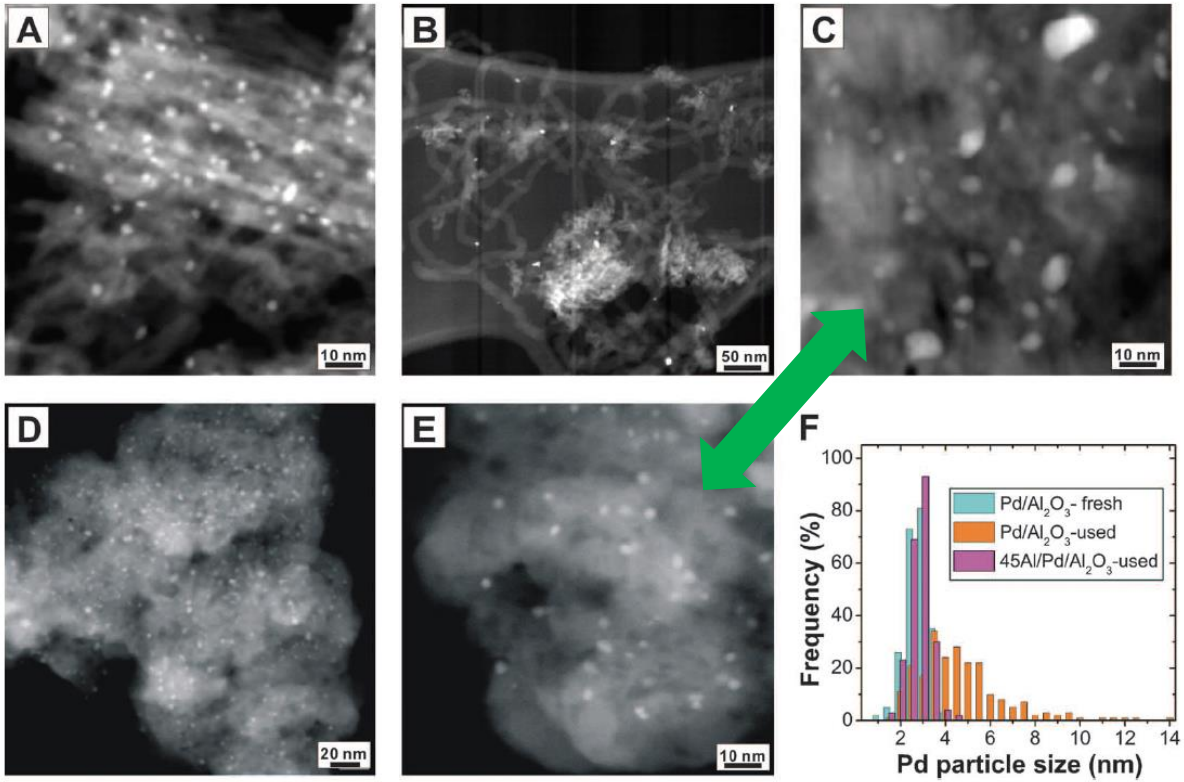


Fig. 2. STEM images of fresh and used samples after ODHE reaction testing. (**A**) The fresh Pd/Al_2O_3 sample. (**B** and **C**) The used Pd/Al_2O_3 sample at 675°C for 30 min at low (B) and high (C) magnification. (**D** and **E**) The used $45Al/Pd/Al_2O_3$ sample at 675°C for ~1700 min at low (D) and high (E) magnification. (**F**) Pd particle size distributions of these three samples.

2012, Lu et al., Coking- and sintering-resistant palladium catalysts achieved through atomic layer deposition, Science 335 (2012) 1205-1208. doi: http://dx.doi.org/10.1126/science.1212906

Case: ethane dehydrogenation with Pd/Al_2O_3 catalysts

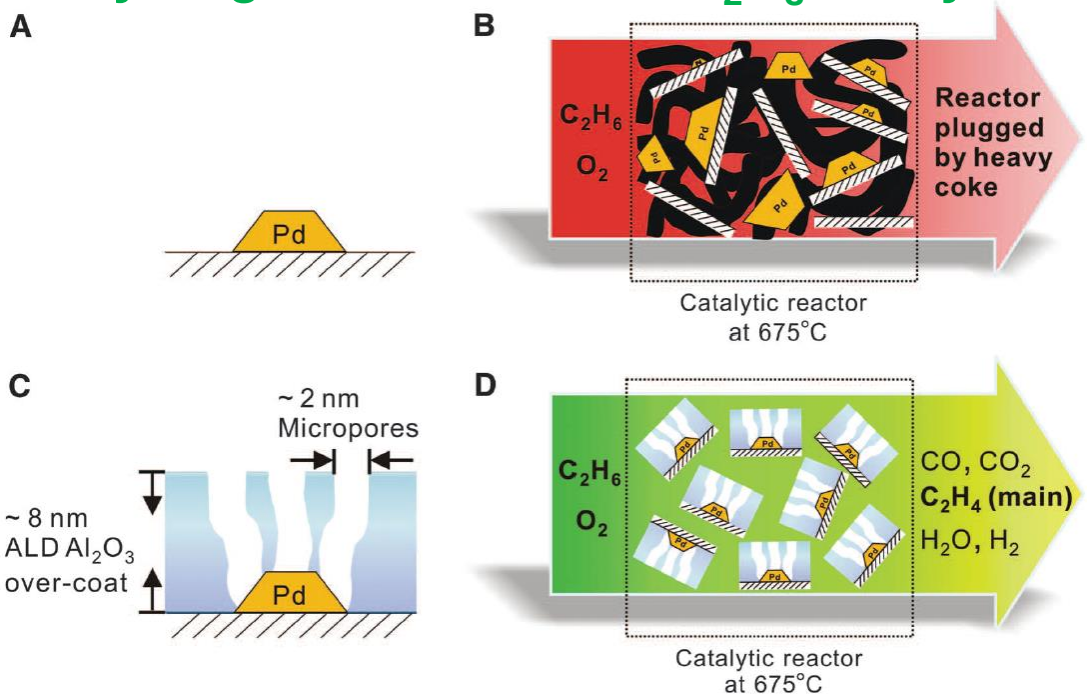


Fig. 4. A schematic model of Pd/Al_2O_3 catalysts with and without ALD Al_2O_3 overcoat during ODHE reaction at 675°C. (**A**) The uncoated Pd/Al_2O_3 catalyst. (**B**) The uncoated Pd/Al_2O_3 catalyst during ODHE reaction, in which filamentous carbon (thick black lines) plugged the reactor and there was substantial sintering and leaching of Pd NPs from the support (barred white lines). (**C**) The Pd catalyst with an ~8-nm ALD Al_2O_3 overcoat, which contained ~2-nm micropores after activation. (**D**) The ALD Al_2O_3–overcoated Pd/Al_2O_3 catalyst during ODHE reaction, on which the microporous Al_2O_3 overcoat trapped and stabilized the Pd NPs, inhibiting Pd NP leaching and coke formation, while greatly enhancing ethylene formation.

2012, Lu et al., Coking- and sintering-resistant palladium catalysts achieved through atomic layer deposition, Science 335 (2012) 1205-1208. doi: http://dx.doi.org/10.1126/science.1212906

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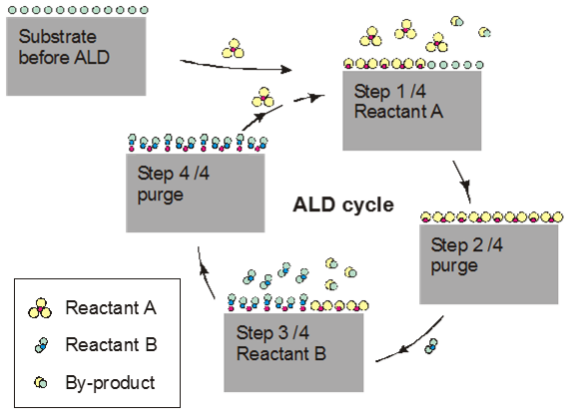
Conclusion & take-home message

Take-home message: Catalysts by ALD

- ALD: repeated saturating, irreversible reactions
- Active development of new processes, not all may be suited for modification of porous catalysts though because of CVD-type side reactions
- In principle, extreme uniformity and monodisperse particles should be obtainable
- Five ways to control the metal loading
- Scienfically, currently, highly interesting → model catalysts



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Once more, Presemo feedback

Go to:

http://presemo.aalto.fi/cheme1130lect5

http://presemo.aalto.fi/cheme1130lect5/screen

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Bonus slides - Additional material for the interested

VPHA website as resource
http://vph-ald.com/

Virtual Project on the History of ALD

VPHA, vph-ald.com: *Worldwide collaborative effort, in an atmosphere of openness, respect and trust*

ALD history

- Home
- Publication Plan
- VPHA open files
- ALD History Blog
- ALD history publications

Virtual Project on the History of ALD (VPHA)

VPHA is an open collaborative effort, whose goal is to clarify open ques
history of the Atomic Layer Deposition (ALD) thin film deposition techni
July 2013. VPHA is based on voluntary efforts, and anyone interested i
welcome to join. All VPHA activities are made in an atmosphere of ope

Key VPHA links:

- Introduction and Invitation to participate
- ALD-history-evolving-file, with continuous open editing
- Publication Plan (v3, April 5, 2015)
- LinkedIn ALD History group
- Open Introduction in SlideShare (no more updated)

Scientific journal articles from VPHA:

- Proceedings article: R. L. Puurunen, "Learnings from an Open Science Effort: Virtual Project on the History of ALD", ECS Transactions 86(6) (2018) 3-17; doi:10.1149/08606.0003ecst. Open access preprint, DOI: 10.1149/osf.io/exyv3.
- Review article: "Recommended reading list of early publications on atomic layer deposition – Outcome of the "Virtual Project on the History of ALD"", Esko Ahvenniemi

http://vph-ald.com/VPHAopenfiles.html -->

VPHA-ALD-thesis-list, link
- in Google docs
- Everyone can comment
- A few ALD History Review co-authors have editing rights
- TO ADD INFO: please put info of the thesis to be added in a file that all can edit, VPHA-thesis-to-be-added.

VPHA-ALD-reviews, link
- in Google docs
- Everyone can comment
- A few ALD History Review co-authors have editing rights
- TO ADD INFO: please put info of reviews and a like to be added in a file which all c VPHA-reviews-to-be-added.

New!

CatALD-reviews, link
- in Google docs, "sister file" of VPHA-ALD-reviews, for catalysis related reviews
- Everyone can comment
- TO ADD INFO: please put the info in the file which all can edit, VPHA-reviews-to-be-added.
- Please email to riikka.puurunen at aalto.fi to send a note that a review should be added to CatALD-reviews

Direct link here

Some ALD reviews mentioned

- **R. L. Puurunen, ” Surface chemistry of atomic layer deposition: a case study for the trimethylaluminum/water process”, J. Appl. Phys. 97 (2005) 121301 1-52. http://dx.doi.org/10.1063/1.1940727, Open Access: http://www.vtt.fi/inf/julkaisut/muut/2010/Puurunen.pdf**
    - Comprehensive review on the surface chemistry of ALD; >1000 references, the world’s 2nd most cited ALD review, cited >1350 times (ISI Web of Science, 24.2.2019)
- **R. L. Puurunen, ” A Short History of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy”, Chem. Vap. Deposition 20 (2014) 332-344. http://dx.doi.org/10.1002/cvde.201402012 (open access)**
    - Essay & story on how it all started (in Finland)
- **V. Miikkulainen, M. Leskelä, M. Ritala, R. L. Puurunen, J. Appl. Phys. 113 (2013) 021301. http://dx.doi.org/10.1063/1.4757907. open access pdf.**
    - Follow-up of http://dx.doi.org/10.1063/1.1940727; ISI highly cited

Highly Cited Paper

Some original ALD-catalysis research papers for the interested (could be many more…)

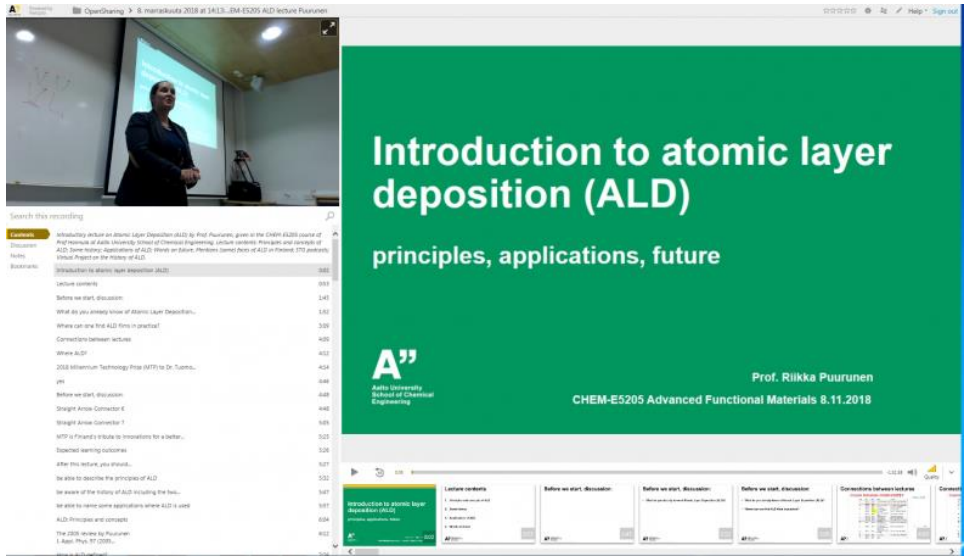
- 2002, Puurunen et al., Cobalt(III) Acetylacetonate Chemisorbed on Aluminum-Nitride-Modified Silica: Characteristics and Hydroformylation Activity, Catal. Lett. 83 (2002) 27-32. https://doi.org/10.1023/A:1020645112790
- 2011, Rui Liu, Yongjing Lin, Lien-Yang Chou, Stafford W. Sheehan, Wangshu He, Fan Zhang, Harvey J. M. Hou, Dunwei Wang, Water Splitting by Tungsten Oxide Prepared by Atomic Layer Deposition and Decorated with an Oxygen-Evolving Catalyst, Angewandte Chemie International Edition, 50 (2011) 499–502. http://dx.doi.org/10.1002/anie.201004801
- 2011, Pagan-Torres et al., Synthesis of Highly Ordered Hydrothermally Stable Mesoporous Niobia Catalysts by Atomic Layer Deposition [biomass-related], ACS Catalysis 1 (2011) 1234-1245. http://dx.doi.org/10.1021/cs200367t
- 2012, Lu et al., Coking- and sintering-resistant palladium catalysts achieved through atomic layer deposition, Science 335 (2012) 1205-1208. doi: http://dx.doi.org/10.1126/science.1212906
- 2013, Mondloch et al., Vapor-Phase Metalation by Atomic Layer Deposition in a Metal–Organic Framework, J. Am. Chem. Soc., 2013, 135 (28), pp 10294–10297, http://dx.doi.org/10.1021/ja4050828
- 2013, Sun et al., Single-atom Catalysis Using Pt/Graphene Achieved through Atomic Layer Deposition, Scientific Reports volume 3, Article number: 1775 (2013). http://dx.doi.org/10.1038/srep01775
- 2014, Zhang et al., Atomic Layer Deposition Overcoating: Tuning Catalyst Selectivity for Biomass Conversion, Angewandte Chemie International Edition 53 (2014) 12132-12136. http://dx.doi.org/10.1002/anie.201407236
- 2015, Kim et al., (Minireview) Artificial Photosynthesis for Sustainable Fuel and Chemical Production, Angewandte Chemie International Edition 54 (2015) 3259–3266. http://dx.doi.org/10.1002/anie.201409116
- 2015, Gao et al., Microscopic silicon-based lateral high-aspect-ratio structures for thin film conformality analysis, Journal of Vacuum Science and Technology A 33 (2015) art. 010601. http://dx.doi.org/10.1116/1.4903941, open access.
- 2018, Alvaro & Yanguas-Gil, Characterizing the field of Atomic Layer Deposition: Authors, topics, and collaborations, PLOS One, 2018. https://doi.org/10.1371/journal.pone.0189137 (open access)

An illustration of ALD

- **Two steps of the $Et_2Zn + H_2O$ process to make ZnO**
- **(illustrative purposes only, not mechanistically correct)**
- https://twitter.com/Ella_Maru/status/900879937607000064
- **Watch at home if you like**
- **works in Chrome, at least**

Introductory general ALD lecture openly available (from fall 2018)

- **Catalysis Professor's Open blog:** https://blogs.aalto.fi/catprofopen/2018/11/09/openteaching-introductory-lecture-on-atomic-layer-deposition-shared/
- **Panopto:** https://aalto.cloud.panopto.eu/Panopto/Pages/Viewer.aspx?id=bd0aee67-7ca5-4973-8216-a99200e888b1
- **Youtube:** https://youtu.be/i-m52yTdZB0
- **SlideShare:** https://pt.slideshare.net/RiikkaPuurunen/introduction-to-atomic-layer-deposition-ald-principles-applications-future
- **LinkedIn:** https://www.linkedin.com/feed/update/urn:li:activity:6466591287486214144/



Latest VPHA submission

On the list collection of doctoral theses on ALD worldwide
http://aldhistory.blogspot.com/2019/02/vpha-communication-ald2019-abstract-submitted.html

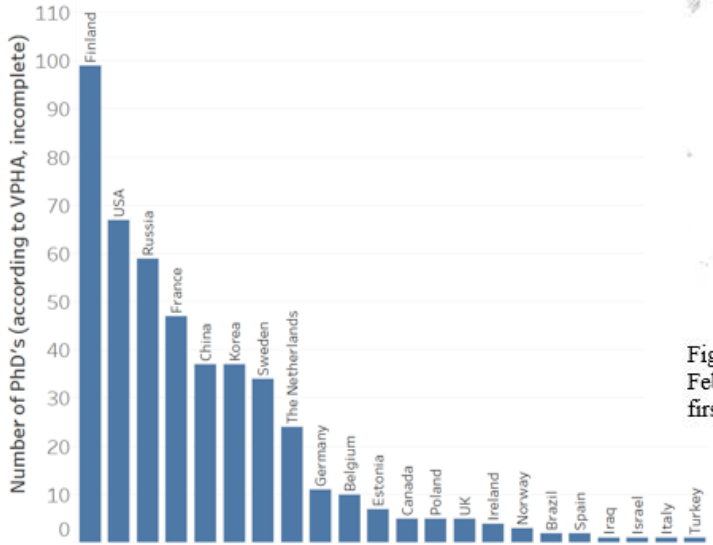


Figure 1. Bar chart summary of doctoral theses on ALD per country, according to information collected in the Virtual Project on the History of ALD, as of February 2019.

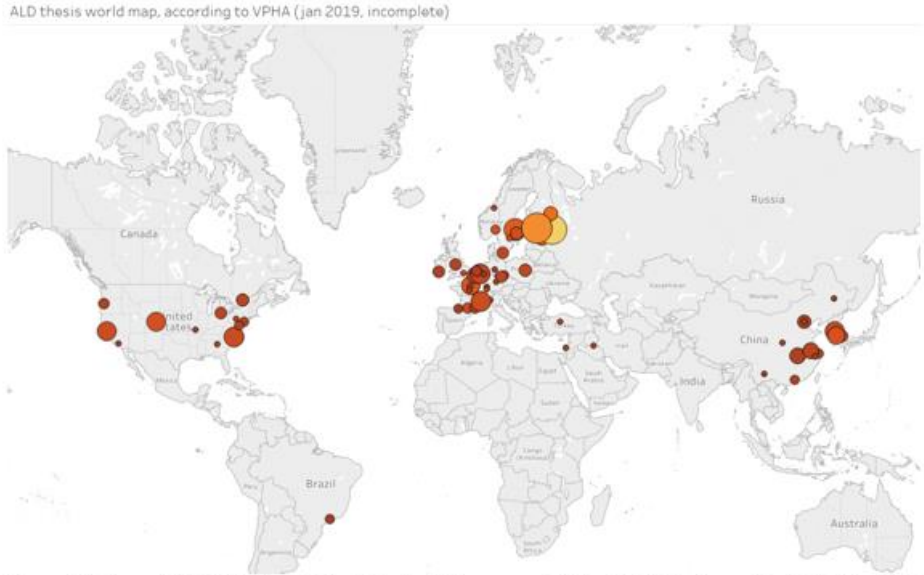


Figure 2: A world distribution plot of doctoral theses on ALD-related topics collected in the VPHA, up to February 2019. The size of the spheres represents the number of records, while the colour represents the first thesis originating from that location. Division per city.

https://twitter.com/rlpuu/status/1096385902971113472

Review on ALD conformality to be published in a few days? Applied Physics Reviews, in press (2019)

Conformality in atomic layer deposition: Current status overview of analysis and modelling

Cite as: Appl. Phys. Rev. 6, 000000 (2019); doi: 10.1063/1.5060967
Submitted: 21 September 2018 · Accepted: 31 January 2019 ·
Published Online: 0 Month 0000

AQ1 Veronique Cremers,[1] Riikka L. Puurunen,[2,3] and Jolien Dendooven[1,a)]

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ABSTRACT

Atomic layer deposition (ALD) relies on alternated, self-limiting reactions between gaseous reactants and an exposed solid surface to deposit highly conformal coatings with a thickness controlled at the submonolayer level. These advantages have rendered ALD a mainstream technique in microelectronics and have triggered growing interest in ALD for a variety of nanotechnology applications, including energy technologies. Often, the choice for ALD is related to the need for a conformal coating on a 3D nanostructured surface, making the conformality of ALD processes a key factor in actual applications. In this work, we aim to review the current status of knowledge about the conformality of ALD processes. We describe the basic concepts related to the conformality of ALD, including an overview of relevant gas transport regimes, definitions of exposure and sticking probability, and a distinction between different ALD growth types observed in high aspect ratio structures. In addition, aiming for a more standardized and direct comparison of reported results concerning the conformality of ALD processes, we propose a new concept, Equivalent Aspect Ratio (EAR), to describe 3D substrates and introduce standard ways to express thin film conformality. Other than the conventional aspect ratio, the EAR provides a measure for the ease of coatability by referring to a cylindrical hole as the reference structure. The different types of high aspect ratio structures and characterization approaches that have been used for quantifying the conformality of ALD processes are reviewed. The published experimental data on the conformality of thermal, plasma-enhanced, and ozone-based ALD processes are tabulated and discussed. Besides discussing the experimental results of conformality of ALD, we will also give an overview of the reported models for simulating the conformality of ALD. The different classes of models are discussed with special attention for the key assumptions typically used in the different modelling approaches. The influence of certain assumptions on simulated deposition thickness profiles is illustrated and discussed with the aim of shedding light on how deposition thickness profiles can

Proof

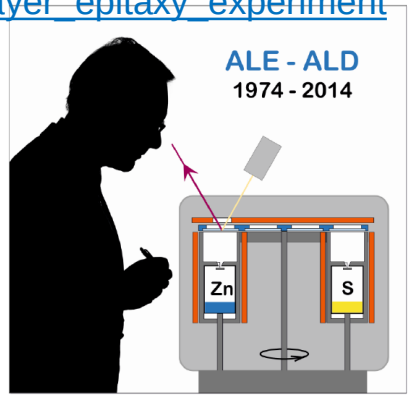
(sceen capture of galley proofs, which the authors need to check, correct if necessary & approve before publication – status as of Feb 24, 2019)

FinALD40 exhibition

FinALD40 materials:

- http://www.aldcoe.fi/events/finald40.pdf
- http://vph-ald.com/UploadedPublications/FinALD40_web_2014-11-29_update2015-01-23.pdf

Image by Puurunen & Suntola donated to Wikimedia Commons with CC BY-SA 4.0 license: https://commons.wikimedia.org/wiki/File:Reconstruction_of_the_first_atomic_layer_epitaxy_experiment_by_Tuomo_Suntola.jpg



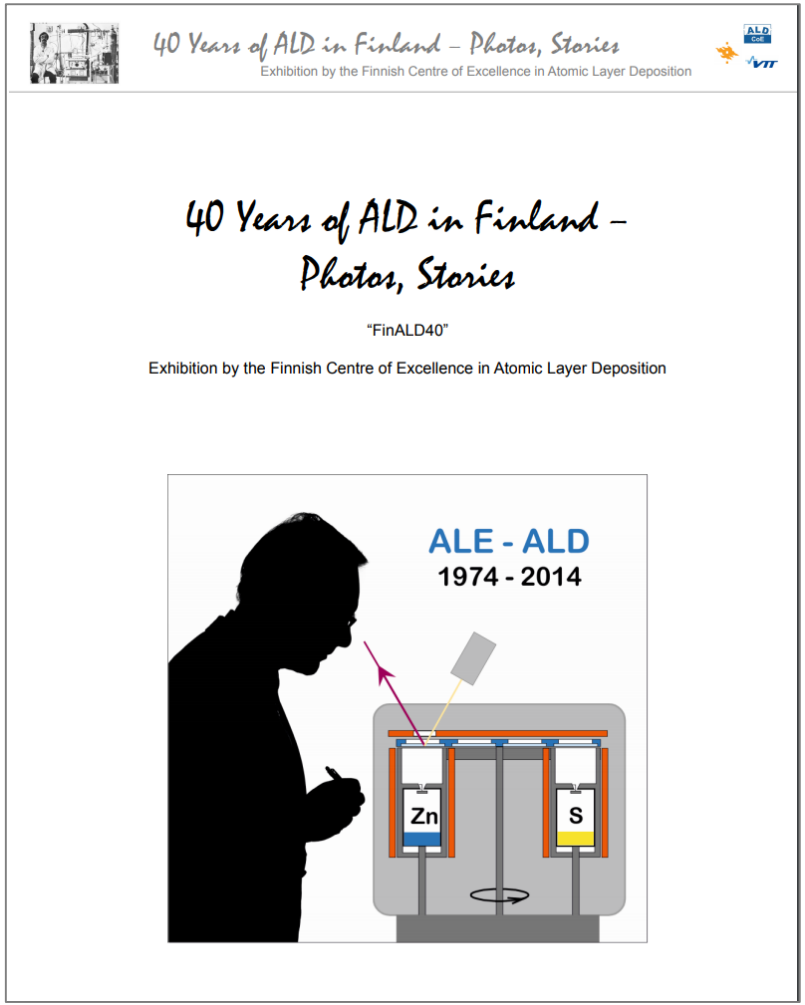


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Photo by Riikka Puurunen, CC BY-SA 4.0 (→ everyone may make edits & share)
https://upload.wikimedia.org/wikipedia/commons/2/2c/Tuomo_Suntola_received_the_Millennium_Technology_Prize_2018.jpg

Atomic Limits

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https://www.atomiclimits.com/2019/02/12/atomic-layer-deposition-process-development-10-steps-to-successfully-develop-optimize-and-characterize-ald-recipes/

Particle ALD interest grows – recent Volkswagen news

https://www.blog.baldengineering.com/2019/01/volkswagen-invests-usd-10-m-in-us-ald.html?m=1

Thursday, January 24, 2019

Volkswagen invests USD 10 M in US ALD start-up Forge Nano for battery material research

The Volkswagen Group is investing US$10 million in the start-up Forge Nano Inc with a view to reinforcing its specialist knowledge in the field of battery research. Forge Nano is investigating a material coating technology that could further improve the performance of battery materials. As a partner, Volkswagen will provide support for industrial trials of this technology. The transaction is still subject to approval by the authorities.

(forgenano.com)

Volkswagen has been collaborating with Forge Nano on advanced battery material research since 2014. The startup with headquarters in Louisville, Colorado, is investigating processes for scaling atomic layer deposition (ALD) to create new core-shell materials, especially for battery applications. ALD is a chemical process for applying atomic scale coatings one atom at a time. With its specific ALD technology, Forge Nano aims to boost energy density of vehicle battery cells.
For example, a higher energy density would have positive effects on the range of electric vehicles. Volkswagen has been lending their automotive and battery expertise towards Forge Nano's applied research efforts.

The Volkswagen Group is consistently forging ahead with its electric offensive and intends to offer more than 50 battery-electric models by 2025, accounting for about a fifth of its entire model portfolio. To safeguard this approach, Volkswagen is cooperating with strategic battery cell suppliers and developing its own specialist know-how in battery research. This also includes targeted venture investments. Volkswagen is increasingly investing in international start-ups to bring innovative technologies forward to production maturity together.

Dr. Axel Heinrich, Head of Volkswagen Group Research, said: "At Volkswagen, we want to be the world's leading provider of e-mobility. We are continually expanding the battery technology know-how required for this purpose. We need to safeguard our technological competence for the future. Cooperation with start-ups is a key element in these efforts. We are acting as a partner to Forge Nano and intend to provide the team with opportunities to carry out industrial trials with its innovative technology."

Dr. Paul Lichty, Founder and CEO of Forge Nano, said: "Our atomically precise surface engineering technology is ushering in a new era of high performance materials. We are excited to partner with a company that has such a strong commitment to commercializing innovation."

https://www.greencarcongress.com/2019/01/20190123-vwforgenano.html

Aalto ALD Forum – internal ”Wiki”

https://wiki.aalto.fi/display/aldforum/Aalto+ALD+Forum

Aalto University Wiki | Spaces | People | Create

Aalto ALD Forum

Pages
Blog

SPACE SHORTCUTS

Here you can add shortcut links to the most important content for your team or project. Configure sidebar.

PAGE TREE
- Groups with ALD-related research
- ALD reactors and related equipment at

Space tools

Pages | Edit | Save for later | Watch | Share

Aalto ALD Forum

Created by Antti Karttunen, last modified on Nov 22, 2018

Aalto ALD Forum is an information hub for all Aalto researchers working on topics related to Atomic Layer Deposition

Building up the Forum has begun recently, please feel free to add relevant content to the following topics:

- Research groups working with ALD at Aalto
- ALD reactors and related equipment at Aalto

Some practical instructions

- If you would like to edit the Forum, but the Wiki tells that you do not have the permissions to do so, please contact antti.karttunen@aalto.fi. The Wiki platform has had some issus with permissions management and not all staff have the proper access rights.
- Please contribute good figures to make the Forum more lively!
- Please try to use your own figures/pictures. If you use figures from other sources, check that the license allows you to do this and attribute the original author properly in the figure caption.

Blog

The most recent ALD-related announcements can be found below. A full listing of blog posts is also available.

Blog Posts

On the "periodic table of ALD processes" created by Riikka Puurunen	Aalto ALD Forum Feb 06, 2019
New review article on ALD conformality created by Riikka Puurunen	Aalto ALD Forum Feb 05, 2019
ELEC-L3221 - Postgraduate Course in Micro and Nanosciences: Atomic layer deposition of nanostructured materials created by Antti Karttunen	Aalto ALD Forum Jan 03, 2019
Visiting lecture: Dr. Mahdi Shirazi on computational simulation of ALD - Micronova Wed 19.12. 14:15 created by Riikka Puurunen	Aalto ALD Forum Dec 11, 2018
Defence of dissertation in the field of Chemistry, M.Sc. Anne Tanskanen created by Riikka Puurunen	Aalto ALD Forum Nov 22, 2018
Visiting lecture, Prof Sean Barry, Precursors and Atomic Layer Deposition of Gold Metal, Nov 27, Ke 2, 10:00 created by Riikka Puurunen	Aalto ALD Forum Nov 22, 2018
Intro and question: who uses ALD and how can we benefit from this Aalto ALD Forum wikispace? created by Riikka Puurunen	Aalto ALD Forum Nov 14, 2018
Introductory lecture on ALD by Puurunen openly shared created by Riikka Puurunen	Aalto ALD Forum Nov 09, 2018
New ebook bought at Aalto: Yanguas-Gil on growth and transport in deposition created by Riikka Puurunen	Aalto ALD Forum Jan 25, 2018
Aalto ALD Forum created created by Antti Karttunen	Aalto ALD Forum Jan 25, 2018

Propose pictogram for ALD? Some recent evolutions…

https://twitter.com/jv3sund/status/1096384848955084800

https://twitter.com/rlpuu/status/1096419723162669056

https://twitter.com/sean_t_barry/status/1096442185065459714

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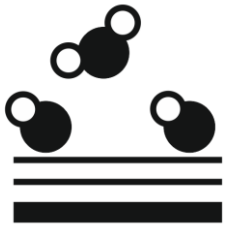
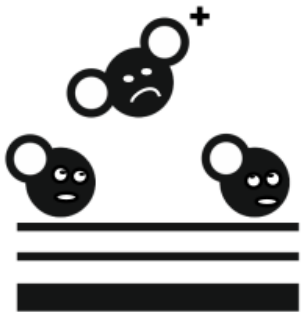


https://twitter.com/JRvanOmmen/status/1096642307049304064



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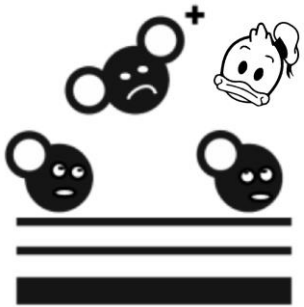
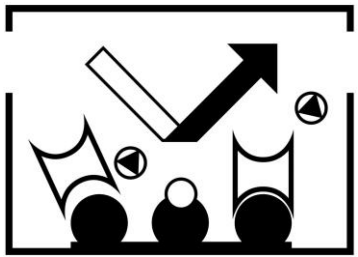


https://twitter.com/JRvanOmmen/status/1097725822587322368



https://twitter.com/Juuhonber/status/1099686334078296065

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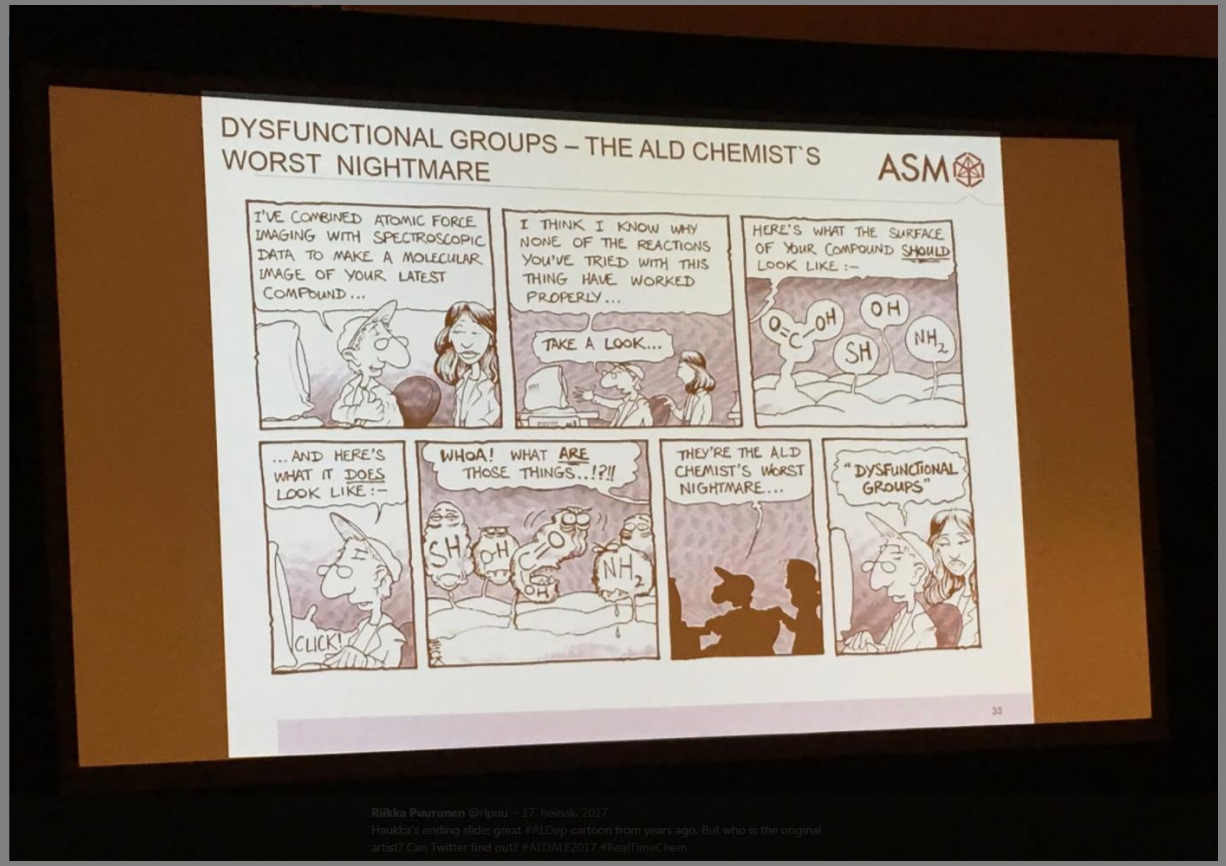

Riikka Puurunen @rlpuu · 17. heinäk. 2017
Haukka's ending slide: great #ALDep cartoon from years ago. But who is the original artist? Can Twitter find out? #ALDALE2017 #RealTimeChem

https://twitter.com/rlpuu/status/887000374795796480
Haukka's ending slide: great #ALDep cartoon from years ago. But who is the original artist? Can Twitter find out? #ALDALE2017 #RealTimeChem

→ Nick Kim: http://www.lab-initio.com