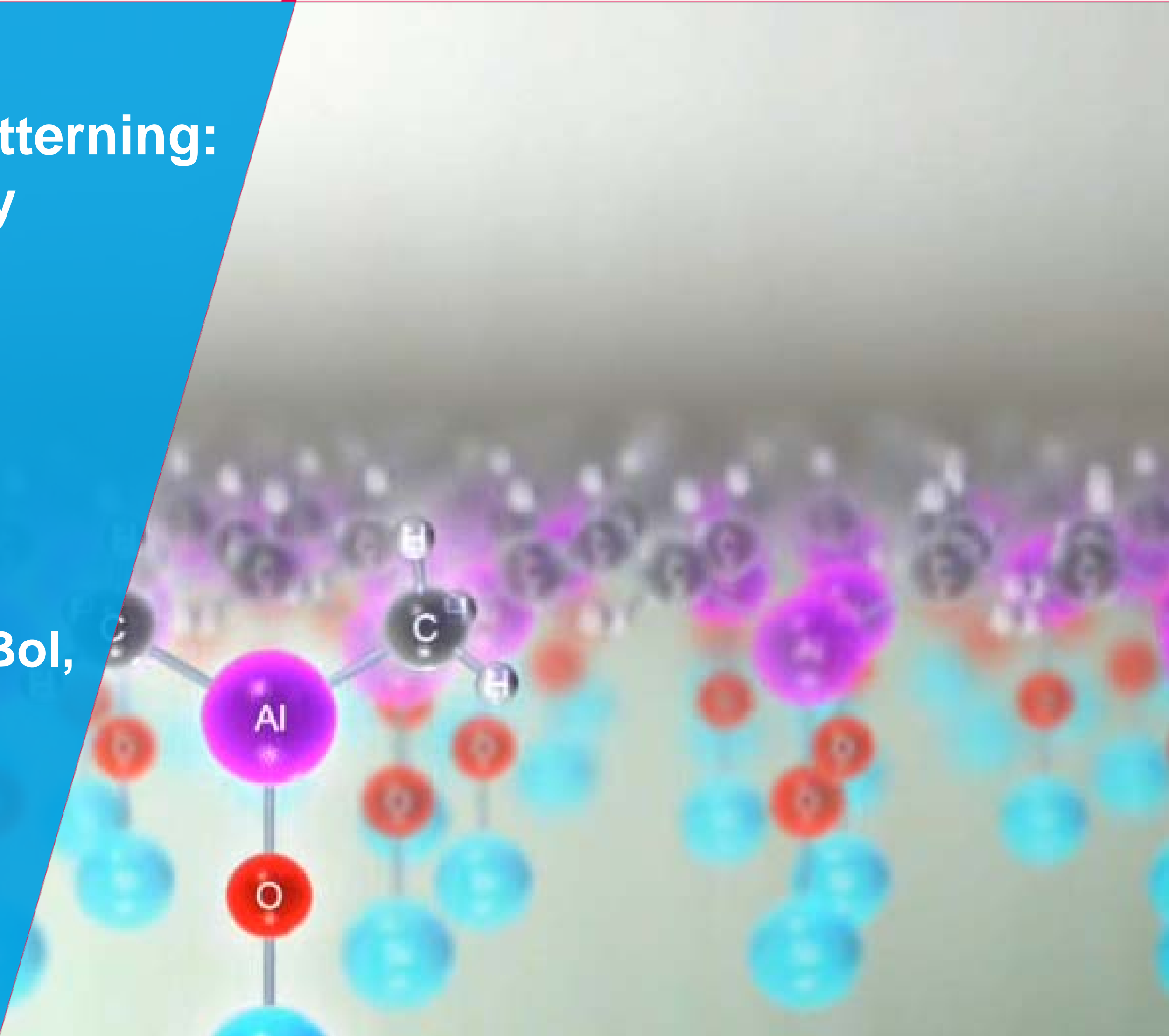
TU/e Technische Universiteit Eindhoven University of Technology

ALD-enabled nanopatterning: area-selective ALD by area-activation



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Outline

- Introduction & Area-selective deposition
- Area-selective ALD by **area-deactivation**
  - Example: **blocking with polyimide**
- Area-selective ALD by **area-activation**
  - Example: **EBID & ALD of Pt (direct-write ALD)**
  - Intermezzo: μ-contact printing & ALD of Ru
  - Example: **μ-plasma printing & ALD of In_2O_3 (direct-write ALD)**
- Summary

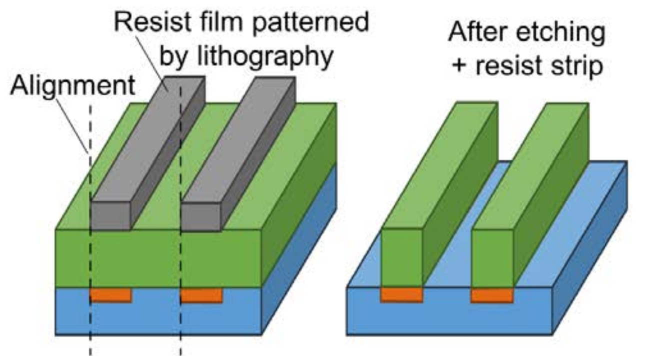
Selective deposition for bottom-up processing

Top-down

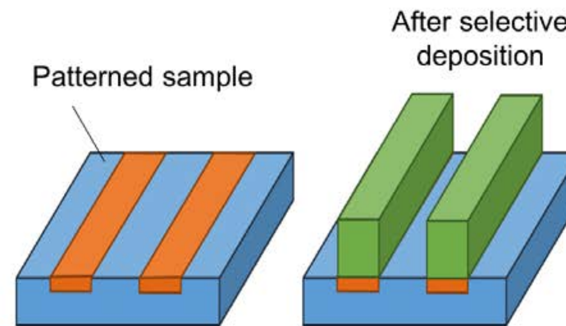
Excavated from solid rock

Bottom-up

Bricks as building blocks



Current process flow
Removal of excess material using etching

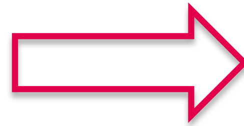


Future: **selective deposition**
Only adding material where needed

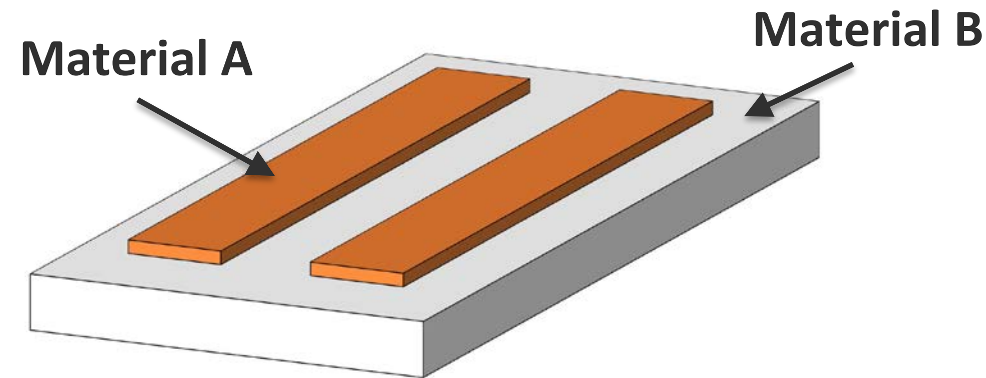
"**Subtractive**" processes "**Additive**" processes

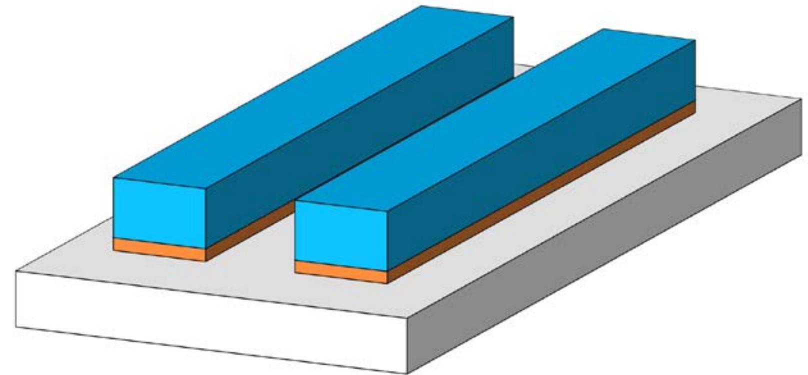
Area-selective deposition

Surface with material A and material B

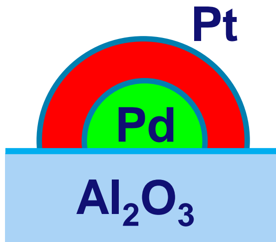


Growth on material A only, not on material B

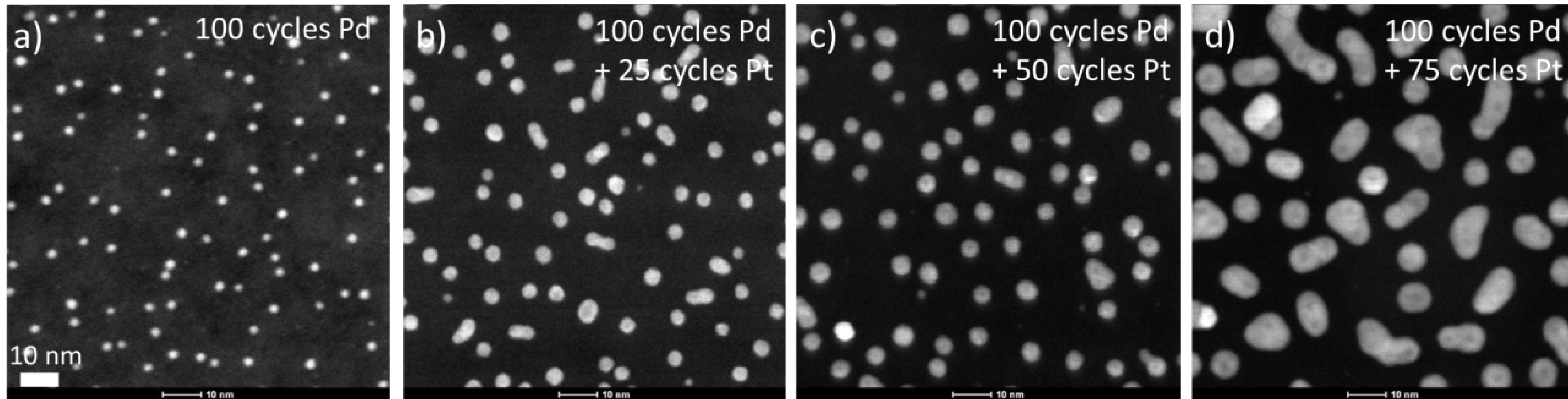




Area-selective deposition: core-shell nanoparticles



1. Deposit Pd nanoparticles by ALD
2. Deposit Pt shell by area-selective ALD on Pd core



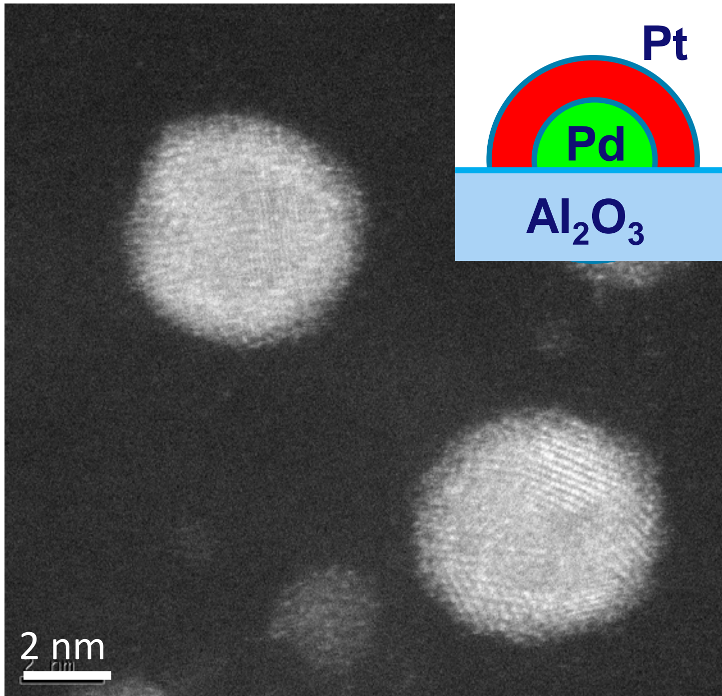
Fixed core diameter (100 cycles Pd)

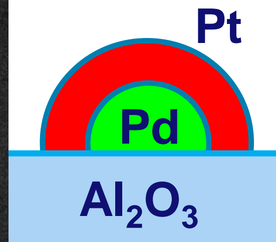
with **varying shell thickness** (0, 25, 50 and 75 cycles Pt)

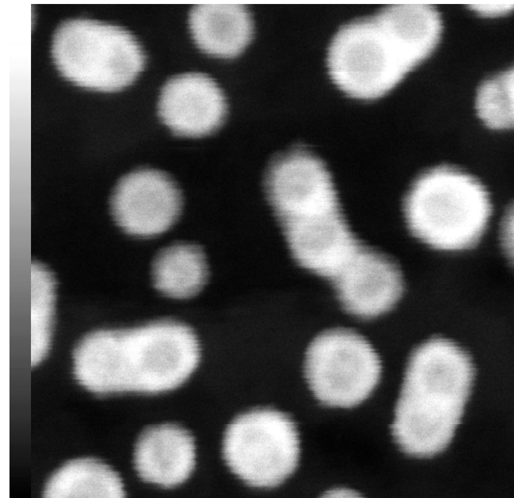
Weber *et al.*, Chem. Mater. 24, 2973 (2012).
Weber *et al.*, Nanotechnology 26, 094002 (2015).

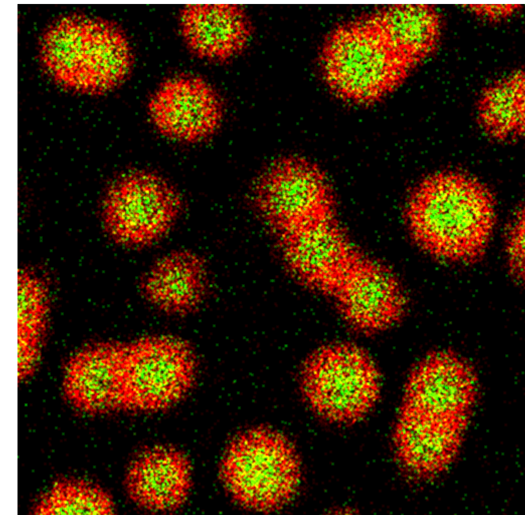
Area-selective ALD: core-shell nanoparticles

HAADF-STEM imaging

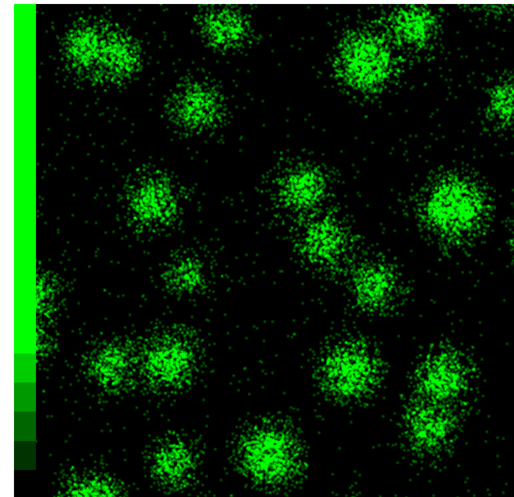


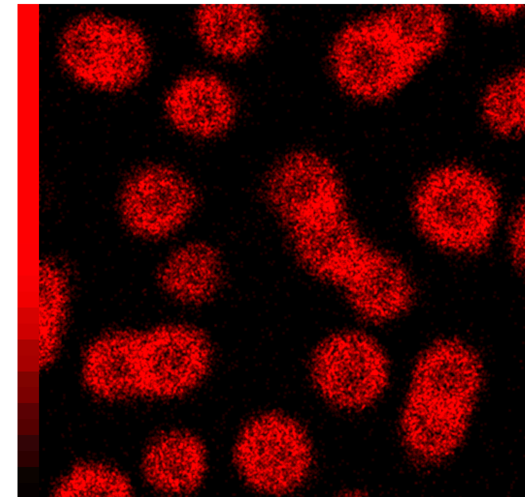






EDS mapping





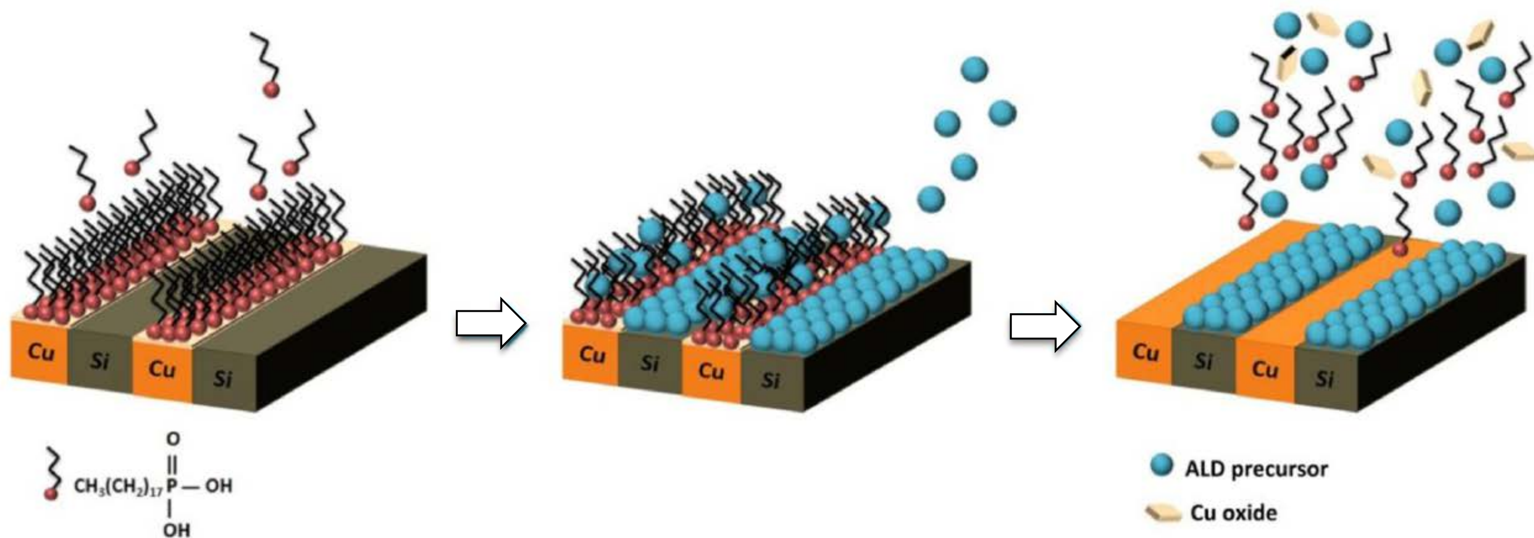
Weber *et al.*, Chem. Mater. 24, 2973 (2012).
Weber *et al.*, Nanotechnology 26, 094002 (2015).

Area-selective deposition: Al_2O_3 on Cu/SiO_2

Patterned Cu/SiO_2: SAMS grow on $Cu(O_x)$

ALD of Al_2O_3 on SiO_2 and (ultimately) on SAMS

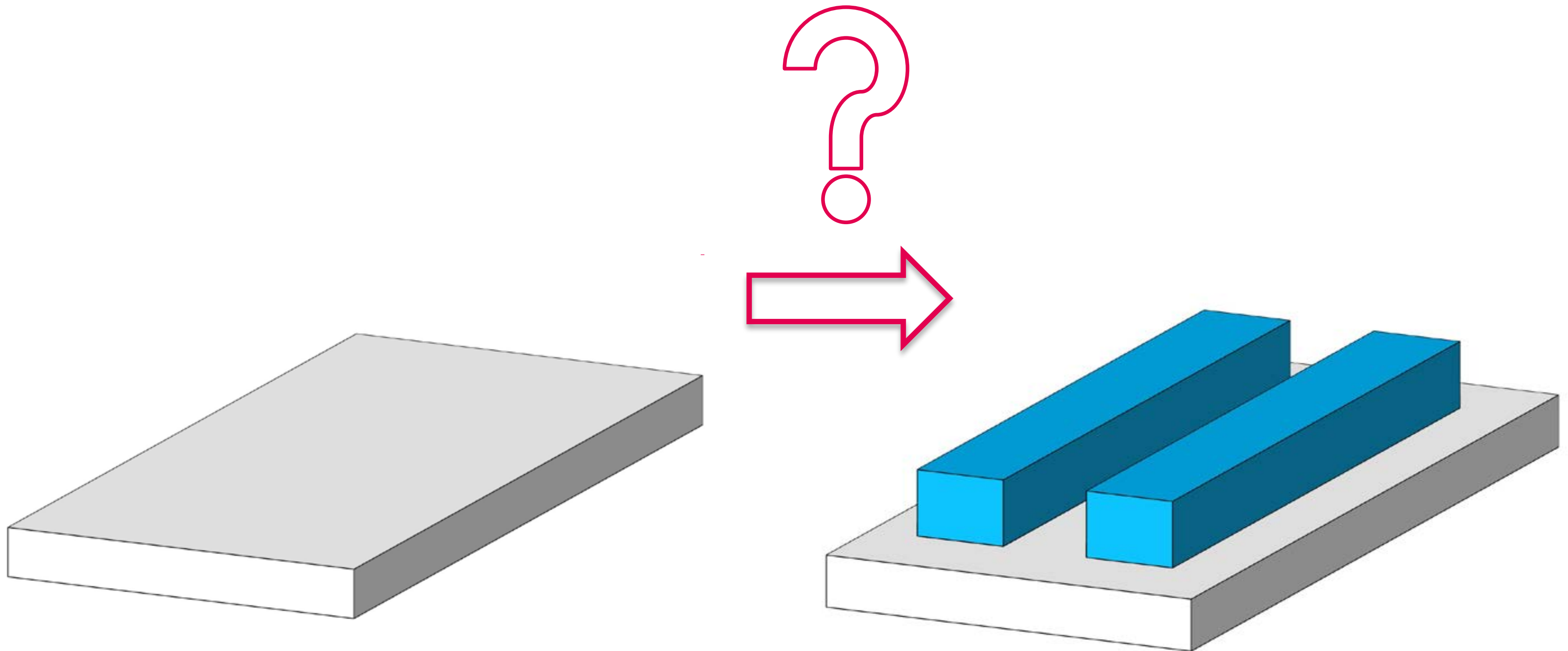
Selective etch of Al_2O_3 and SAMS



- The SAMS grow **selectively** on the Cu(Ox) and not on the SiO_2
- Al_2O_3 grows on **both the SiO_2 and on the SAMS** (albeit with some delay and with a lower quality)

Minaye Hashemi *et al.*, ACS Nano 9, 8710 (2015).

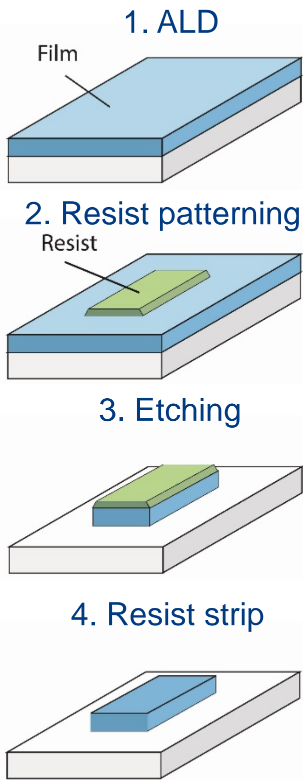
Nanopatterning using area-selective ALD?



ALD-enabled patterning

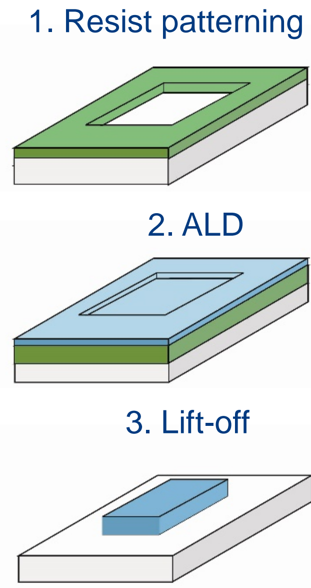
Conventional:

Etching

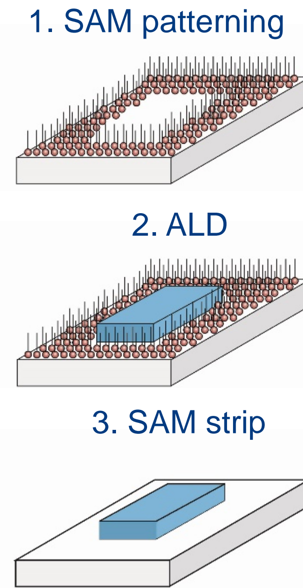


ALD-enabled:

Lift-off

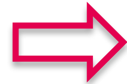
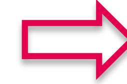


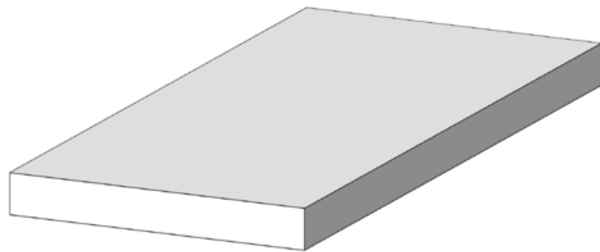
Area-selective ALD by area-deactivation

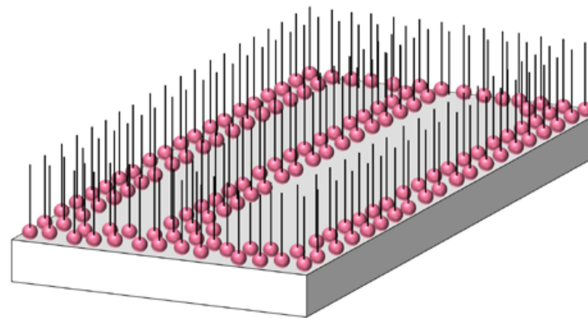


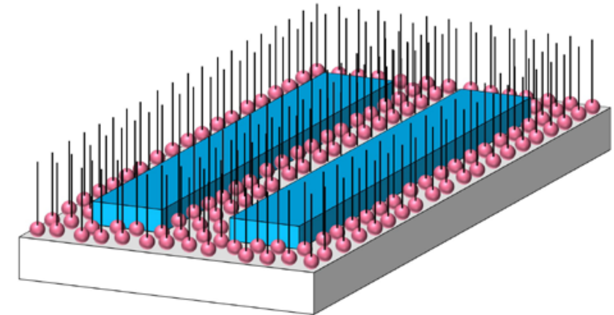
Mackus *et al.*, Nanoscale 6, 10941 (2014).

Area-selective ALD by area-deactivation

Blank substrate  Areas masked by photosensitive material or SAMs  ALD on open areas only





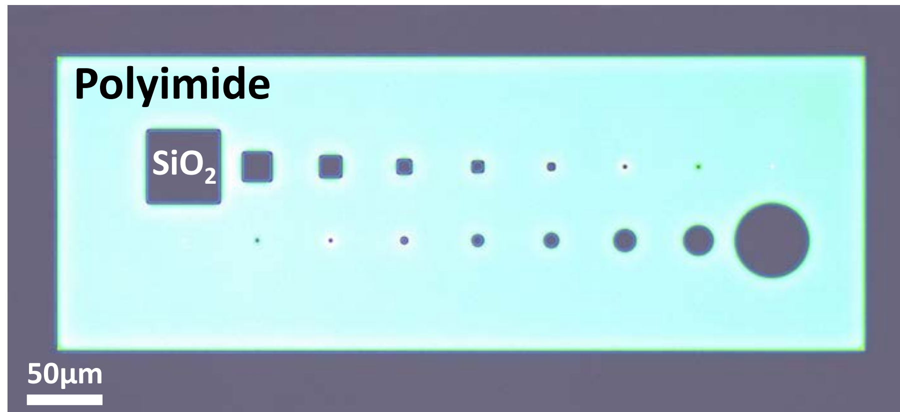


No deposition on the masking material (otherwise lift-off)

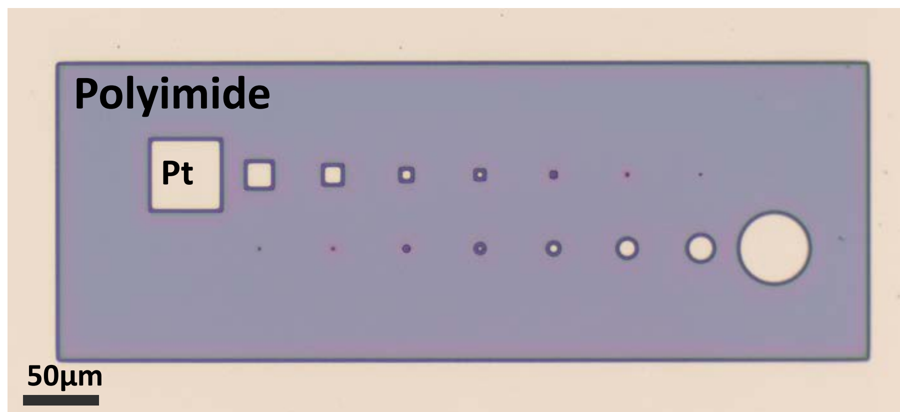
The masking of the substrate by photosensitive material or by SAMs requires a patterning step (typically subtractive)!

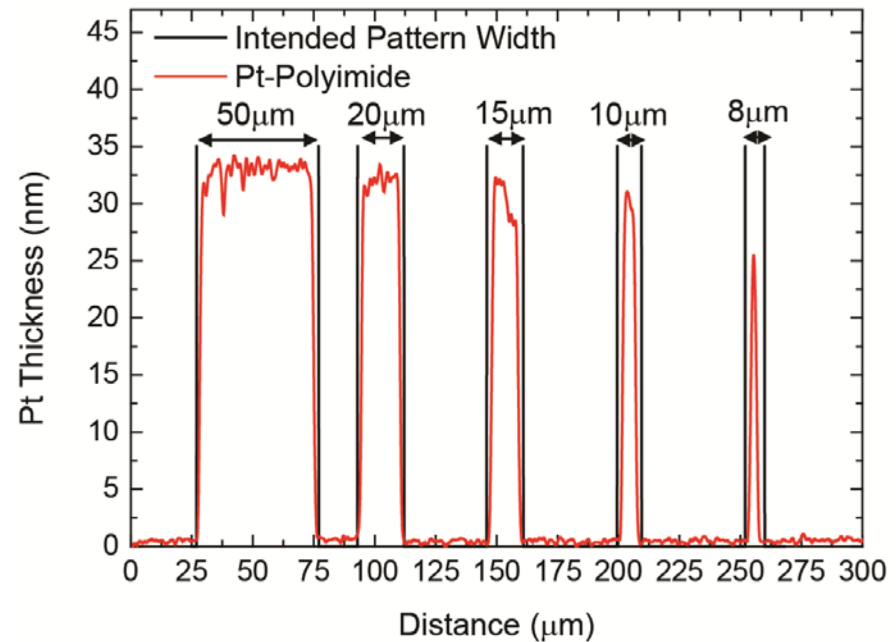
AS-ALD by area-deactivation: using polyimide

After polyimide photolithography patterning



After 1000 cycles Pt ALD (300 °C)

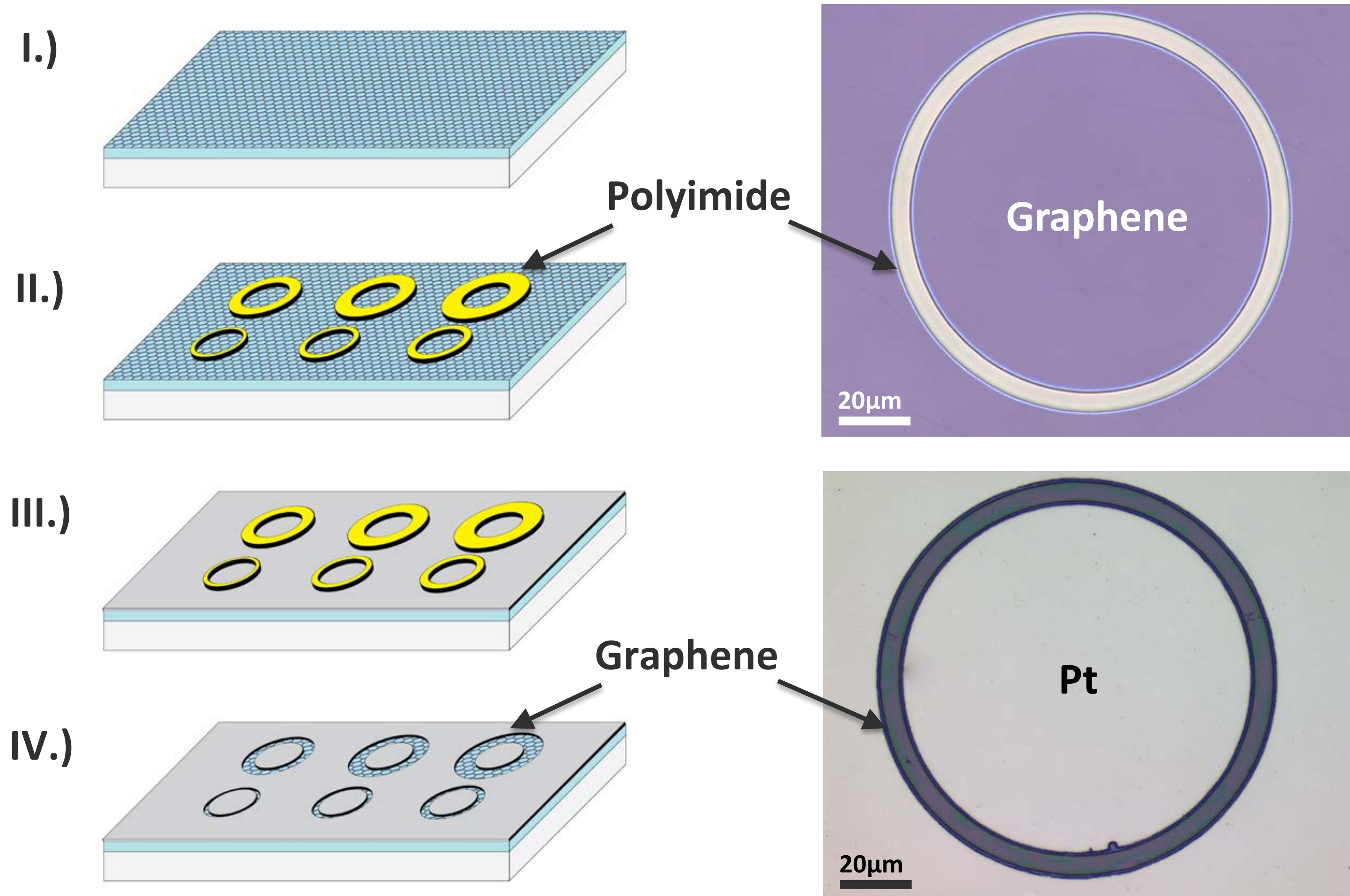




- Pt does not deposit on polyimide so **no lift-off**
- Polyimide does not "flow" at 300 ° C so **well-controlled pattern width**

Vervuurt *et al.*, Nanotechnology 27, 405302 (2016).

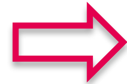
AS-ALD by area-deactivation: using polyimide



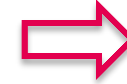
Vervuurt *et al.*, Nanotechnology 27, 405302 (2016).

Area-selective ALD by area-deactivation

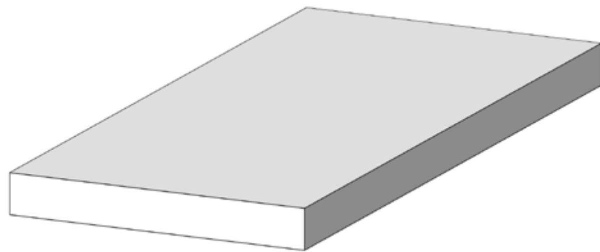
Blank substrate

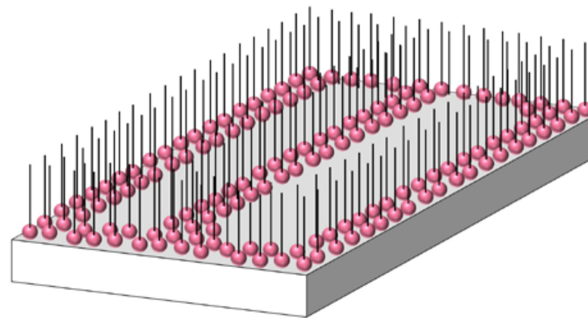


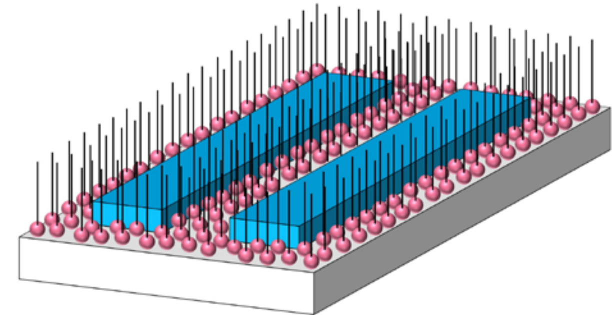
Areas masked by photosensitive material or SAMs



ALD on open areas only







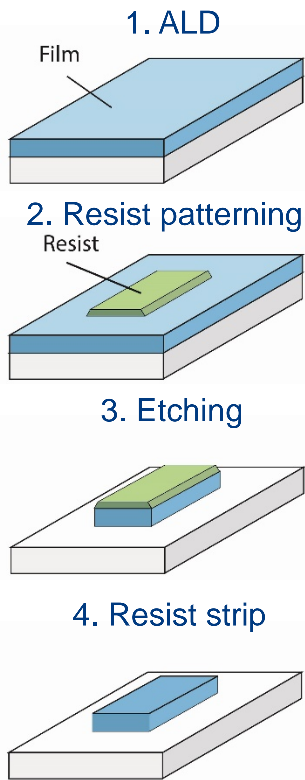
No deposition on the masking material (otherwise lift-off)

The masking of the substrate by photosensitive material or by SAMs requires a patterning step (typically subtractive)!

Summary: ALD-enabled patterning

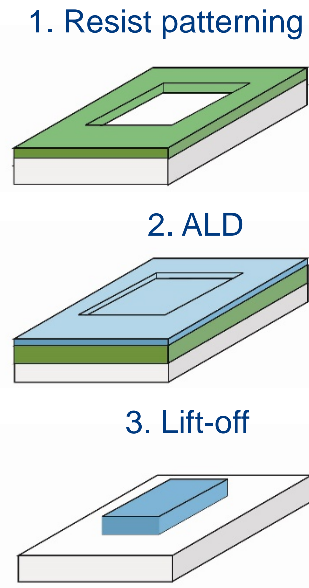
Conventional:

Etching

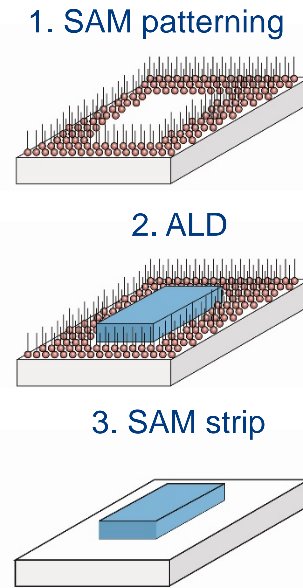


ALD-enabled:

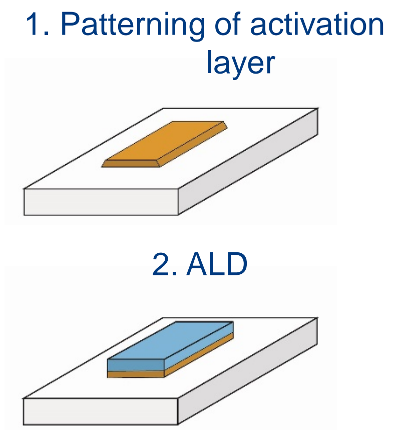
Lift-off



Area-selective ALD by area-deactivation



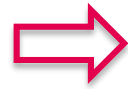
Area-selective ALD by area-activation



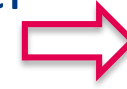
Mackus *et al.*, Nanoscale 6, 10941 (2014).

Area-selective ALD by area-activation

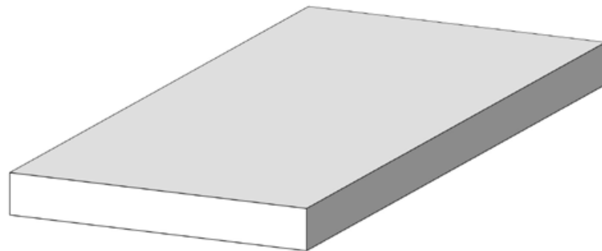
Blank substrate

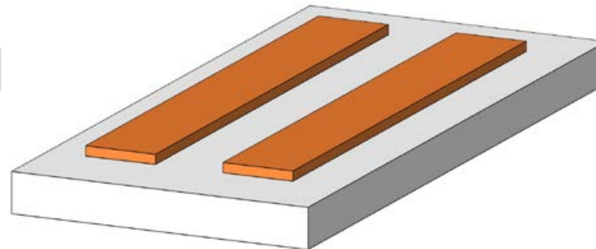


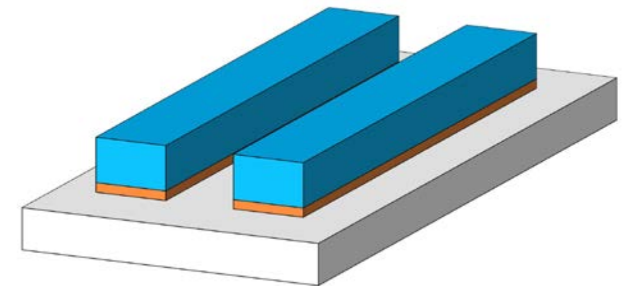
Local activation of surface by seed layer or modification surface groups, etc.



ALD on activated areas only





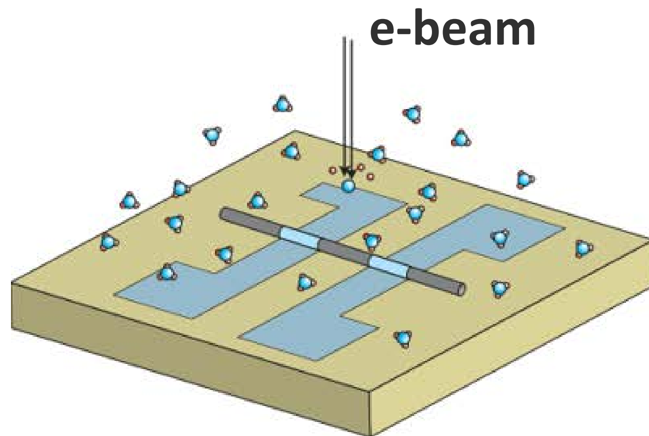


The local activation is a patterning step but it is not subtractive!

AS-ALD by area-activation: EBID & ALD of Pt

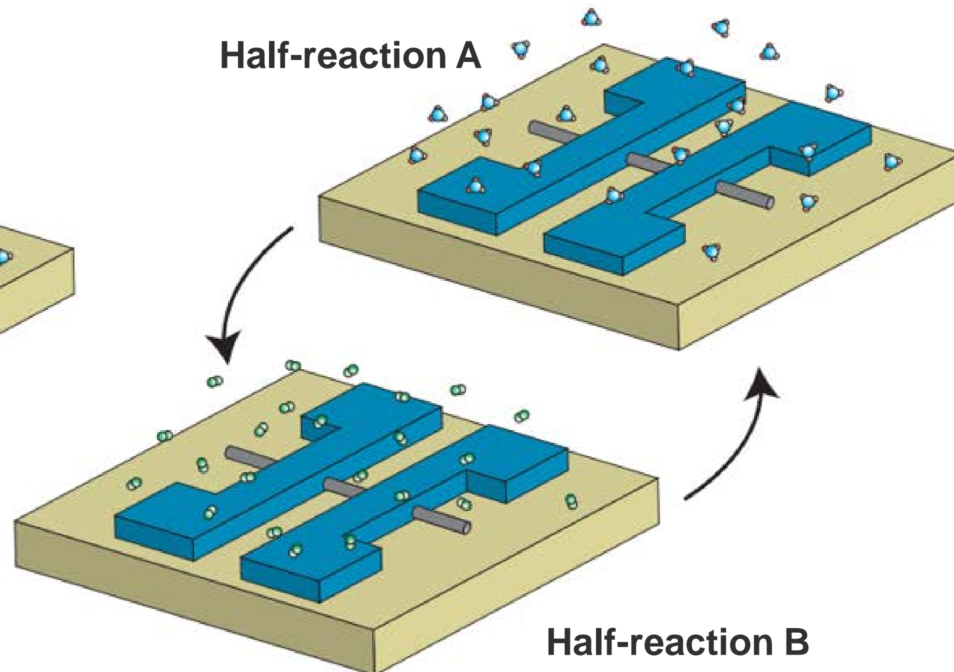
1. Patterning step:

e-beam induced deposition (EBID)



2. Building step:

Atomic layer deposition (ALD)



Two-step process:

- Patterning: ultrathin (<1 ML) seed layer on oxide by **EBID**
- Building: **area-selective ALD** on seed layer

FEI COMPANY™ Tools for Nanotech

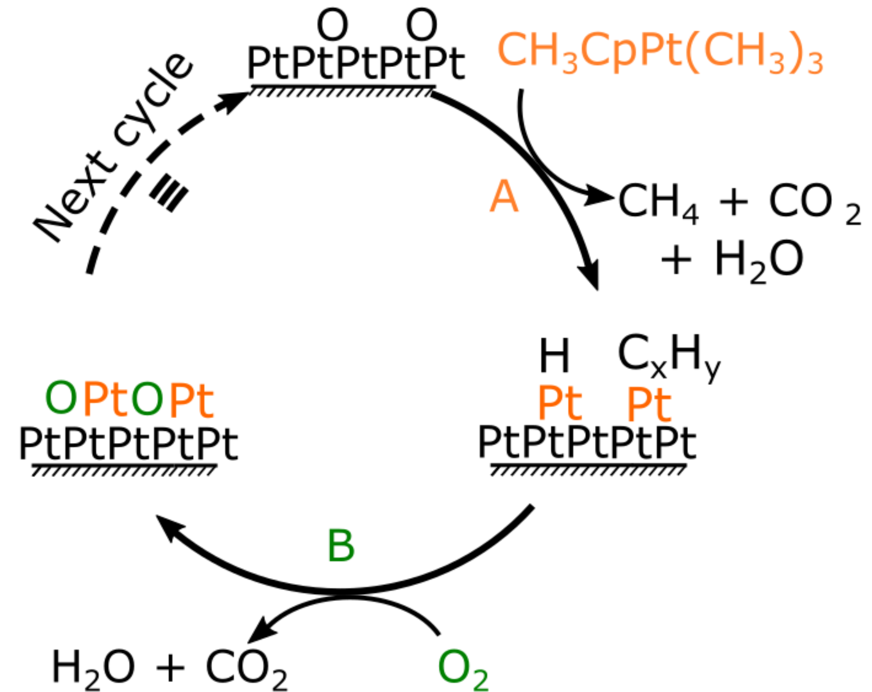
Mackus *et al.*, Nanoscale 4, 4477 (2012).
US patent: 8,268,532 (2012).

AS-ALD by area-activation: EBID & ALD of Pt

1. **Patterning step:** EBID

2. **Building step:** ALD

FEI Nova Nanolab 600



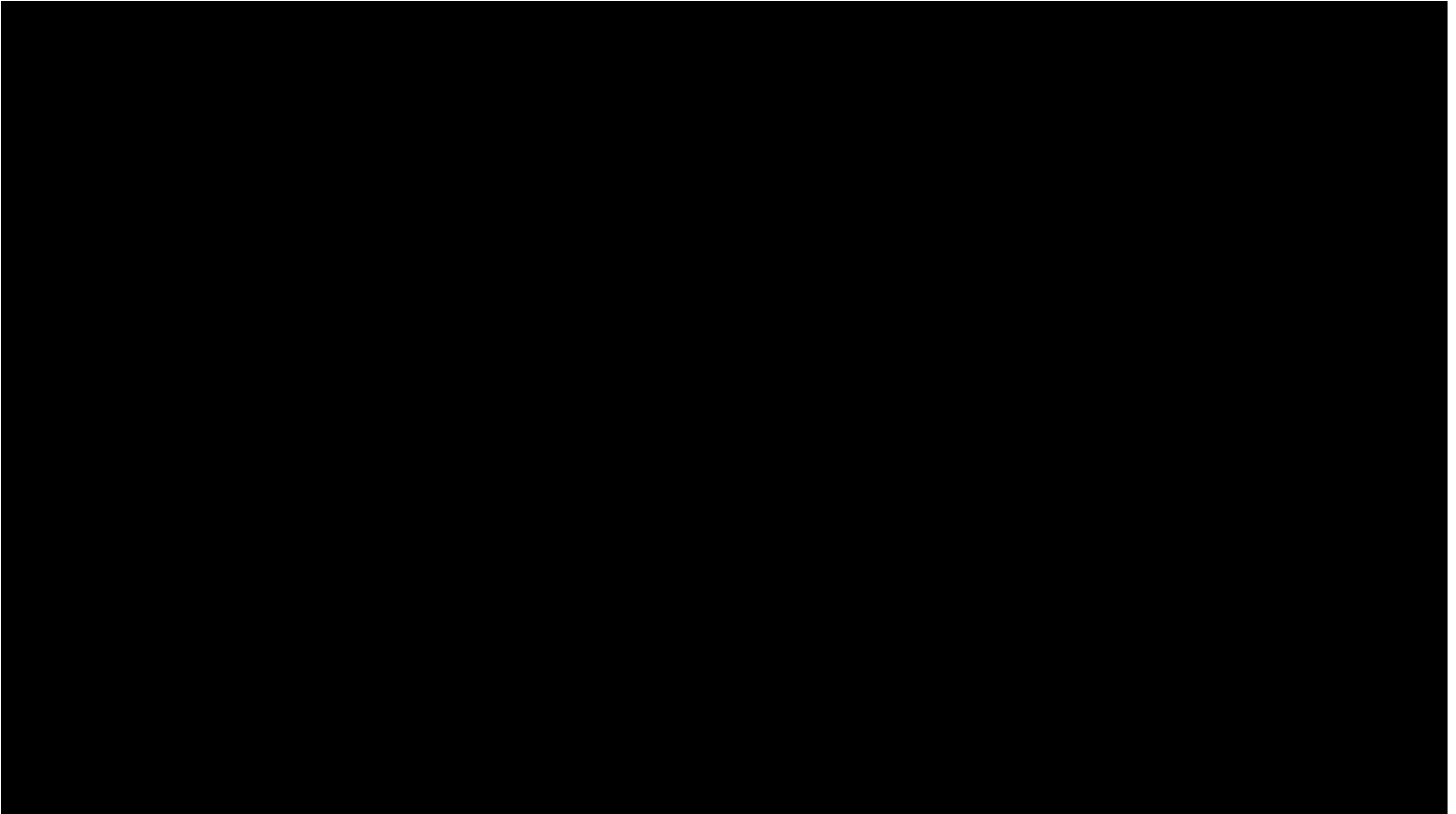
Pattering with:

- **Nanoscale resolution** of electron beam induced deposition (EBID)
- High Pt **material quality** as obtained by ALD

FEI COMPANY™ TOOLS FOR NANOTECH

Mackus *et al.*, Nanoscale 4, 4477 (2012).
US patent: 8,268,532 (2012).

Direct-write ALD with e-beam patterning

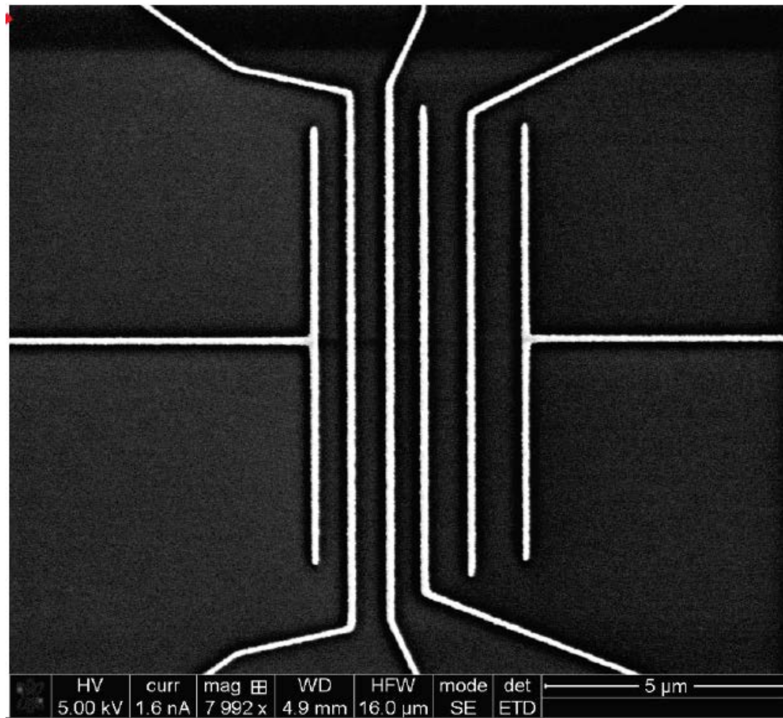


Direct-write: maskless and “templateless” patterning

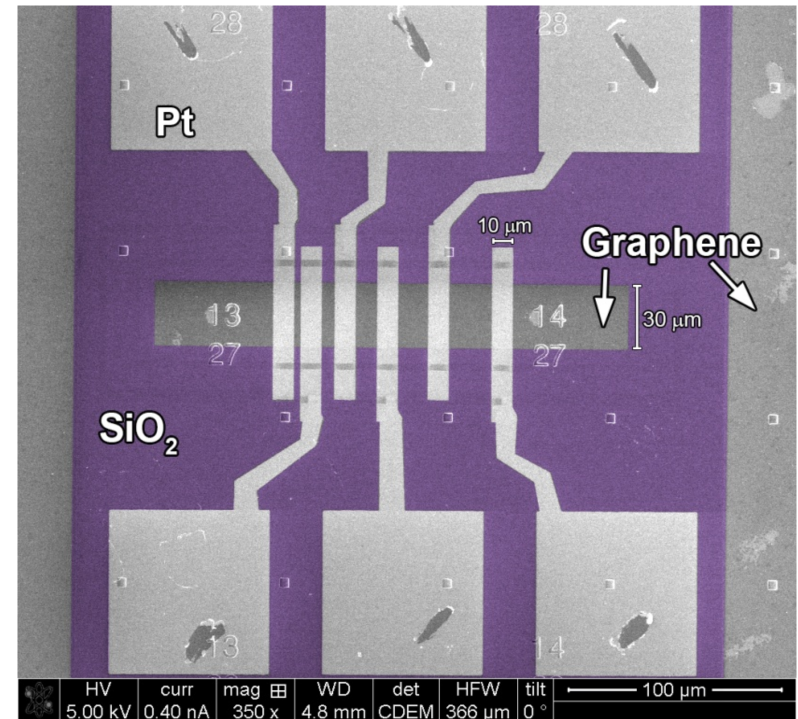
Mackus *et al.*, Nanoscale 4, 4477 (2012).
US patent: 8,268,532 (2012).

Direct-write ALD of Pt contacts

Back-gated (**single-wall**) **CNTFET** with direct-write ALD **Pt** contacts



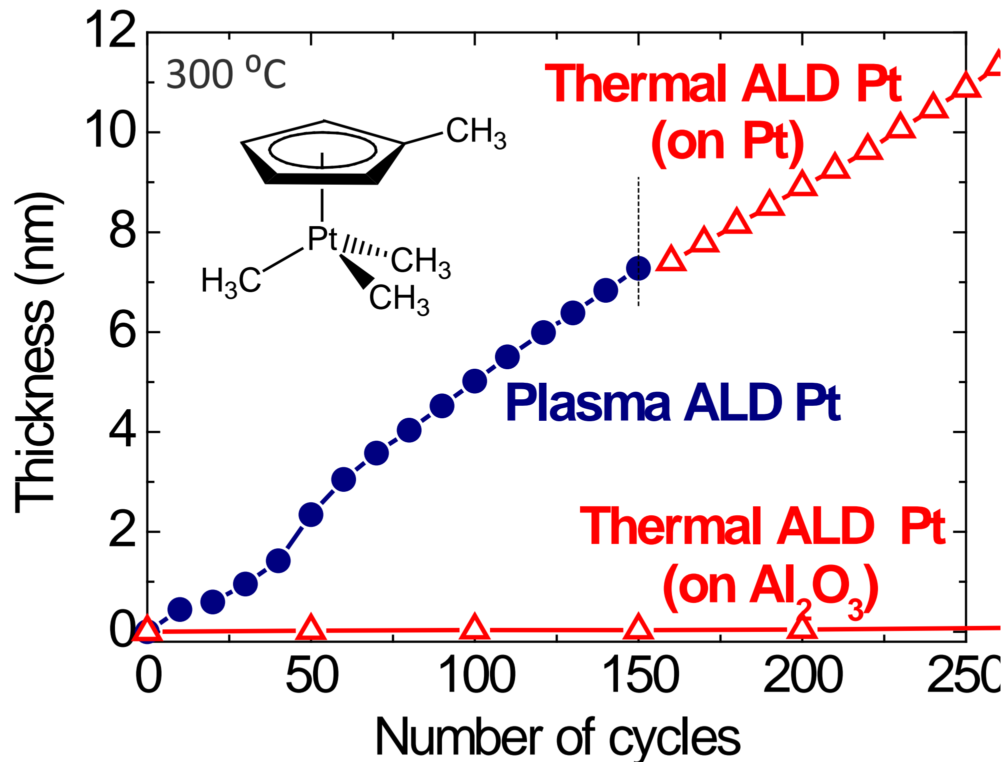
TLM structure on **graphene** with direct-write ALD **Pt** contacts

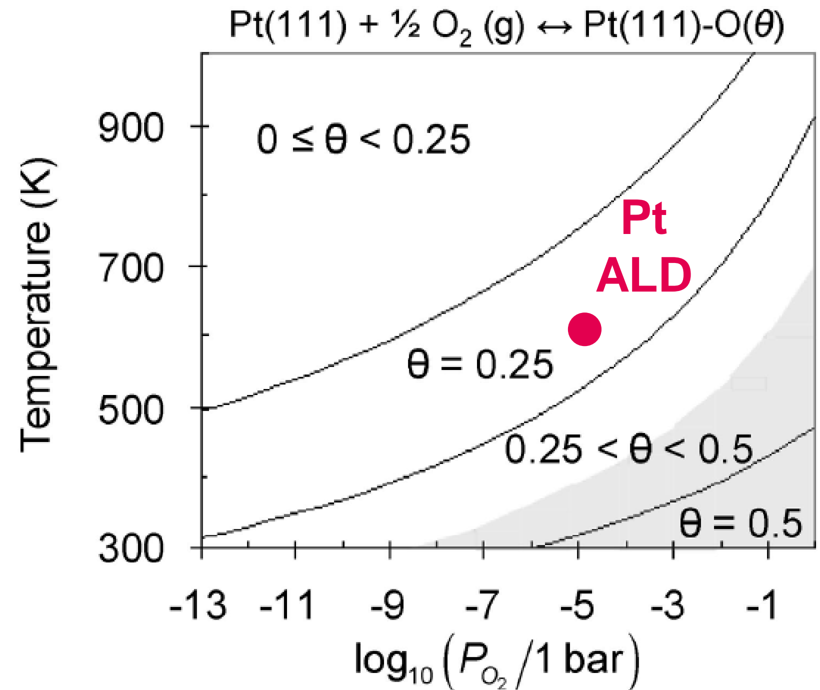


FEI COMPANY™ TOOLS FOR NANOTECH

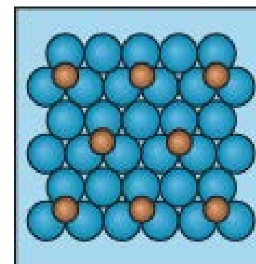
Mackus *et al.*, Appl. Phys. Lett. 110, 013101 (2017).
Thissen *et al.*, 2D Mater. 4, 025046 (2017).

Underlying surface science: Pt dissociates O_2





Pt nucleates **poorly** on oxides
Nucleation depends on **O_2 pressure** and **sample temperature**



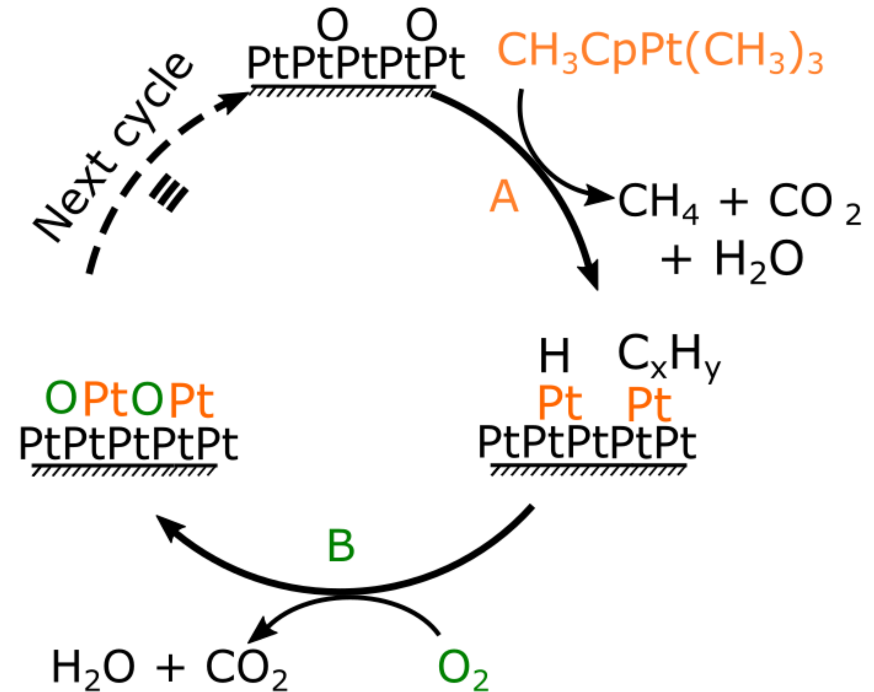
Mackus *et al.*, Chem. Mater. 25, 1905 (2013)
Getman *et al.*, J. Phys. Chem. C 112, 26 (2008)

AS-ALD by area-activation: EBID & ALD of Pt

1. Patterning step: EBID

2. Building step: ALD

FEI Nova Nanolab 600



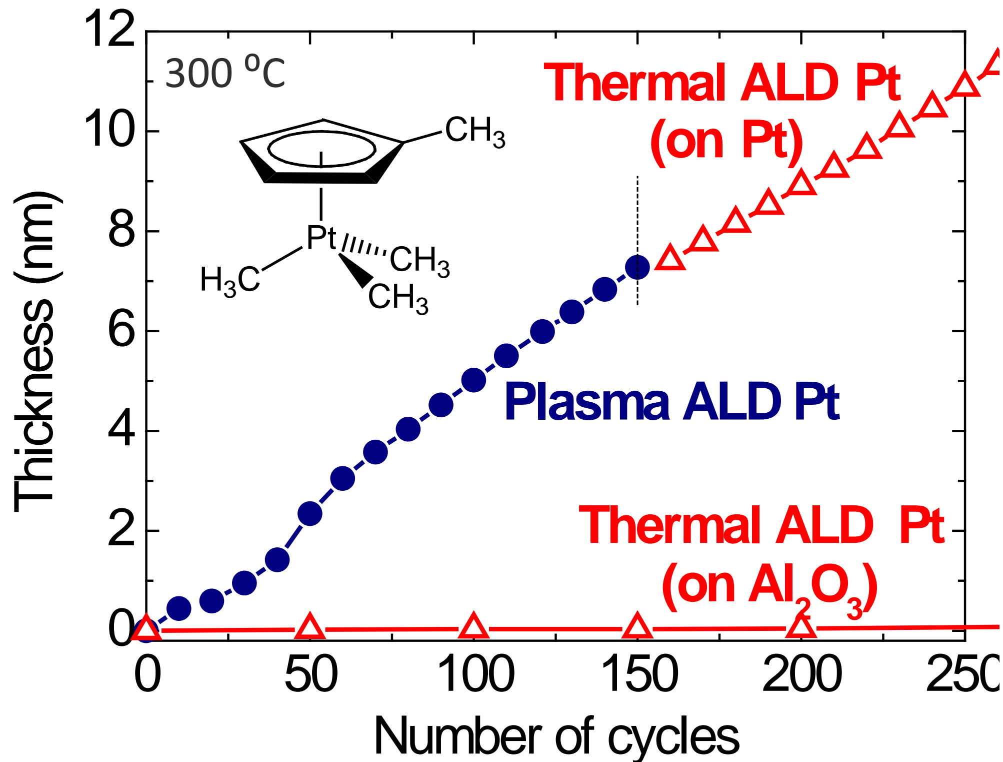
Pattering with:

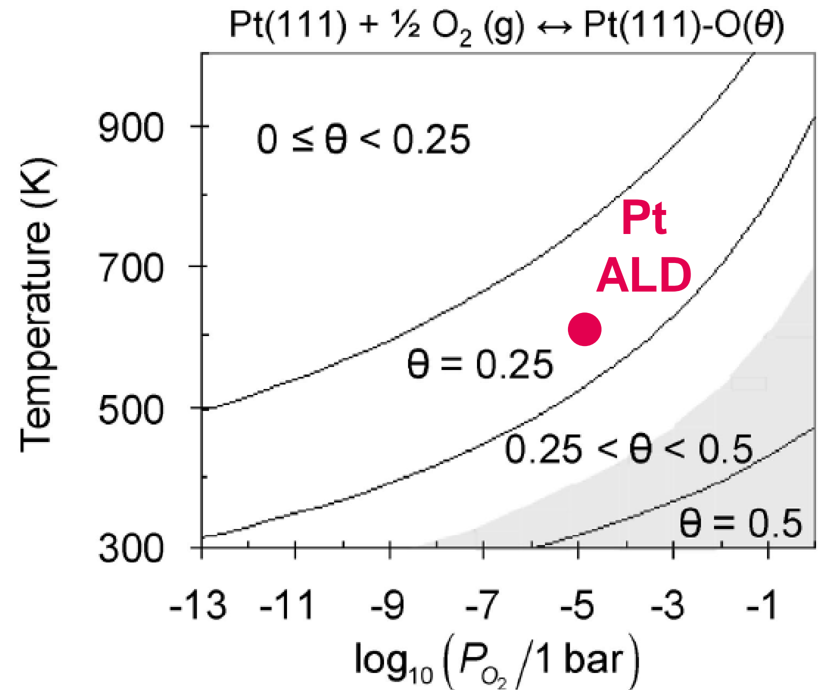
- **Nanoscale resolution** of electron beam induced deposition (EBID)
- High Pt **material quality** as obtained by ALD

FEI COMPANY™ TOOLS FOR NANOTECH

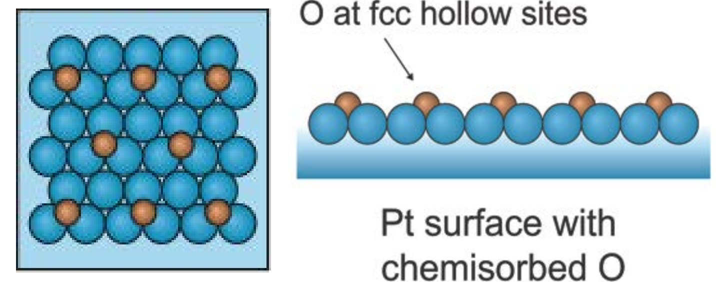
Mackus *et al.*, Nanoscale 4, 4477 (2012).
US patent: 8,268,532 (2012).

Underlying surface science: Pt dissociates O_2



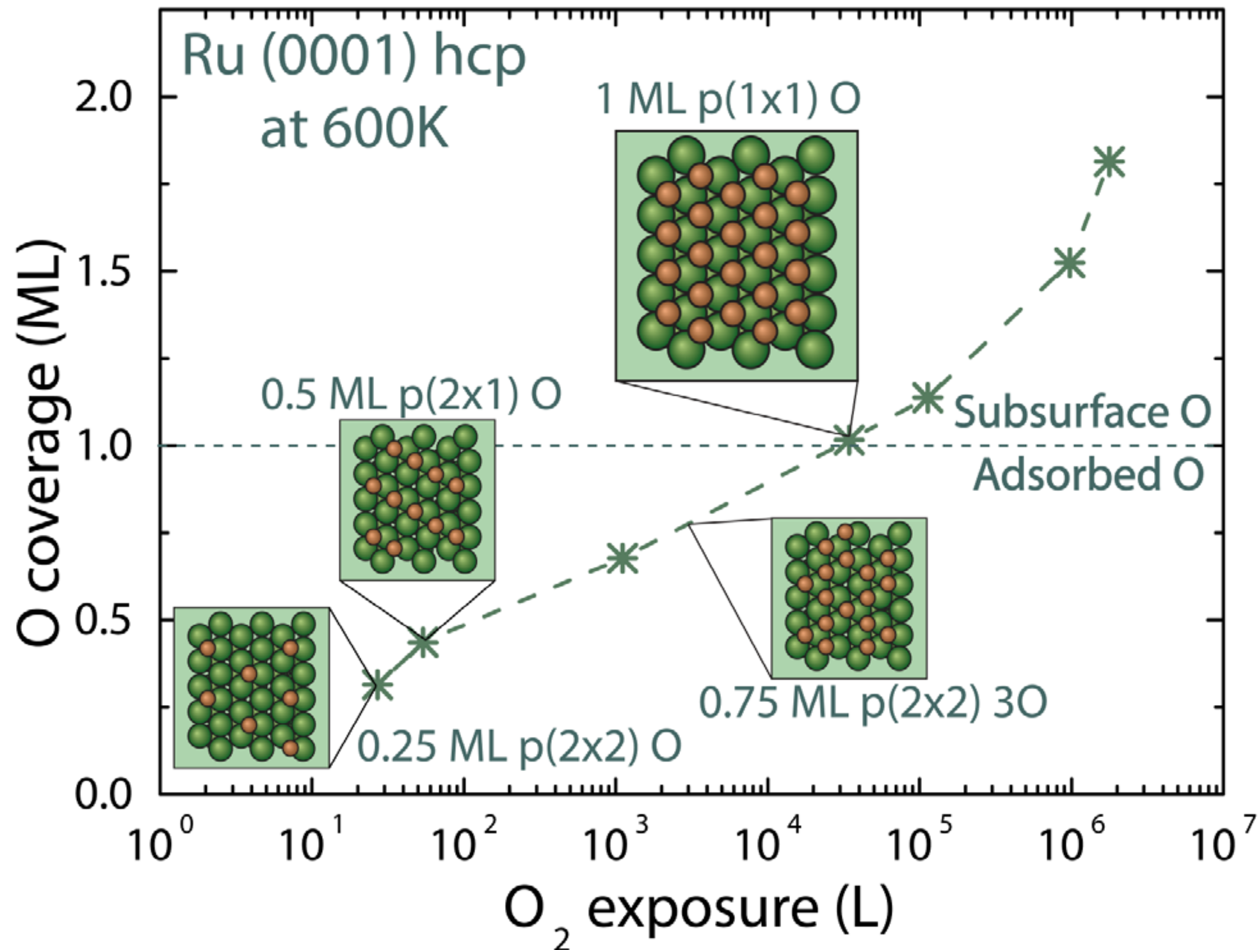


Pt nucleates **poorly** on oxides
Nucleation depends on **O_2 pressure** and **sample temperature**



Mackus *et al.*, Chem. Mater. 25, 1905 (2013).
Getman *et al.*, J. Phys. Chem. C 112, 26 (2008).

Underlying surface science: Ru dissociates O_2

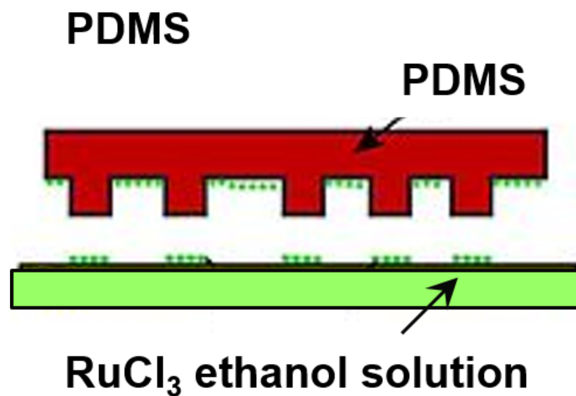


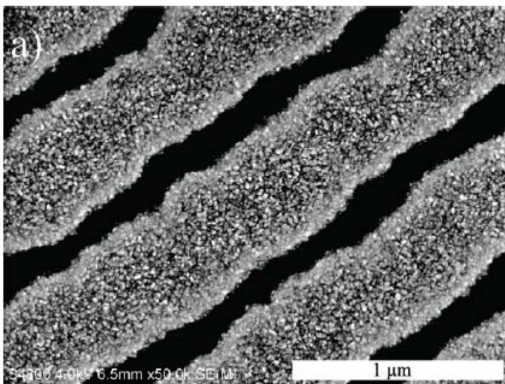
Leick *et al.*, J. Phys. Chem. C 117, 21320 (2013) and references therein.

AS-ALD by area-activation: μ-CP & ALD of Ru

1. Patterning step:

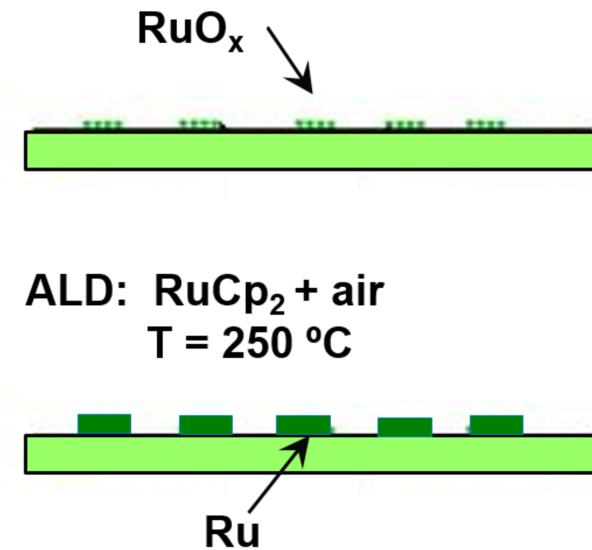
Micro-contact printing





2. Building step:

Atomic layer deposition (ALD)



Ru temperature window = 275 – 400 ^{o}C

Ru does **not nucleate** just below temperature window: **250 ^{o}C**

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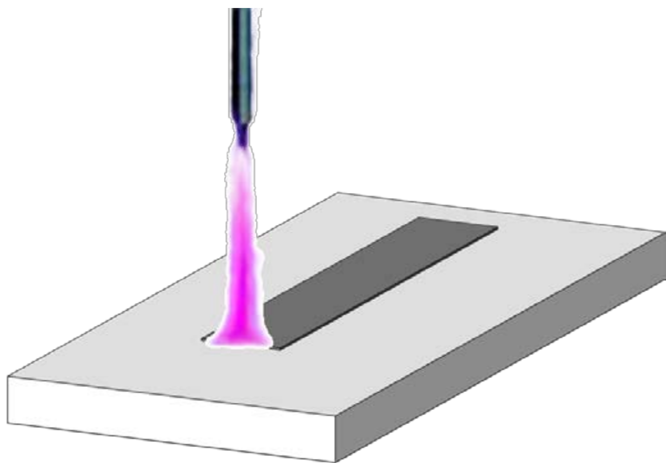
Färm *et al.*, Chem. Mater. 24, 275 (2012).

Outline

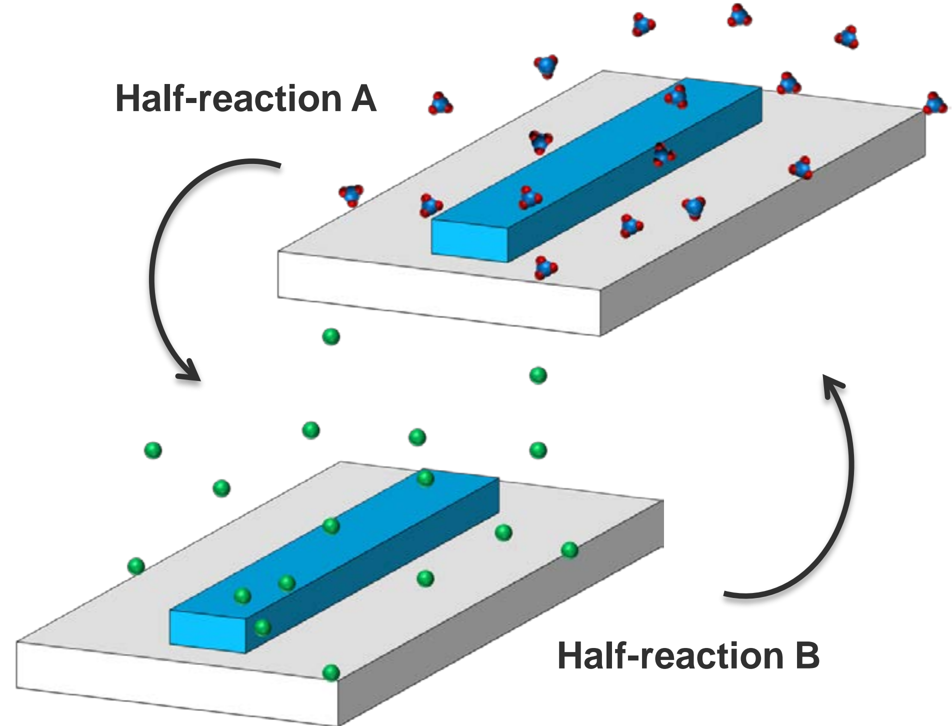
- Introduction & Area-selective deposition
- Area-selective ALD by **area-deactivation**
  - Example: **blocking with polyimide**
- Area-selective ALD by **area-activation**
  - Example: **EBID & ALD of Pt (direct-write ALD)**
  - Intermezzo: μ-contact printing & ALD of Ru
  - Example: **μ-plasma printing & ALD of In_2O_3 (direct-write ALD)**
- Summary

AS-ALD by area-activation: μPP & ALD of In_2O_3

1. Patterning step:
μ-plasma printer (in air)



2. Building step:
Atomic layer deposition (ALD)



Two-step process:

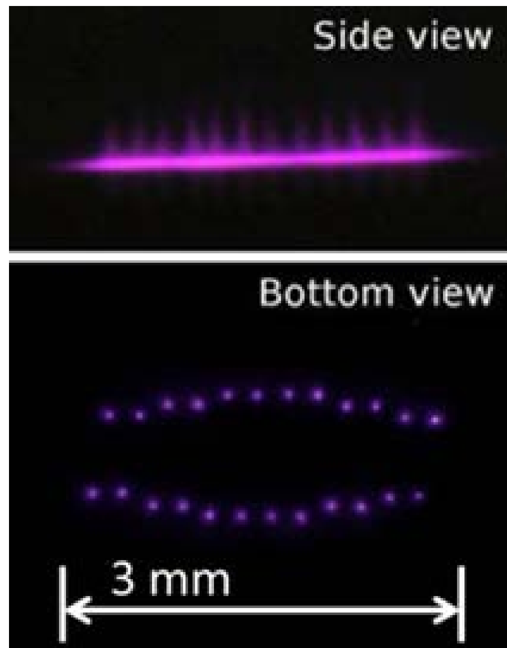
- Patterning: **plasma treatment** of H-terminated silicon surface
- Building: **area-selective ALD** on treated area

Mameli *et al.*, Chem. Mater. 29, 921 (2017).

AS-ALD by area-activation: µ-PP & ALD of In_2O_3

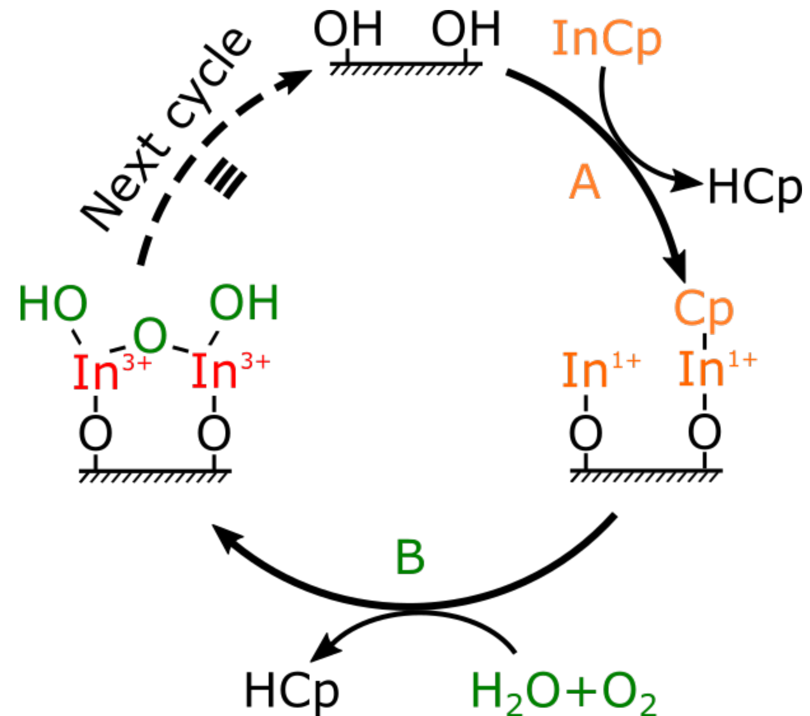
1. Patterning step:

µ-plasma printer (in air)



2. Building step:

Atomic layer deposition (ALD)



Pattering with:

- **Sub-mm resolution** of µ-plasma printer
- High In_2O_3 **material quality** as obtained by ALD

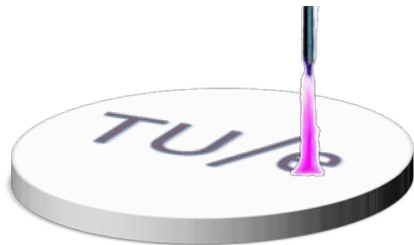
Libera *et al.*, Chem. Mater. 23, 21150 (2011).
Mameli *et al.*, Chem. Mater. 29, 921 (2017).

Direct-write ALD of In_2O_3

1)

Blank H-terminated surface

2)

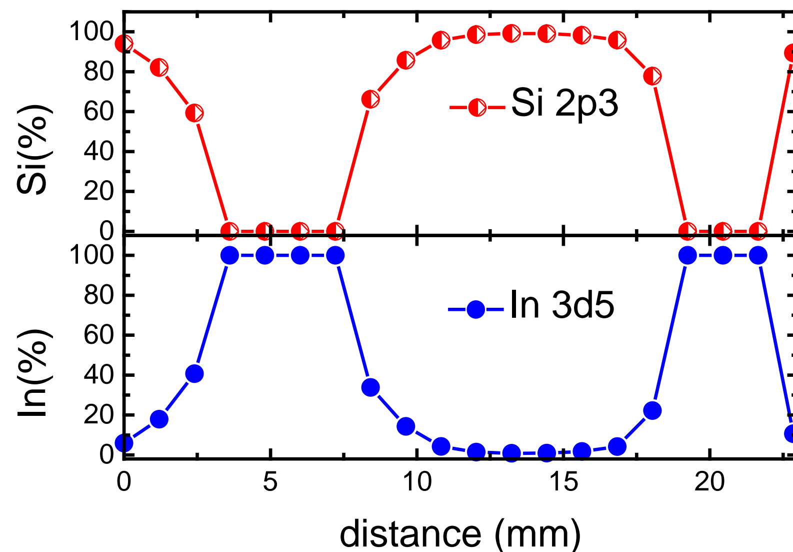


μ-plasma activation

3)

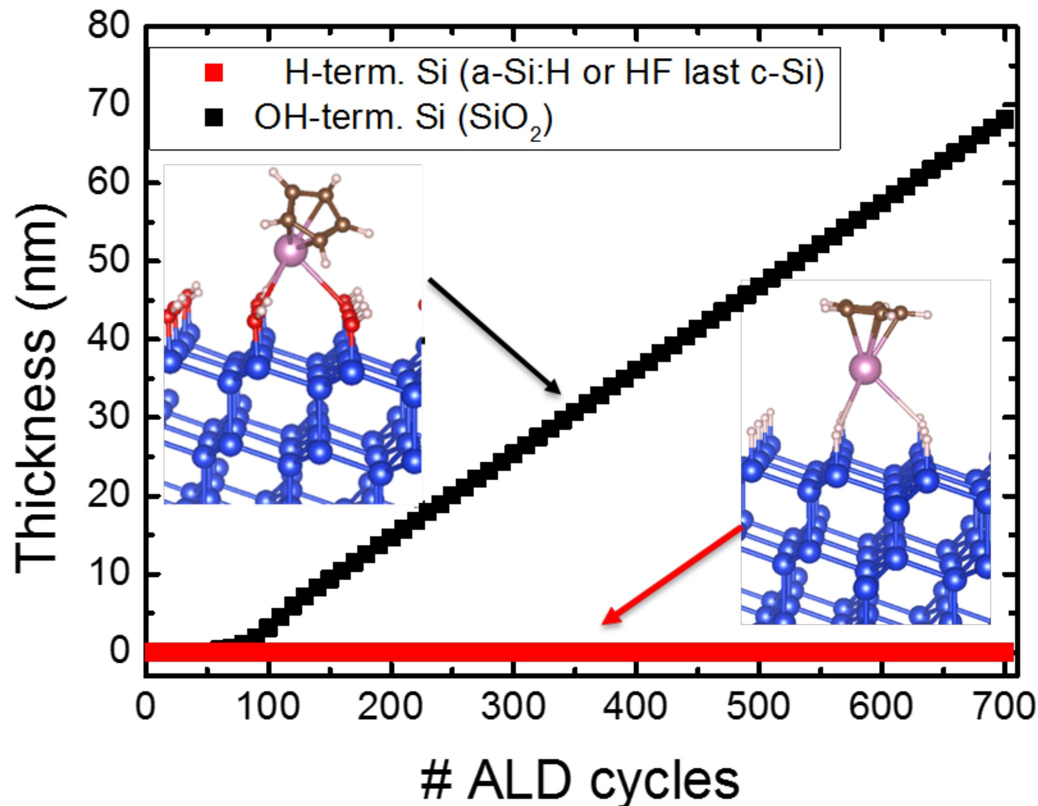
ALD

XPS linear scan



Mameli *et al.*, Chem. Mater. 29, 921 (2017).

Underlying surface science: InCp adsorption



Adsorption energies of InCp (in eV)

Si(111)-H

PBE (Avg.)	-0.021
PBE-D3 (Avg.)	-0.258

Si(111)-OH

PBE (Avg.)	-0.048
PBE-D3 (Avg.)	-0.385

Calculations in progress: Adsorption on Si(111)-OH seems thermodynamically more favorable

ALD In_2O_3 using InCp as precursor exhibits a **large nucleation delay** on **H-terminated surfaces**

Mameli *et al.*, Chem. Mater. 29, 921 (2017).

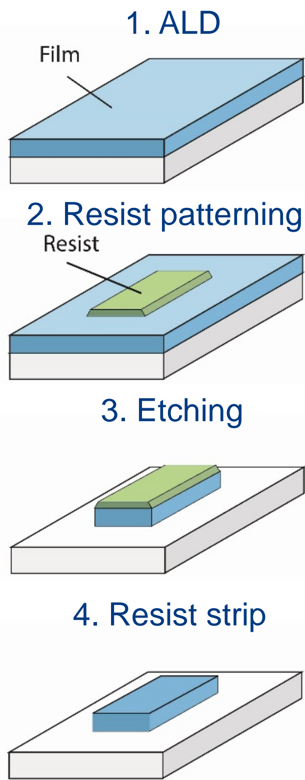
Summary

- Area-selective deposition will provide **processing solutions** for upcoming technology nodes
- There is especially interest in area-selective ALD as ALD is **starting surface dependent**
- Preferably also **nanopatterning** by area-selective ALD
- We can distinguish two approaches:
  - Area-selective ALD by **area-deactivation**
  - Area-selective ALD by **area-activation**
- Area-selective ALD by area-activation is the ultimate dream as the **surface on which no film needs to be deposited remains untouched**
- Presented two approaches that can be categorized as **direct-write ALD**
- To be continued… !

Summary: ALD-enabled patterning

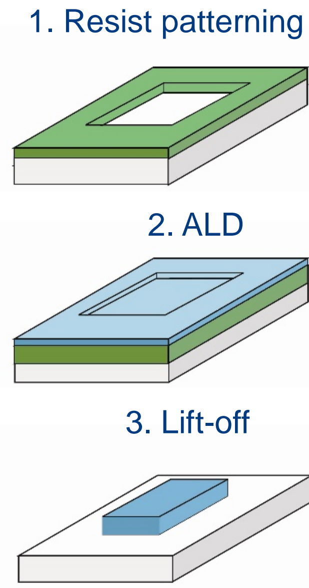
Conventional:

Etching

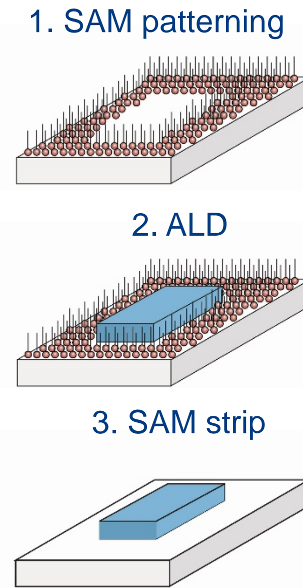


ALD-enabled:

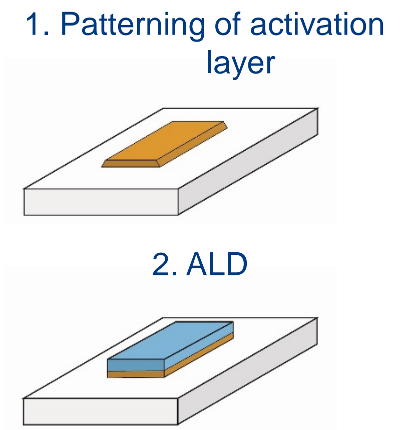
Lift-off



Area-selective ALD by area-deactivation



Area-selective ALD by area-activation



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

Review paper

Nanoscale

REVIEW

Cite this: *Nanoscale*, 2014, 6, 10941

The use of atomic layer deposition in advanced nanopatterning

A. J. M. Mackus, A. A. Bol* and W. M. M. Kessels

Atomic layer deposition (ALD) is a method that allows for the deposition of thin films with atomic level control of the thickness and an excellent conformality on 3-dimensional surfaces. In recent years, ALD has been implemented in many applications in microelectronics, for which often a patterned film instead of full area coverage is required. This article reviews several approaches for the patterning of ALD-grown films. In addition to conventional methods relying on etching, there has been much interest in nanopatterning by area-selective ALD. Area-selective approaches can eliminate compatibility issues associated with the use of etchants, lift-off chemicals, or resist films. Moreover, the use of ALD as an enabling technology in advanced nanopatterning methods such as spacer defined double patterning or block copolymer lithography is discussed, as well as the application of selective ALD in self-aligned fabrication schemes.

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www.rsc.org/nanoscale

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

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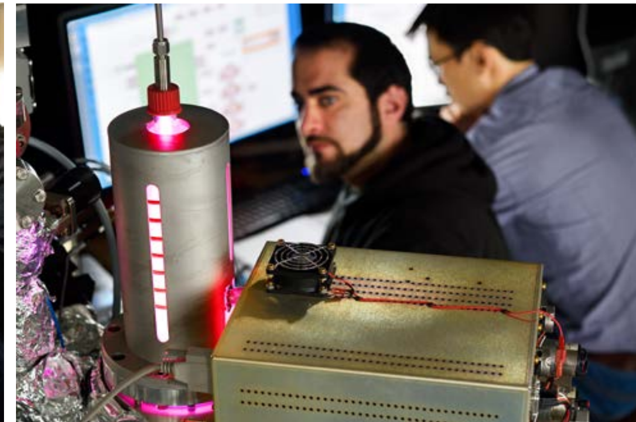

Patterning of graphene with polyimide

René Vervuurt

Direct-write ALD of Pt

Nick Thissen

Direct-write ALD of In_2O_3

Alfredo Mameli

Yinghuan Kuang

Morteza Aghaee

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Fred Roozeboom