TU/e Technische Universiteit
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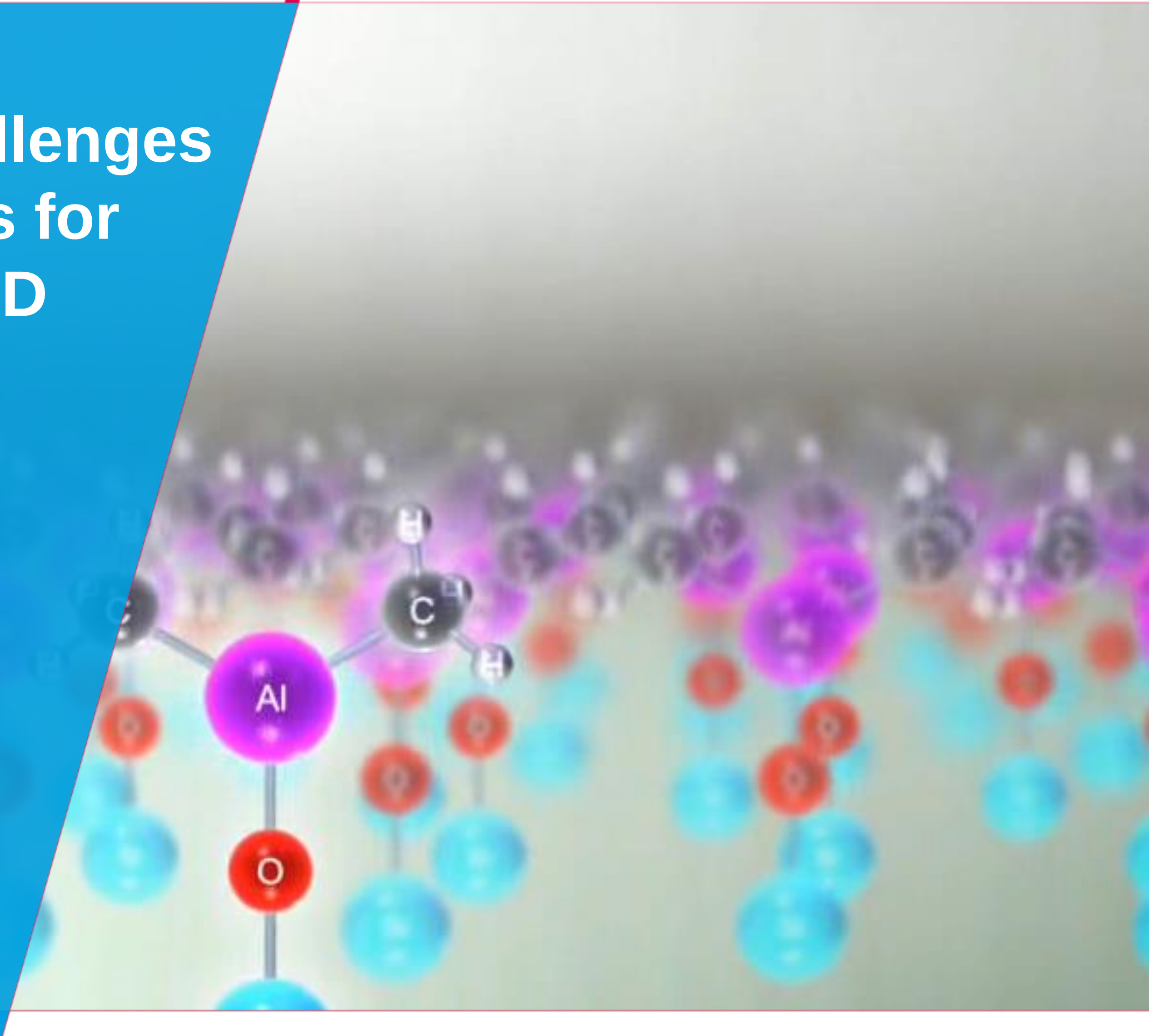
University of Technology

Approaches, challenges and opportunities for area-selective ALD

Adrie Mackus

Eindhoven University of Technology



Where innovation starts

Area-selective ALD for bottom-up processing

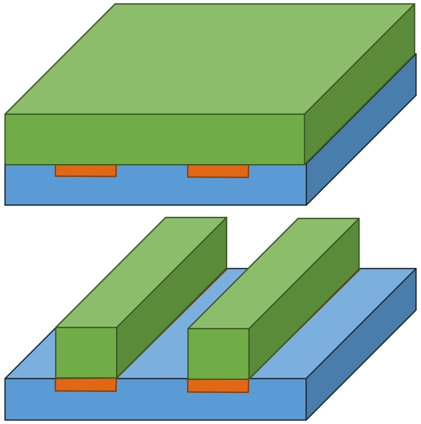
Top-down **Bottom-up**

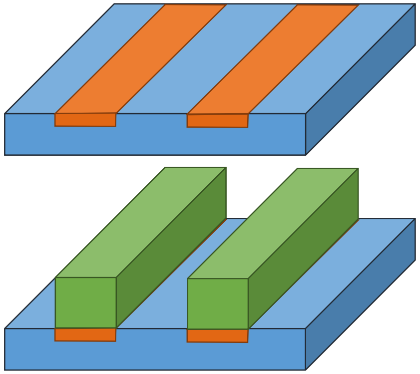
Building technology

Excavated from solid rock

Bricks as building blocks

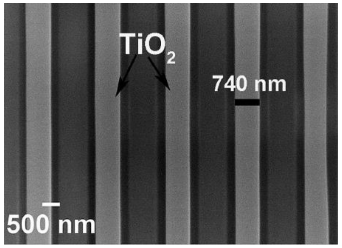
Semiconductor fabrication



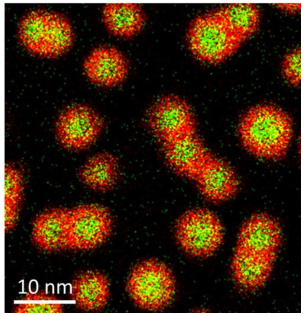


Subtractive **Additive** processing

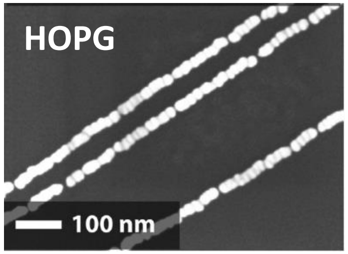
What is area-selective ALD?



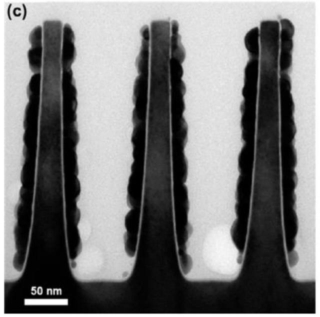
Haider *et al.*, *RSC Adv.* **6**, 106109 (2016)



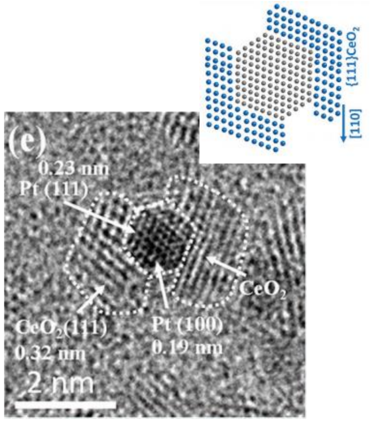
Weber *et al.*, *Nanotechnology* **26**, 094002 (2015)



Lee *et al.*, *Nano Lett.* **13**, 457 (2013)



Kim *et al.*, *ACS Nano* **10**, 4451 (2016)



Cao *et al.*, *Small* 17006483 (2017)

Area-selective ALD = bottom-up fabrication by deposition of atoms at specific locations

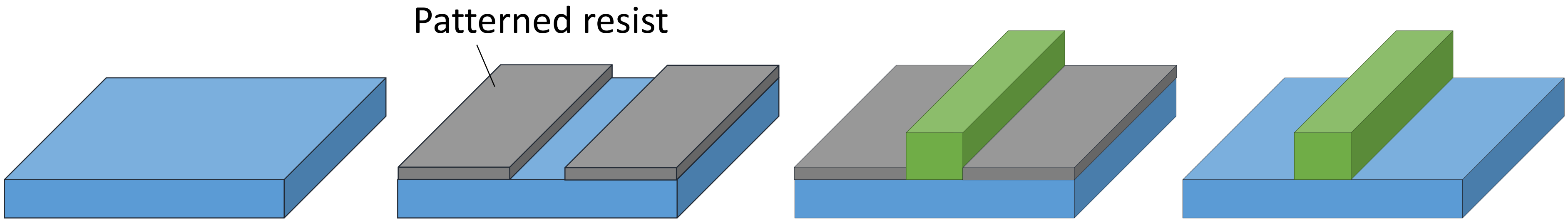
Lecture Richard Feynman "*There is plenty of room at the bottom*"

*What could we do with **layered structures** with just the right layers? What would the properties of materials be if we could really **arrange the atoms the way we want them**? ….. when we have some control of the arrangement of things on small scale, we will get an enormously greater range of possible properties that substances can have…*

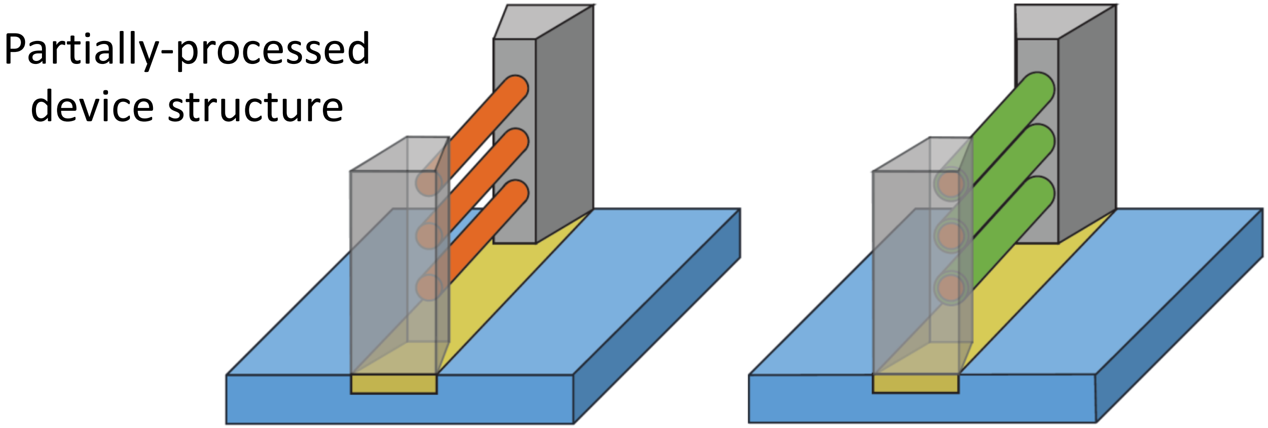
Richard Feynman, American Physical Society meeting, Caltech, Dec 29 1959

What is area-selective ALD?

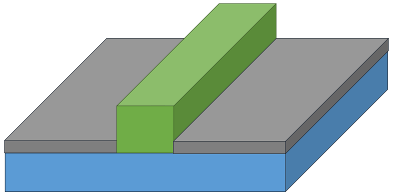
Area-selective ALD involving patterning steps



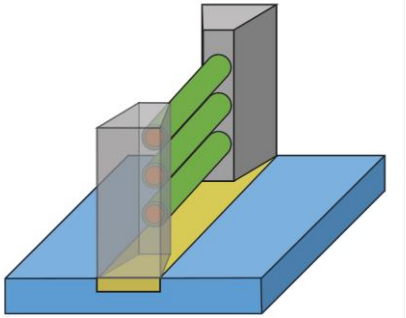
Area-selective ALD on a device structure



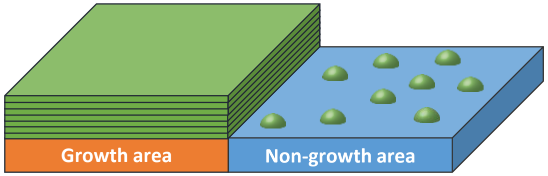
Outline



1. **Patterning of ALD-grown films**
   - Area-selective ALD by area-deactivation
   - Area-selective ALD by area-activation

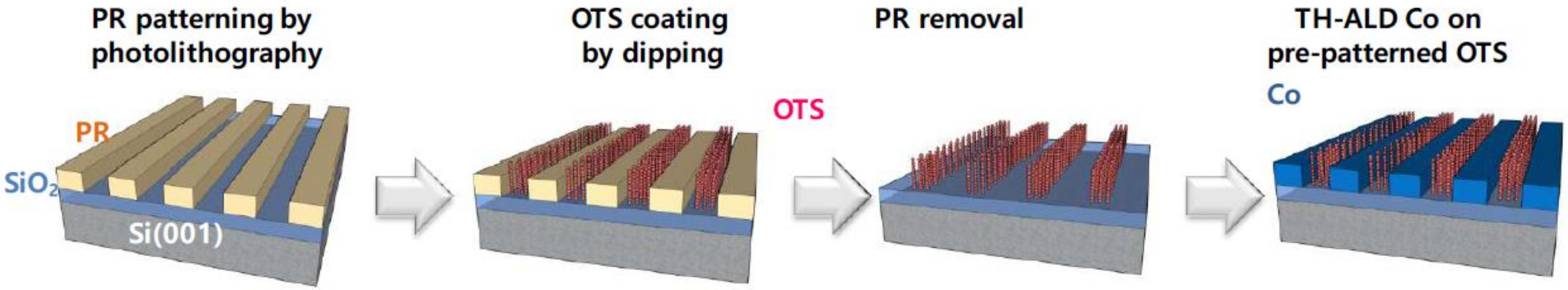


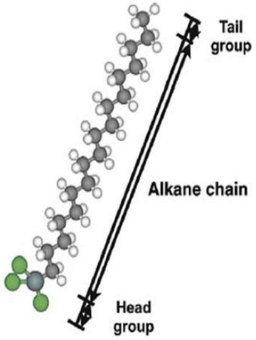
2. **Approaches for obtaining area-selective growth**
   - Motivation: self-aligned fabrication
   - Selective precursor adsorption
   - Selective co-reactant adsorption

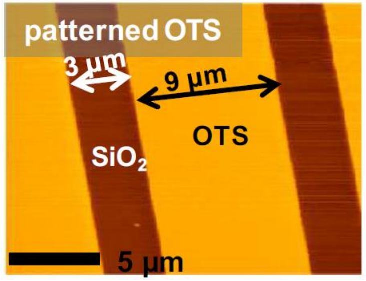


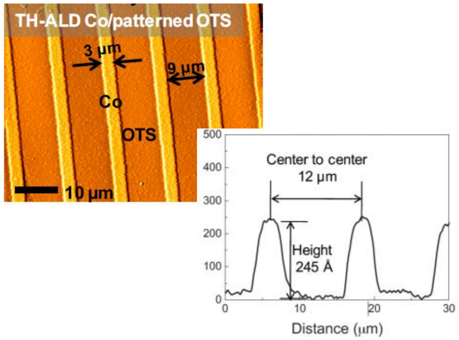
3. **Discussion of challenges**
   - Achieve high selectivity
   - Geometrical effects
   - Classes of selectivity

Area-selective ALD on SAM-functionalized surface

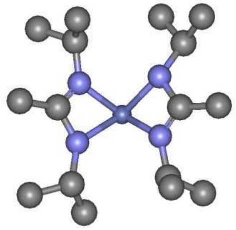




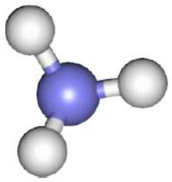




Co(iPr-AMD)$_2$



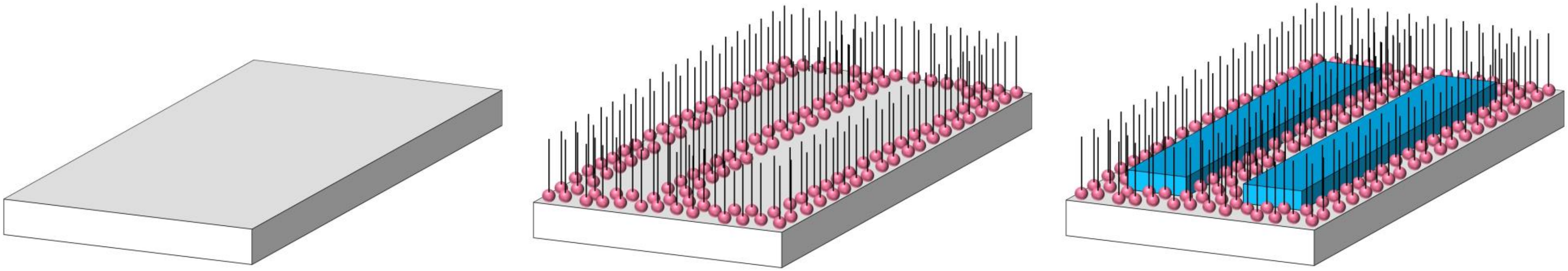
NH$_3$



- Patterning by photolithography
- Adsorption of octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM)
- Area-selective ALD of Co from Co(iPr-AMD)$_2$ + NH$_3$

Lee *et al.*, *J. Electrochem. Soc.* **157**, D10 (2010)
Kim, Area Selective Deposition workshop, Leuven, Belgium (2016)

Area-selective ALD by area-deactivation



Blank substrate ⇨ Areas masked by self-assembled monolayer (SAM) ⇨ ALD on open areas only

- ALD growth deactivation by self-assembled monolayer (SAM)
- No growth occurs on the SAM

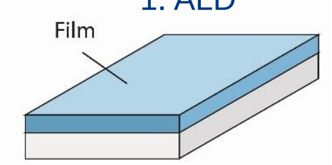
Book chapter: *Nanopatterning by area-selective ALD*
Lee and Bent, in *ALD of nanostructured materials*, Wiley, 2012

Patterning of ALD-grown films

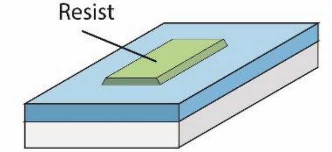
Conventional:

Etching

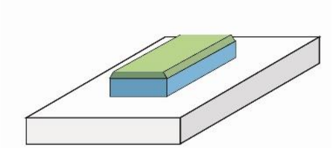
1. ALD



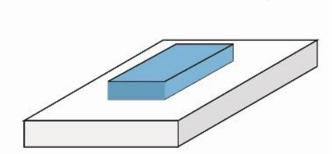
2. Resist patterning



3. Etching

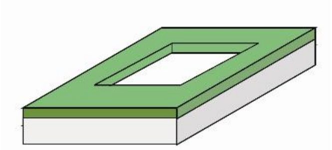


4. Resist strip

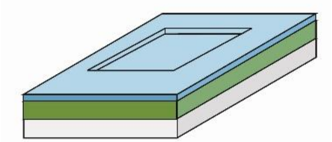


Lift-off

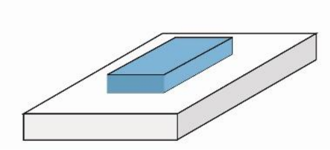
1. Resist patterning



2. ALD



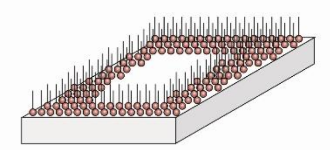
3. Lift-off



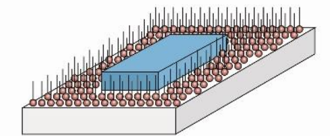
ALD-enabled:

Area-selective ALD by area-deactivation

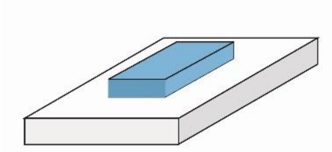
1. SAM patterning



2. ALD



3. SAM strip

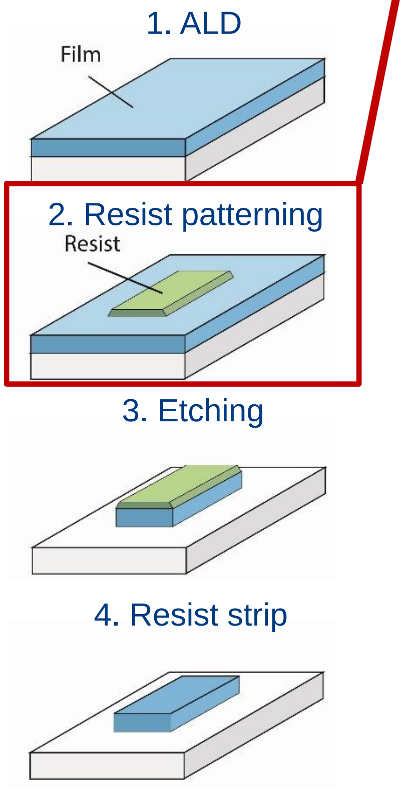


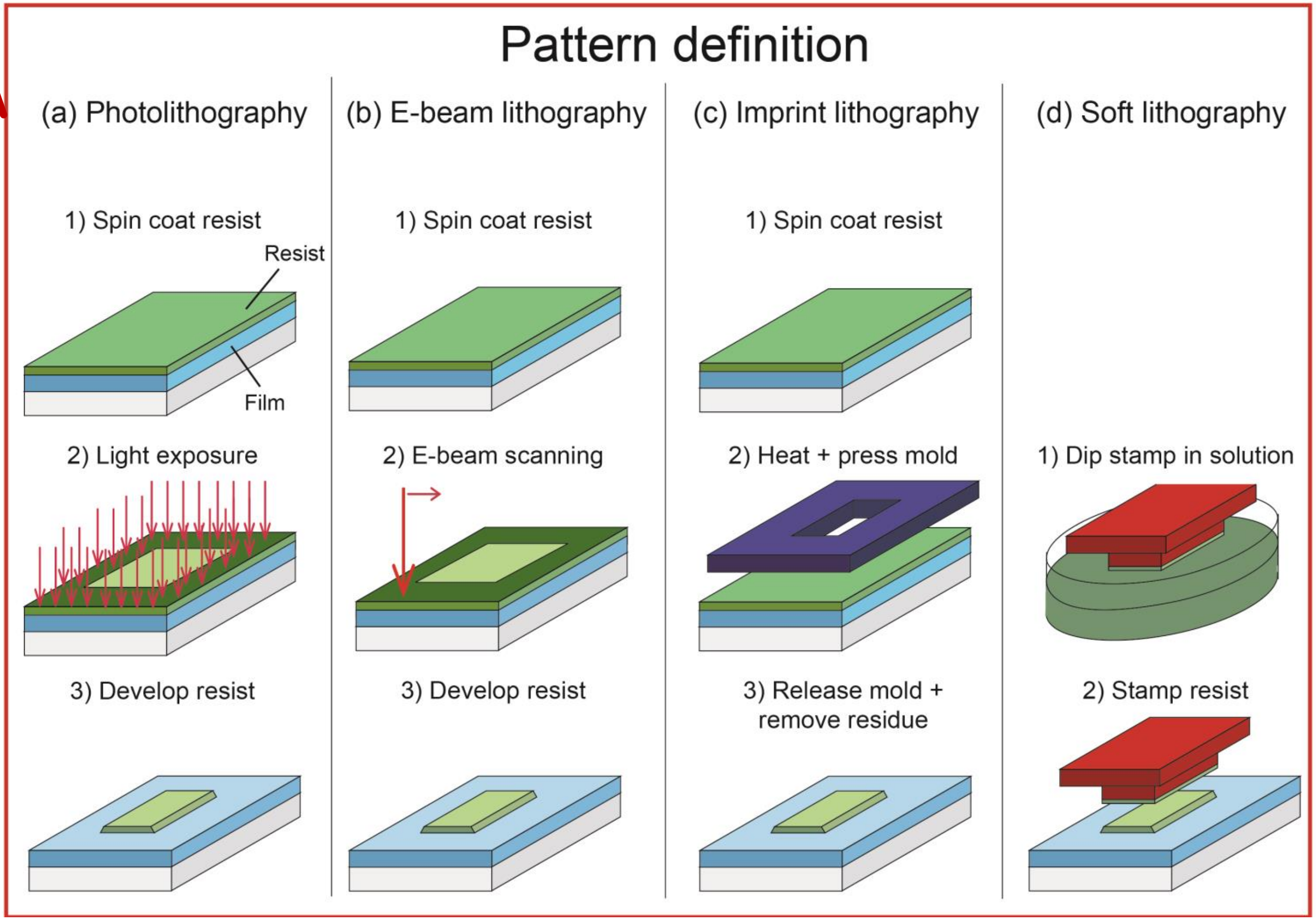
Review paper: *The use of ALD in advanced nanopatterning*
Mackus *et al.*, *Nanoscale* **6**, 10941 (2014)

Patterning of ALD-grown films

Conventional:

Etching

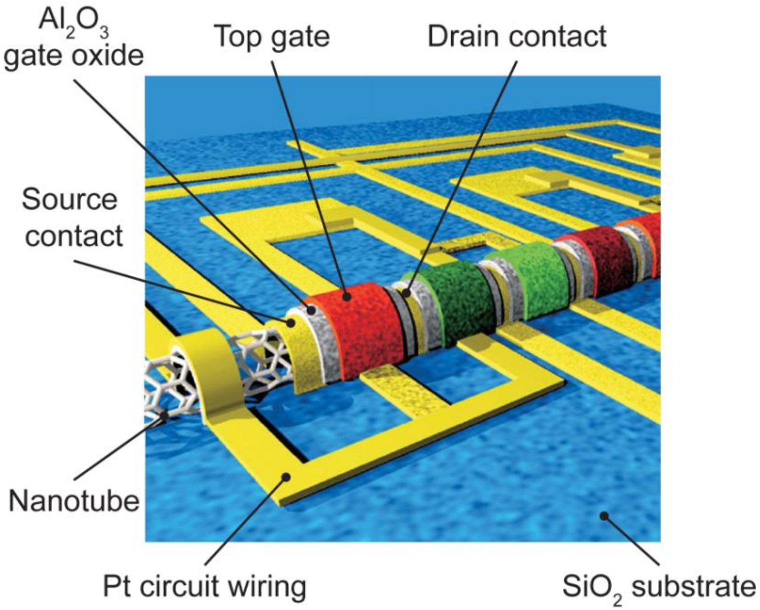

1. ALD
2. Resist patterning
3. Etching
4. Resist strip



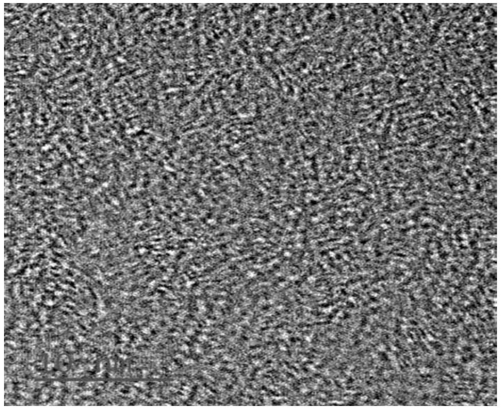
Review paper: *The use of ALD in advanced nanopatterning*
Mackus *et al.*, *Nanoscale* **6**, 10941 (2014)

Motivation: Elimination of compatibility issues

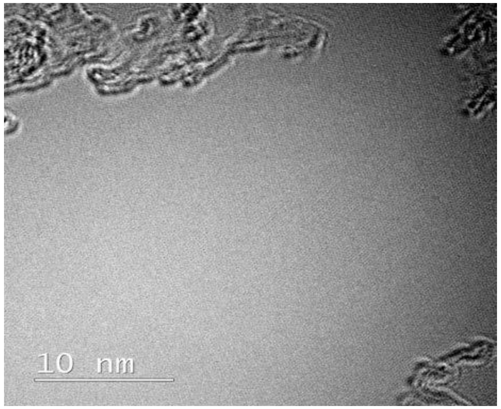
Example: Contacting carbon nanotubes or graphene



Graphene / PMMA residue



"Clean" graphene



Not compatible with sensitive CNT surface:

- Etching chemicals
- Lift-off methods (due to delamination)
- Resist films

→ **Bottom-up method desired**

Avouris, *Physics Today* **62**, 34 (2009)

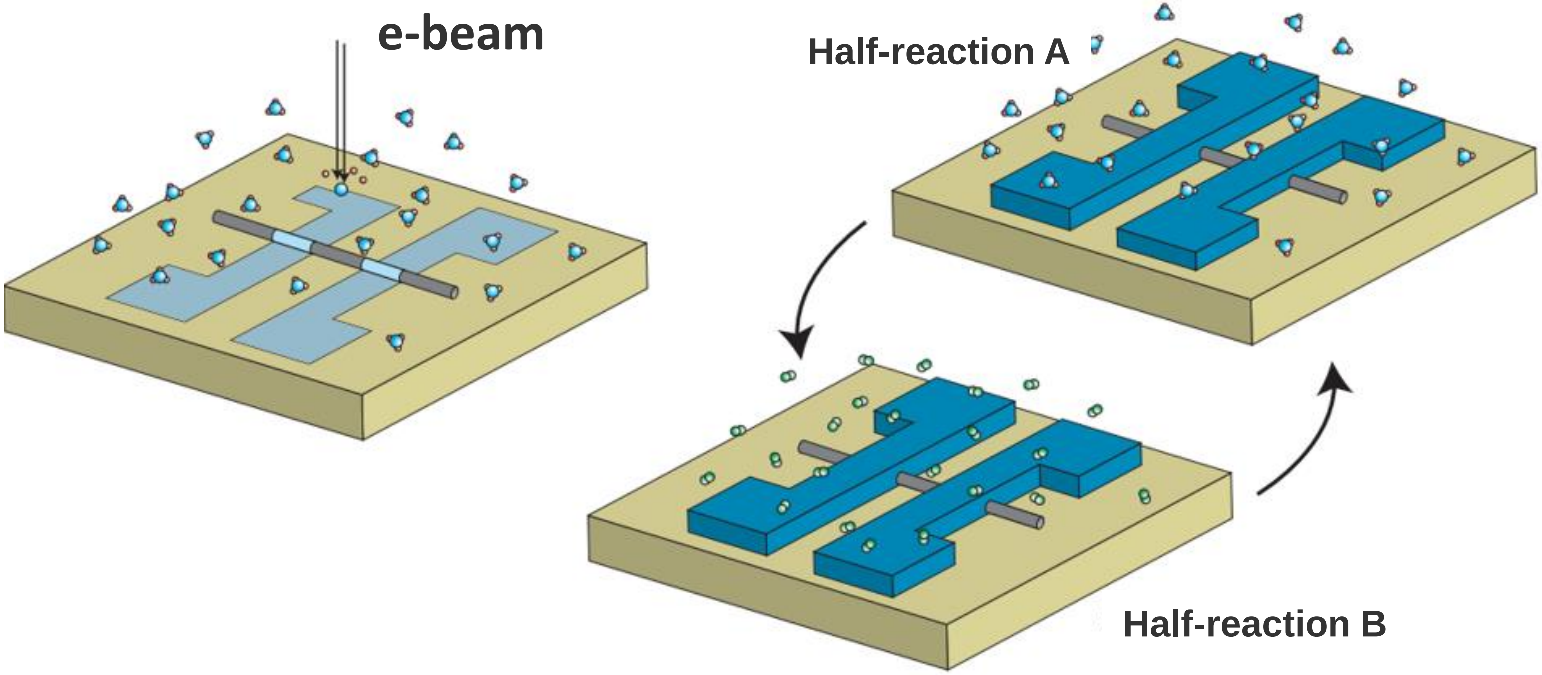
Example area-activation: EBID & ALD of Pt

1. Patterning step:

e-beam induced deposition (EBID)

2. Building step:

Atomic layer deposition (ALD)



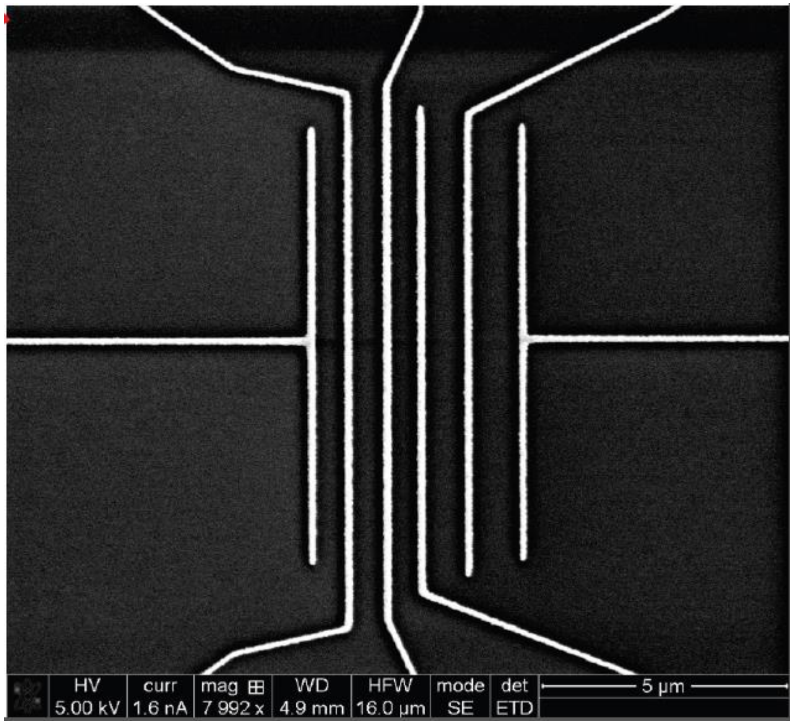
Two-step process:

- Patterning: ultrathin (<1 ML) seed layer on oxide by **EBID**
- Building: **area-selective ALD** of Pt ($MeCpPtMe_3 + O_2$) on seed layer

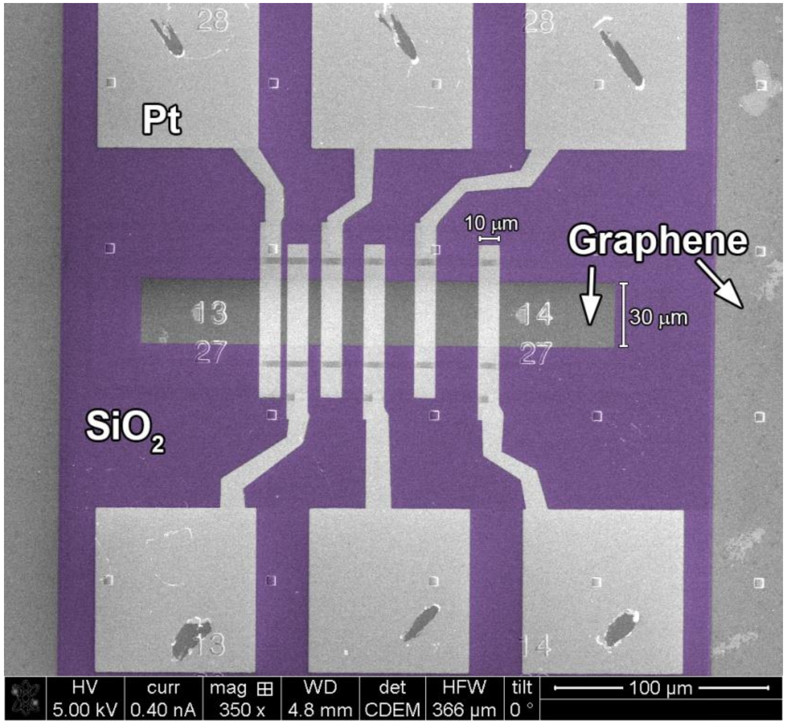
Mackus *et al.*, *Nanoscale* **4**, 4477 (2012)
US patent: 8,268,532 (2012)

Direct-write ALD of Pt contacts

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



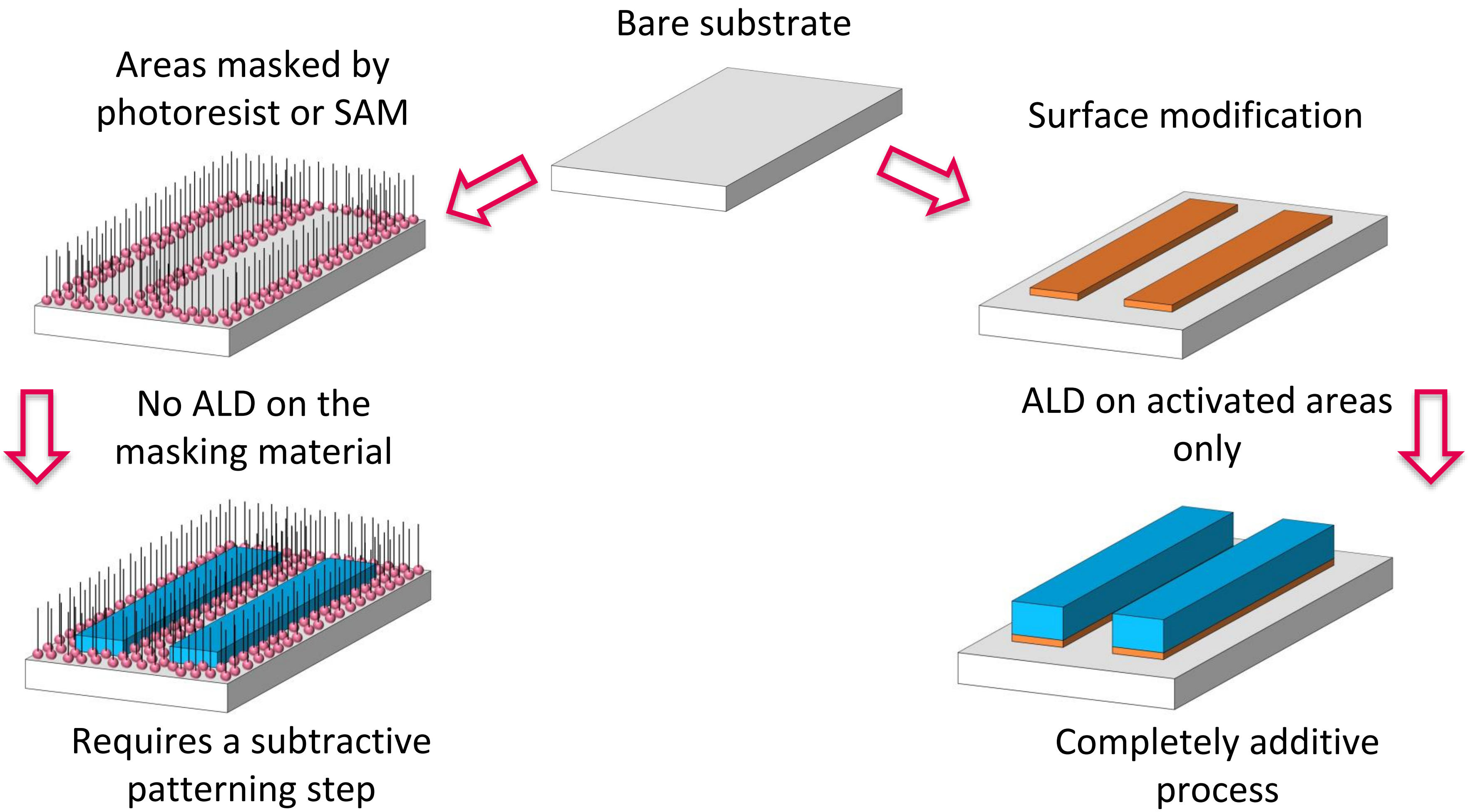
TLM structure on **graphene**
with direct-write ALD **Pt** contacts



- Bottom-up patterning: **eliminates use of resists and etching steps**

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

Area-deactivation versus area-activation



Bare substrate

Areas masked by photoresist or SAM

No ALD on the masking material

Requires a subtractive patterning step

Surface modification

ALD on activated areas only

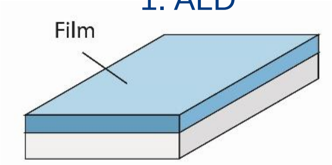
Completely additive process

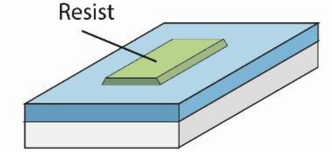
Review paper: *The use of ALD in advanced nanopatterning*
Mackus *et al.*, *Nanoscale* **6**, 10941 (2014)

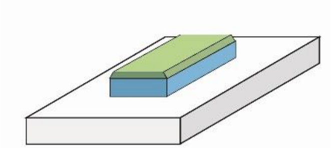
Patterning of ALD-grown films

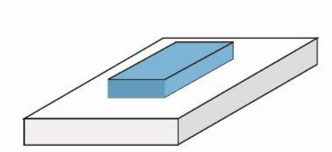
Conventional:

Etching

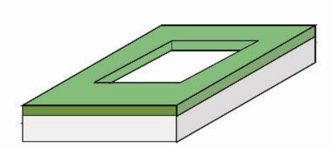

1. ALD


2. Resist patterning


3. Etching


4. Resist strip

Lift-off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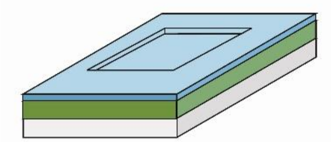
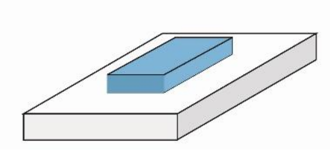
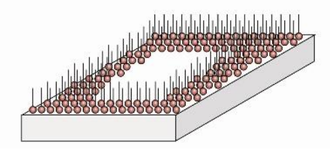

2. ALD


3. Lift-off

Subtractive

ALD-enabled:

Area-selective ALD by area-deactivation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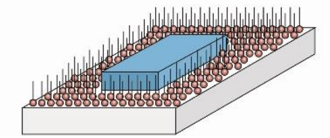
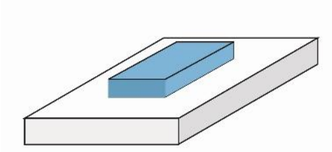
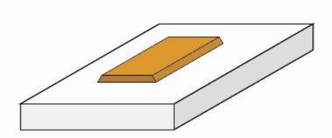
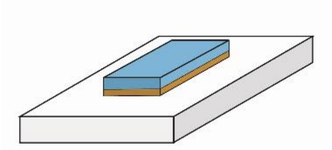

2. ALD


3. SAM strip

Area-selective ALD by area-activation

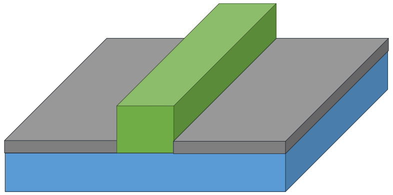

1. Patterning of activation layer


2. ALD

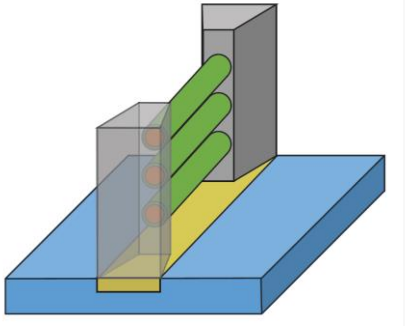
Additive

Review paper: *The use of ALD in advanced nanopatterning*
Mackus *et al.*, *Nanoscale* **6**, 10941 (2014)

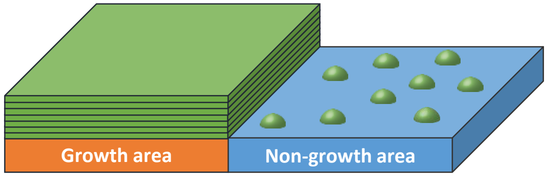
Outline



1. **Patterning of ALD-grown films**
   - Area-selective ALD by area-deactivation
   - Area-selective ALD by area-activation

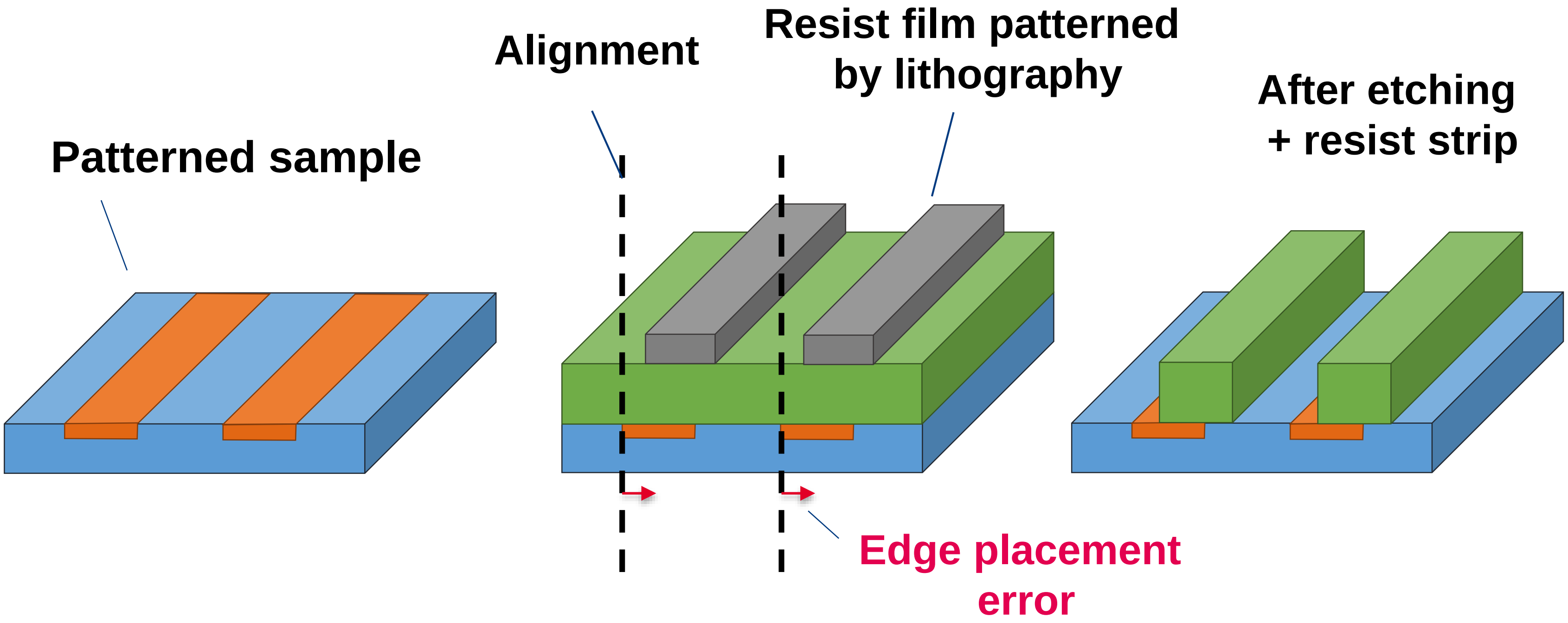


2. **Approaches for obtaining area-selective growth**
   - Motivation: self-aligned fabrication
   - Selective precursor adsorption
   - Selective co-reactant adsorption



3. **Discussion of challenges**
   - Achieve high selectivity
   - Geometrical effects
   - Classes of selectivity

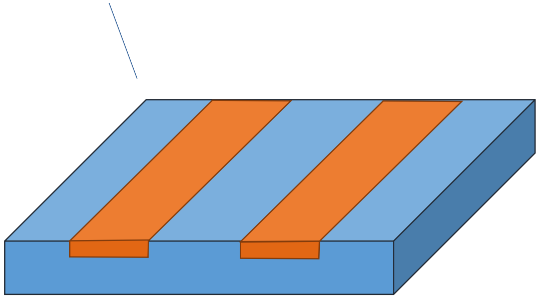
The challenge of alignment at the nanoscale



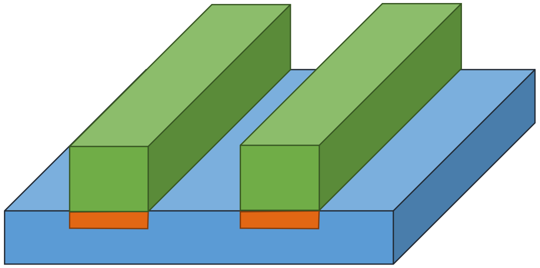
- Alignment becomes extremely challenging in future technology nodes

Motivation: Enabling self-aligned fabrication

Patterned sample



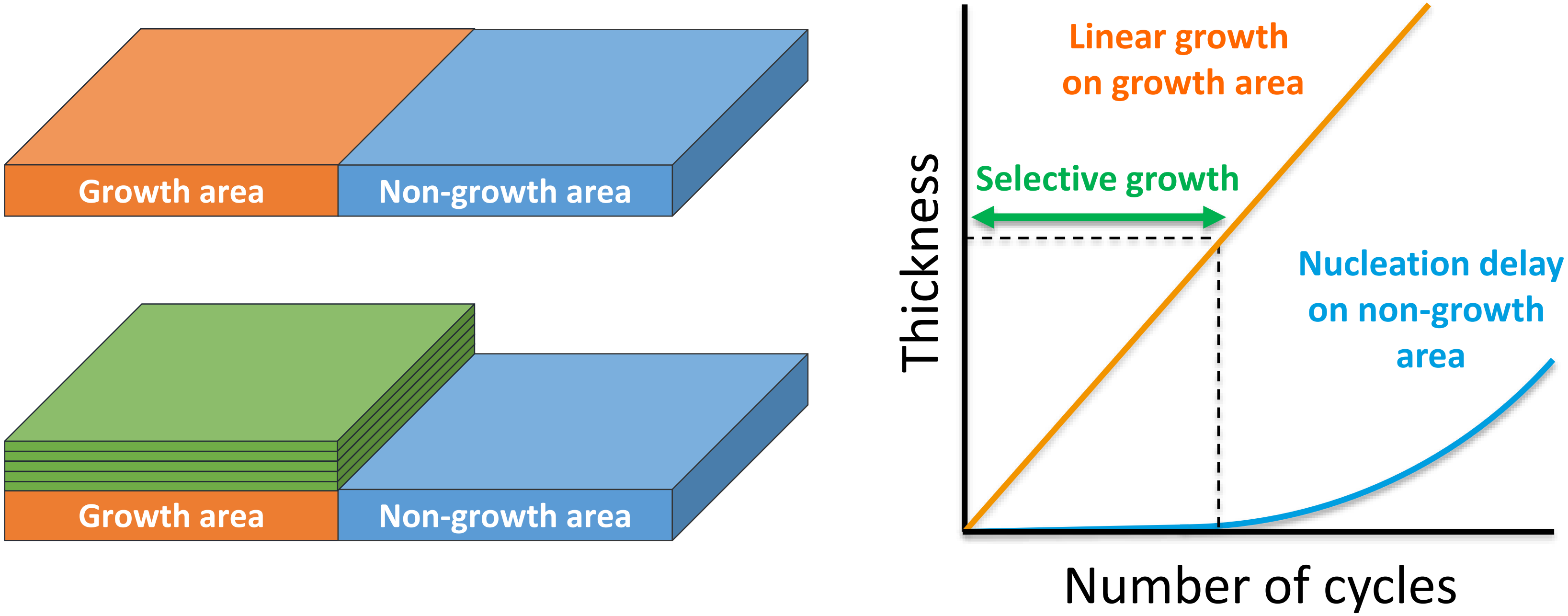
Selective deposition



Area-selective ALD:

- Fewer lithography and etch steps
- Eliminates alignment issues
- **Self-aligned fabrication scheme**

Area-selective ALD on a specific material



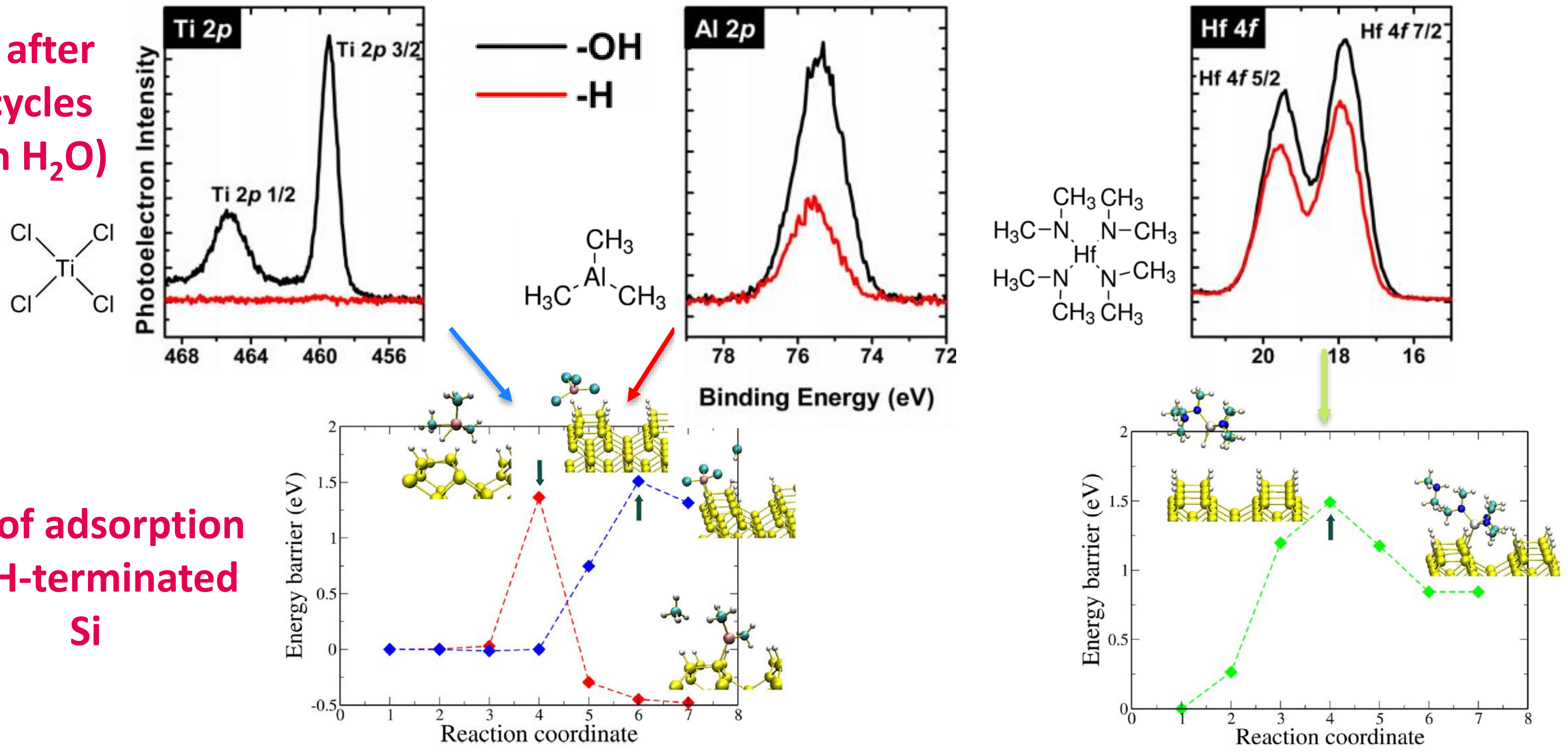
- Growth area = material on which deposition should occur
- Non-growth area = material(s) on which no deposition should occur

Differences in nucleation behavior are often exploited to achieve area-selective ALD

Selective precursor adsorption

XPS after 10 cycles (with H_2O)

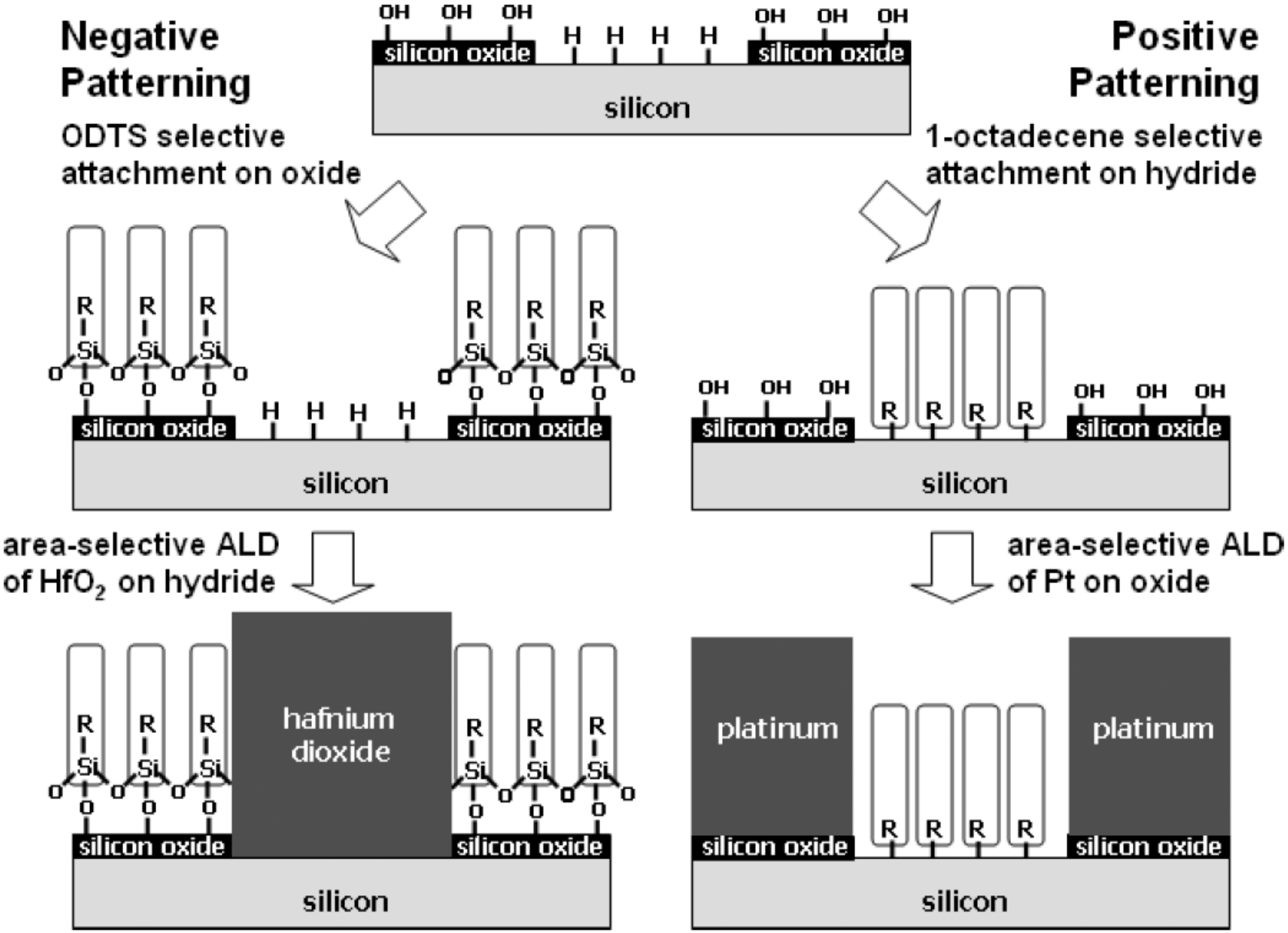
DFT of adsorption on H-terminated Si



- Adsorption of $TiCl_4$ is the most endothermic reaction (1.30 eV)
- Chemoselective adsorption of precursor allows for area-selective ALD of films of a few nanometers thick

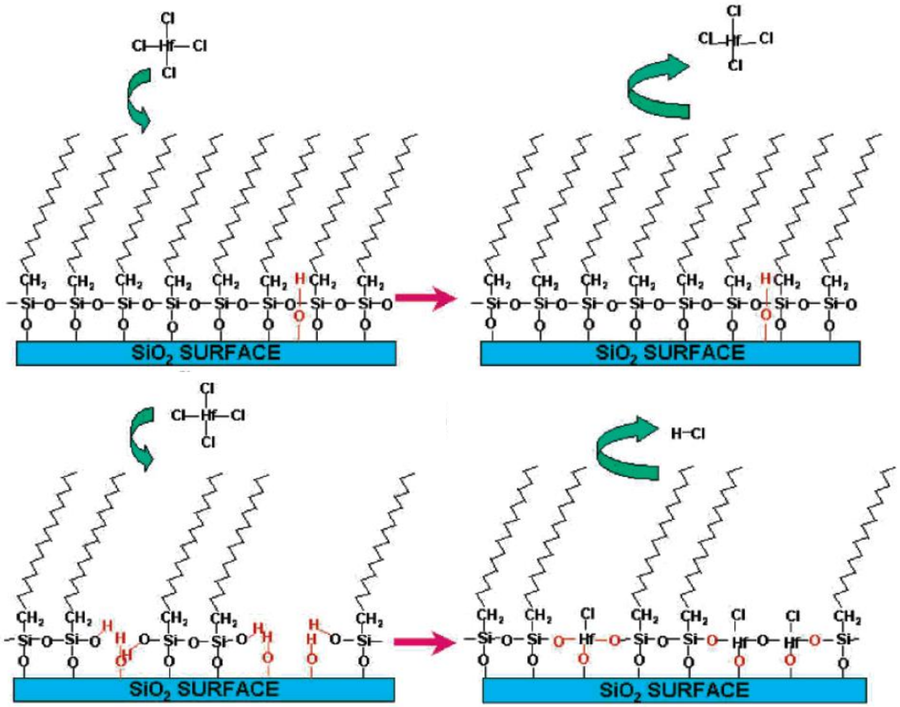
Longo *et al.*, *J. Vac. Sci. Technol. B*, **32** O3D112-1 (2014)

Selective adsorption of SAM

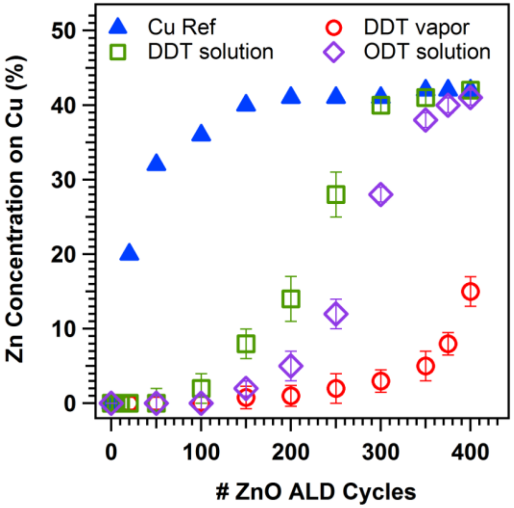


Chen and Bent, *Adv. Mater.* **18**, 1086 (2006)

Precursor blocking by SAM prior to deposition



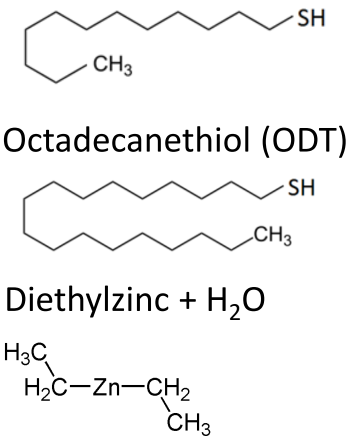
XPS on Cu

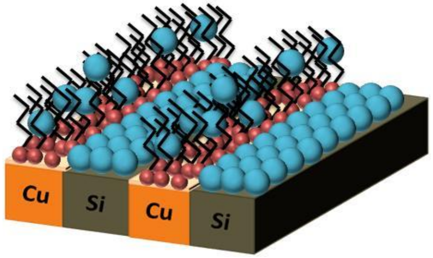


Dodecanethiol (DDT)

Octadecanethiol (ODT)

Diethylzinc + H_2O





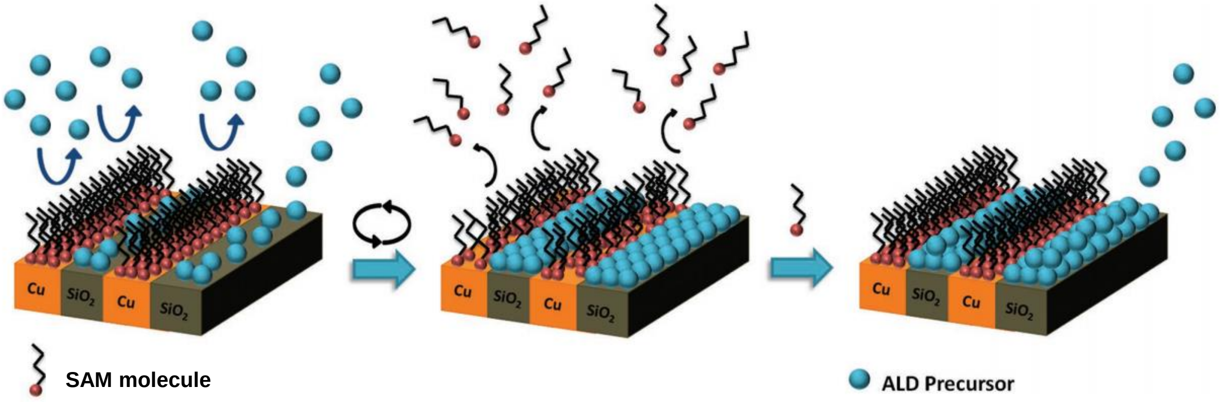
Role of SAMs is twofold:

1. Remove hydroxyl groups from the surface
2. Prevent precursor molecules from reaching the surface

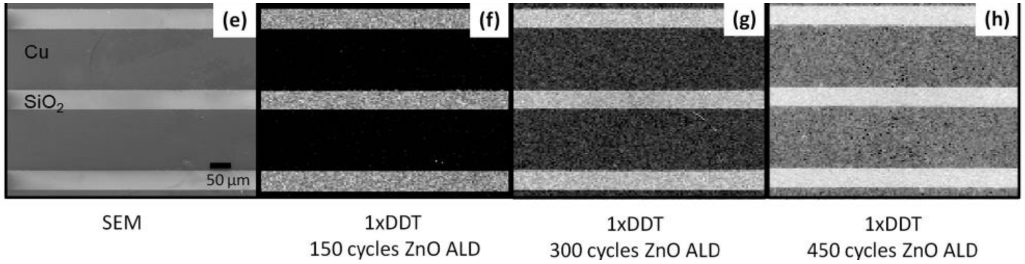
- At some point selectivity is lost, due to desorption or degradation of SAM

Chen *et al.*, *Chem. Mater.* **17**, 536 (2005)
Minaye Hasehemi *et al.*, *ACS Appl. Mater. Interfaces* **8**, 33264 (2016)

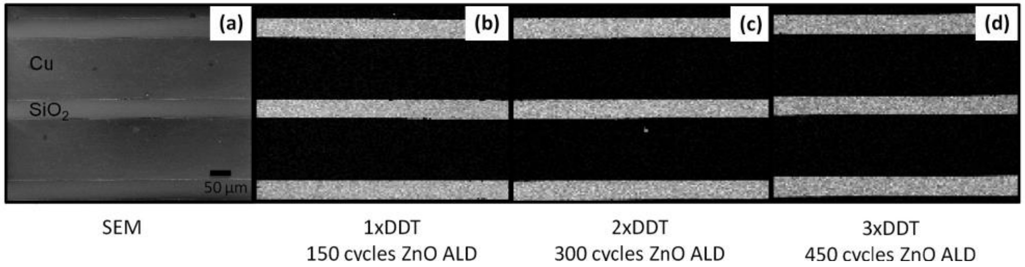
Regeneration of SAM



Reference



Re-dosing



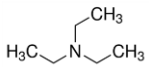
- Results in area-selective ALD of 3 x thicker ZnO films

Minaye Hasehemi and Bent, *Adv. Mater. Interfaces* **3**, 1600464 (2016)

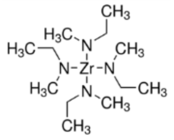
Precursor blocking during every ALD cycle

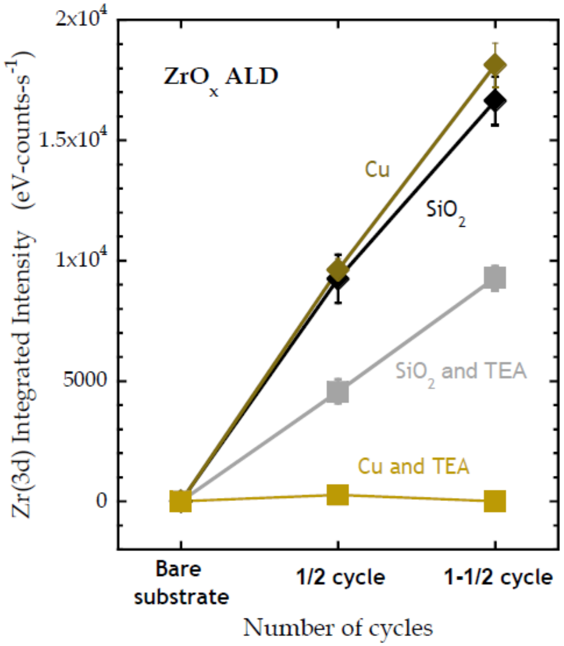
Co-dosing inhibitor

Triethylamine (TEA)



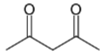
TEMAZ



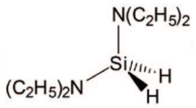


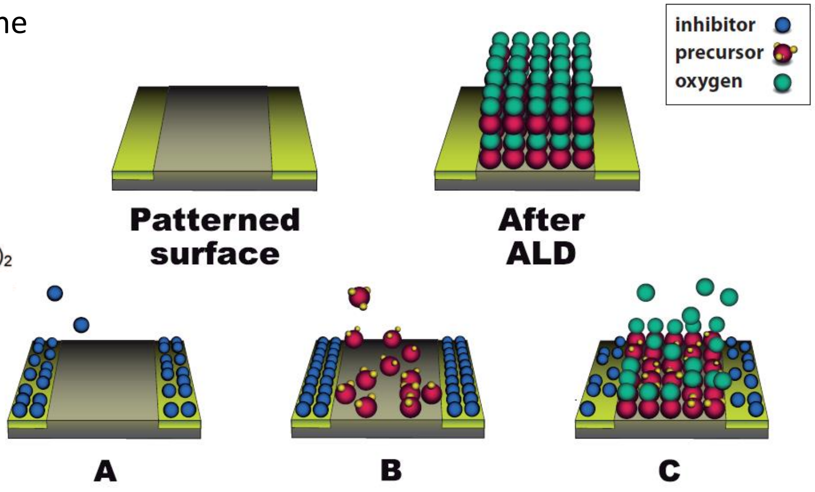
ABC-type cycle with inhibitor

Acetylacetone (Hacac)



BDEAS





Use of **inhibitor molecules** during every ALD cycle:

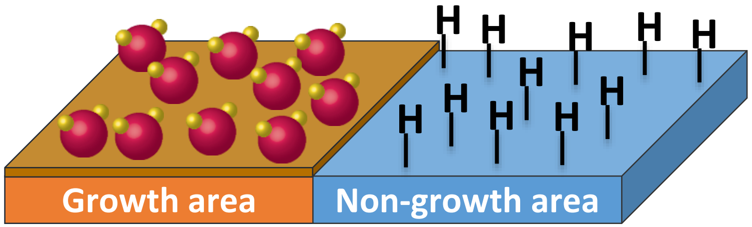
- Co-dosing during precursor pulse (Engstrom and co-workers)
- ABC-type cycle (Mameli *et al.*)

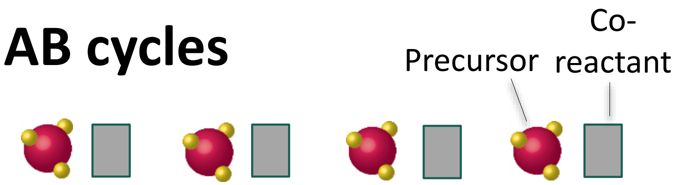
Benefit: **compatible with plasma-assisted or ozone-based ALD**

MSc report Taewon Suh, Cornell University, 2017
Mameli *et al.*, submitted

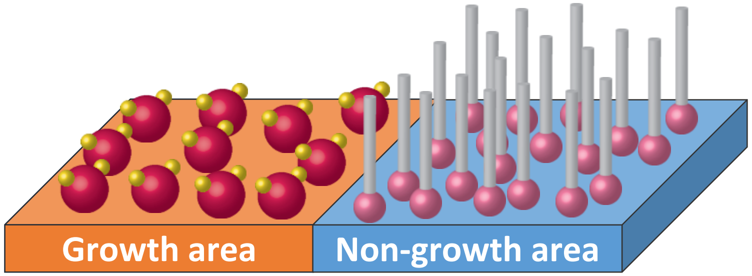
Approaches for selective precursor adsorption

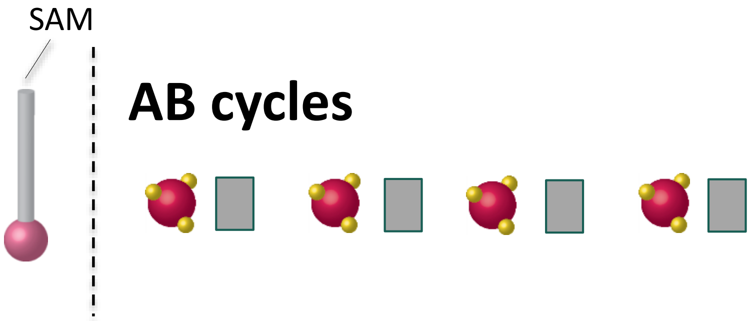
1a. Selective precursor adsorption



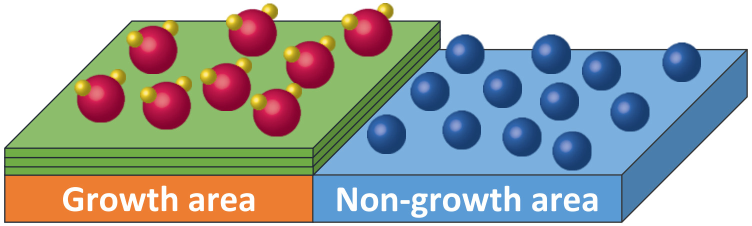


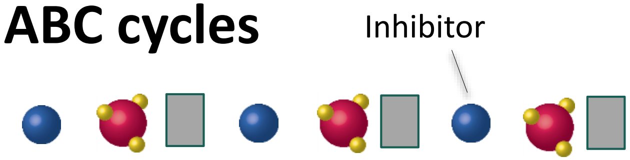
1b. Precursor blocking prior to deposition



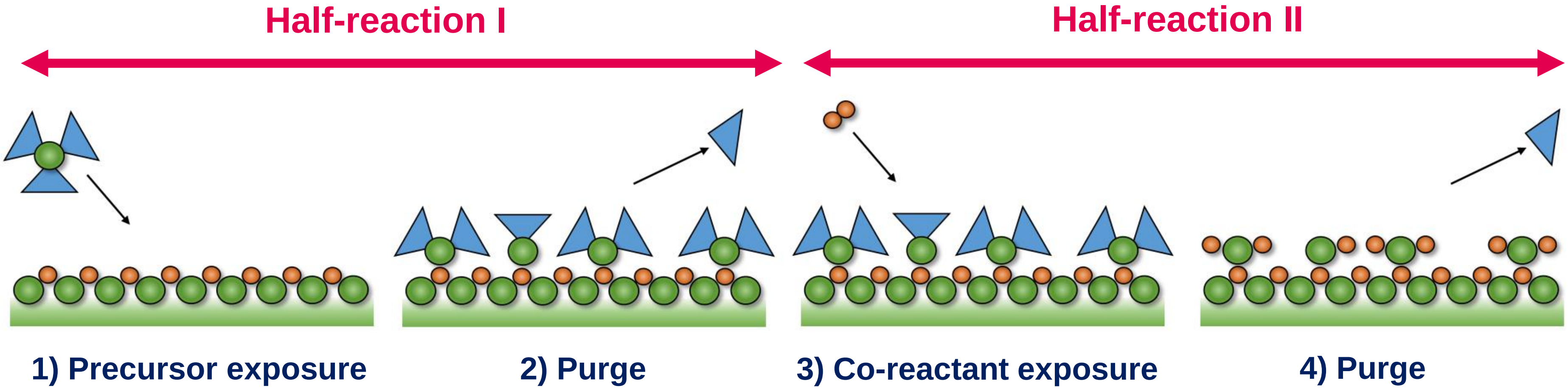


1c. Precursor blocking during every cycle





Approaches for achieving area-selective growth



Half-reaction I

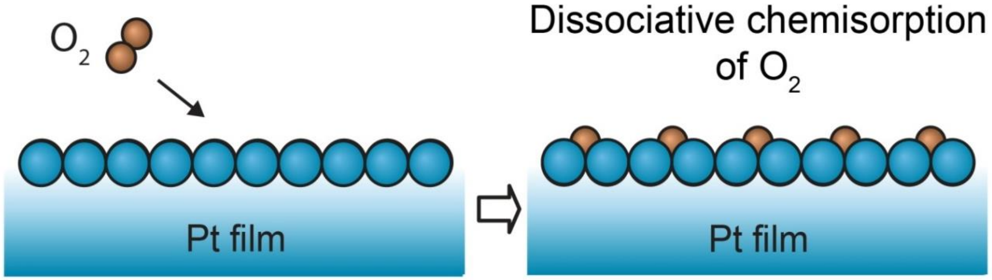
1. Selective precursor adsorption on growth area

a. Selective precursor adsorption
b. Precursor blocking prior to deposition
c. Precursor blocking during every cycle

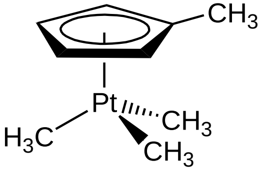
Half-reaction II

2. Selective co-reactant adsorption on growth area

Catalytic activation of the co-reactant



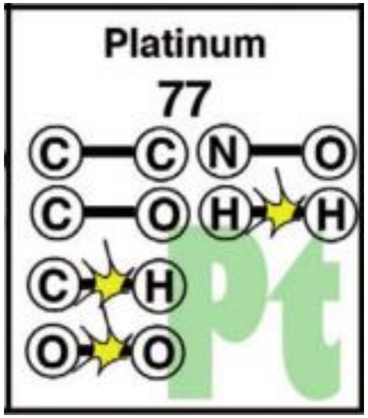
Pt ALD process:



$MeCpPtMe_3$ + O_2 gas

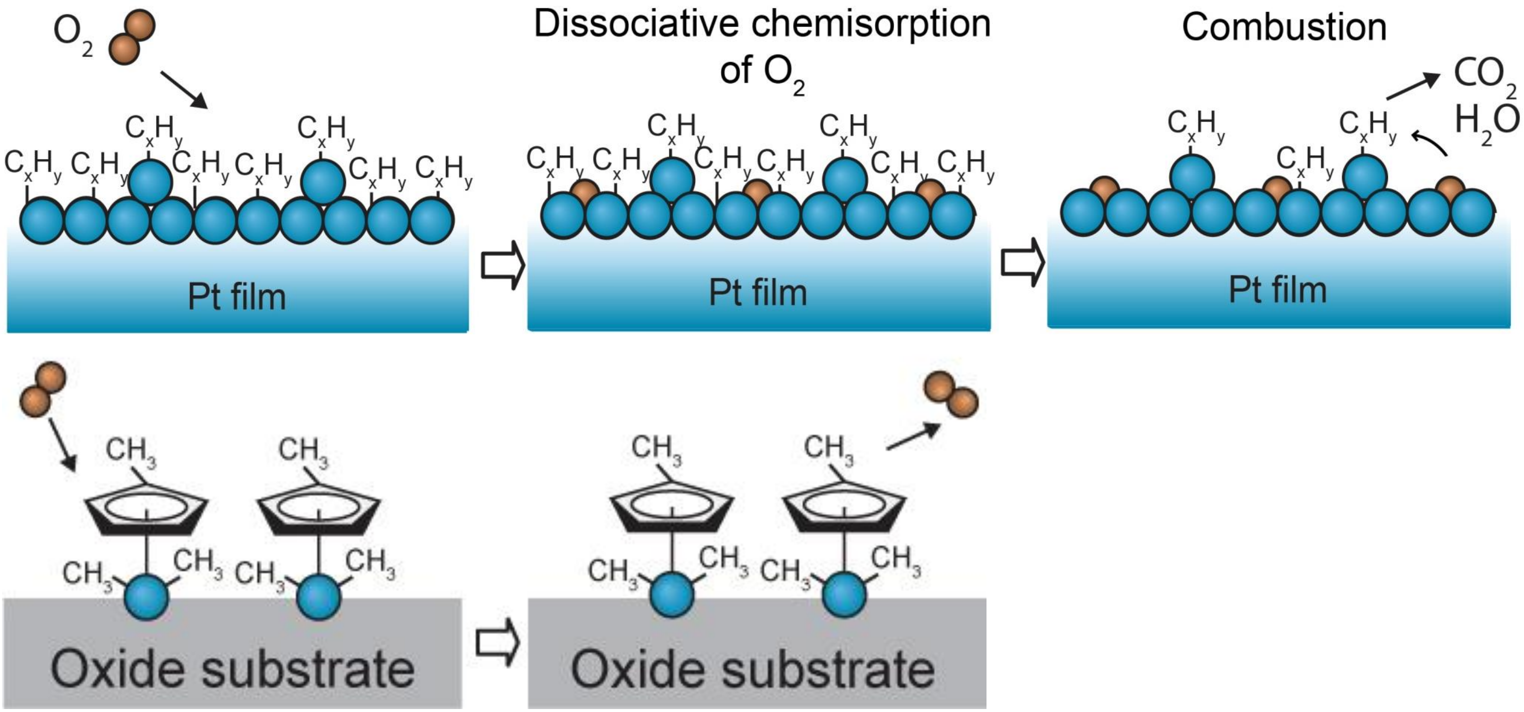
200-300 ˚C

- O-O bond breaking: **Dissociative chemisorption of O_2**



Aaltonen *et al.*, *Electrochem. Solid-State Lett.* **6**, C130 (2003)
Freyschlag and Madix., *Materials Today* **14**, 134 (2011)

Catalytic activation of the co-reactant

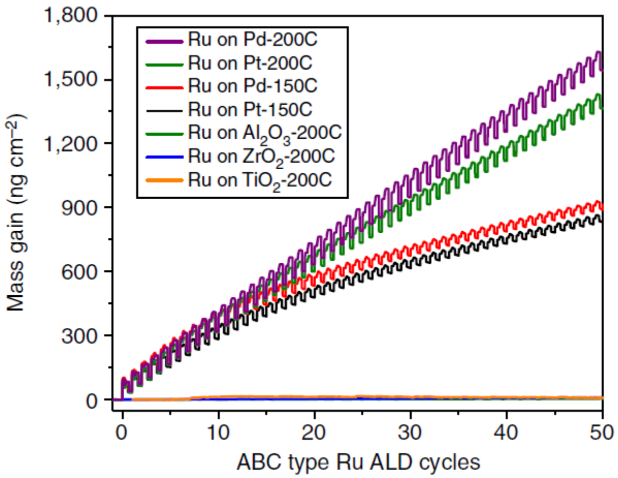


- **Selective adsorption of O_2 on metal growth area**
- Precursor ligands are not eliminated from non-growth area
- Approach for metal-on-metal deposition

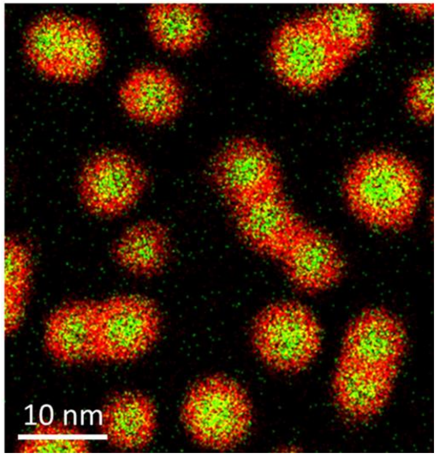
Aaltonen *et al.*, *Electrochem. Solid-State Lett.* **6**, C130 (2003)
Mackus *et al.*, *Chem. Mater.* **24**, 1752 (2012)

Core/shell synthesis by metal-on-metal ALD

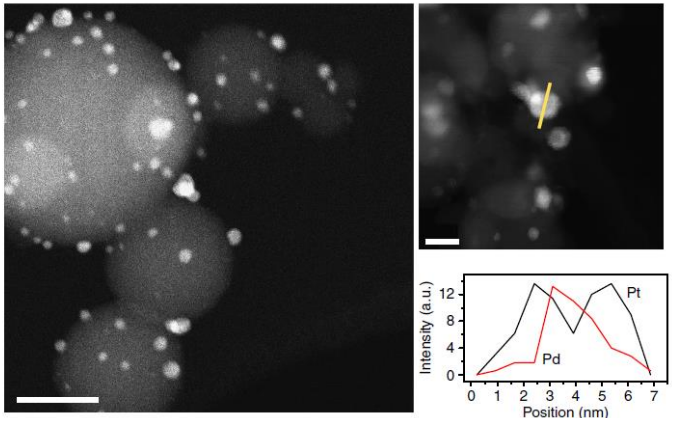
Ru deposition on Pd or Pt



Pd/Pt core/shell



Pd/Pt core/shell



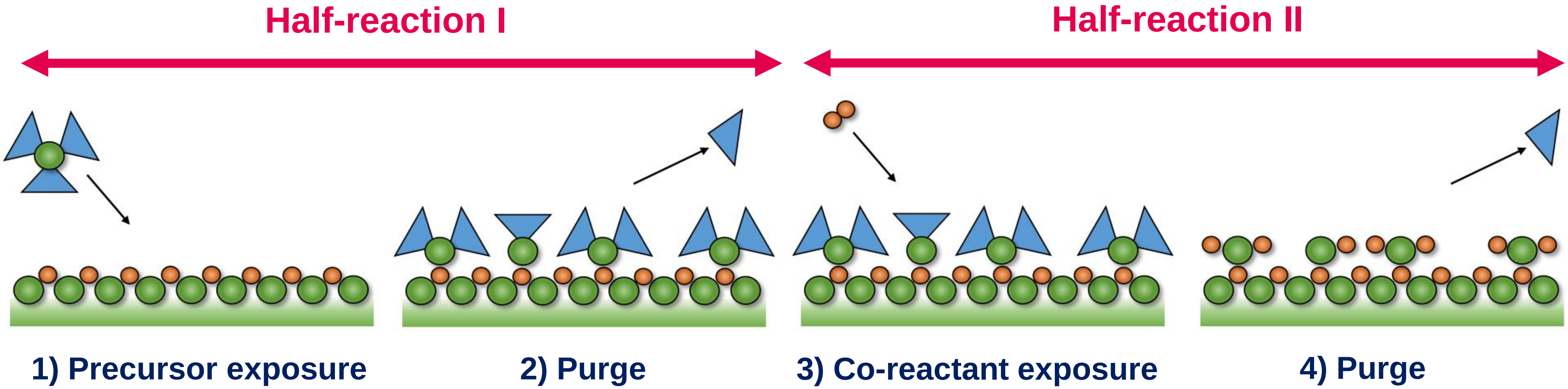
Catalytic activation of the co-reactant has been used extensively for the synthesis of core/shell and bimetallic particles

- Area-selective ALD of Pd on Pt, Pt on Pd, Pd on Ru, etc.

Motivation for area-selective ALD: Controlled synthesis of nanostructures

Weber *et al.*, *Nanotechnology* **26**, 094002 (2015)
Lu *et al.*, *Nat. Commun.* **5**, 3264 (2014)

Approaches for achieving area-selective growth



Half-reaction I

1. Selective precursor adsorption on growth area

a. Selective precursor adsorption
b. Precursor blocking prior to deposition
c. Precursor blocking during every cycle

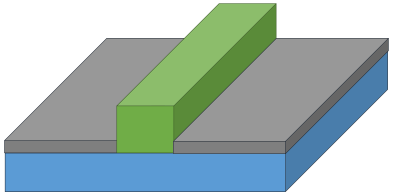
Half-reaction II

2. Selective co-reactant adsorption on growth area

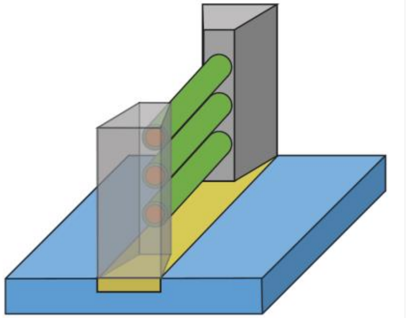
a. Catalytic activation of co-reactant on the growth area

Outline

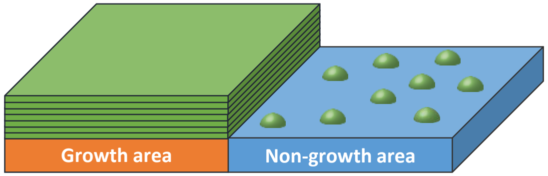
1. **Patterning of ALD-grown films**
   - Area-selective ALD by area-deactivation
   - Area-selective ALD by area-activation



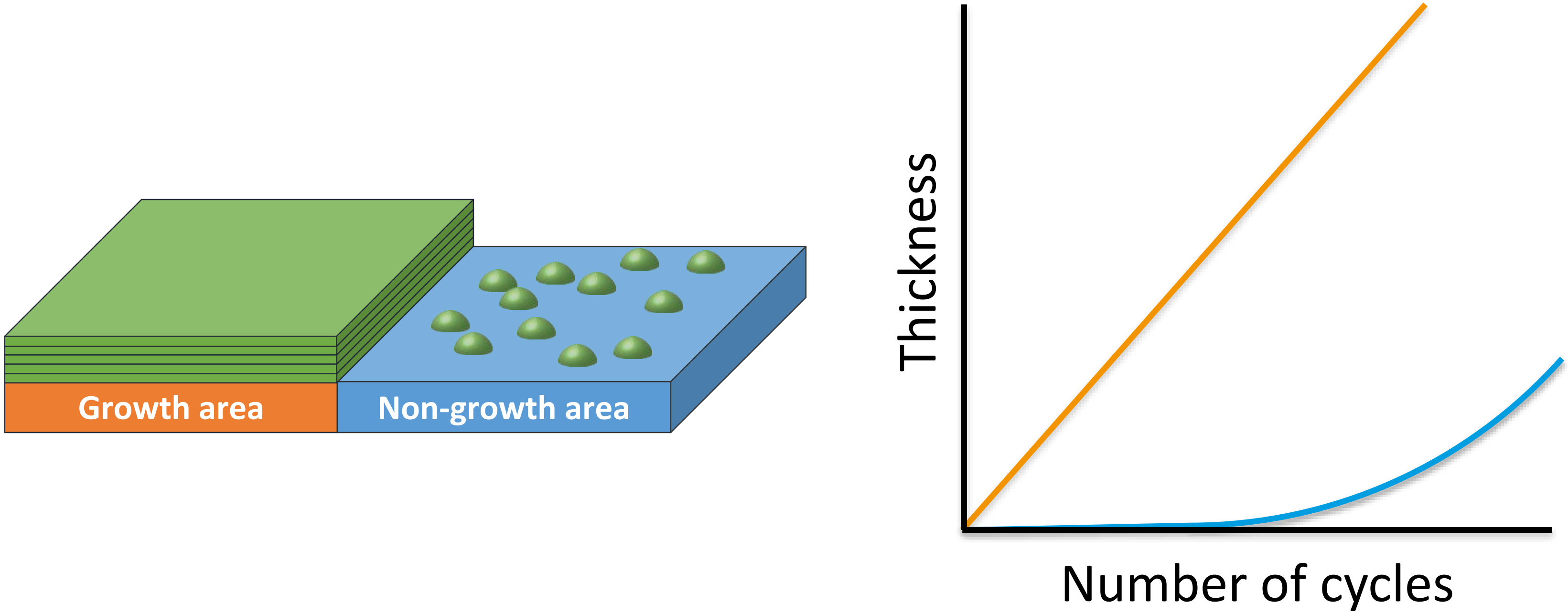
2. **Approaches for obtaining area-selective growth**
   - Motivation: self-aligned fabrication
   - Selective precursor adsorption
   - Selective co-reactant adsorption



3. **Discussion of challenges**
   - Achieve high selectivity
   - Geometrical effects
   - Classes of selectivity



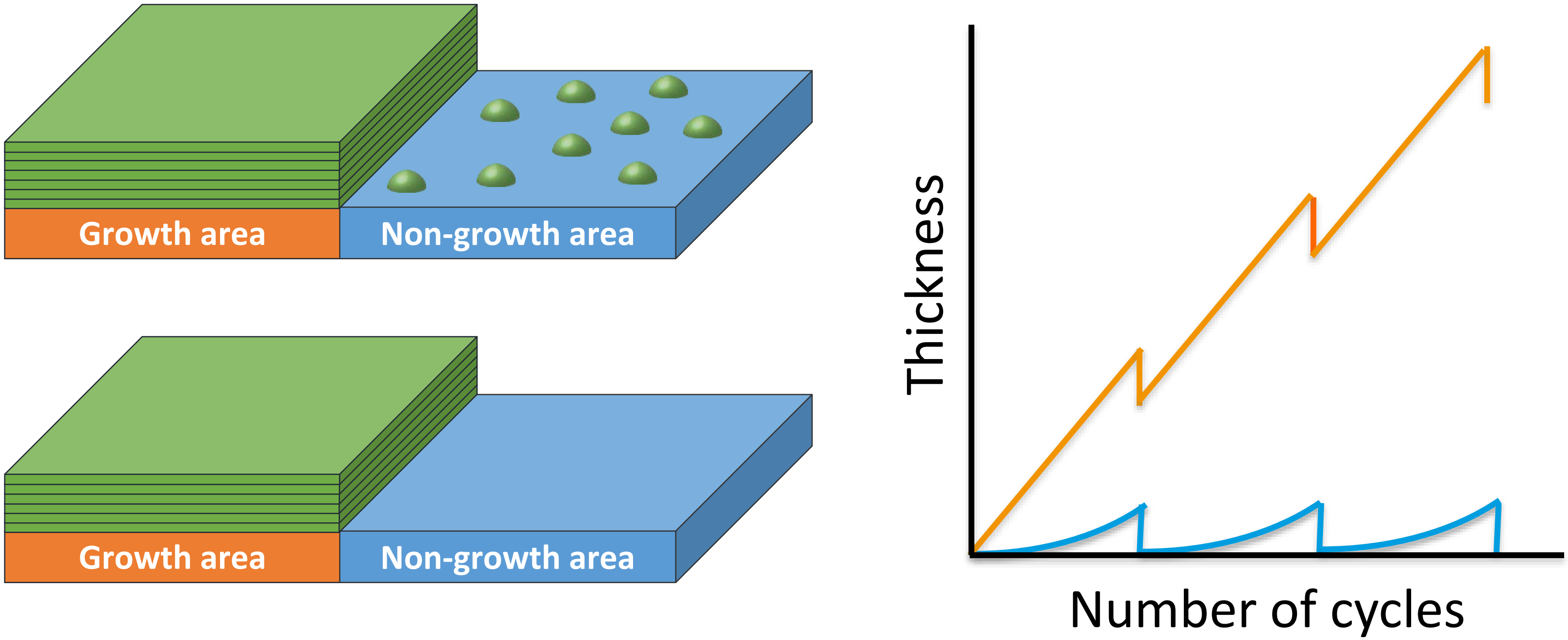
Main challenge: achieve high selectivity



- Selectivity in ALD refers to ratio of amount of material deposited on growth and non-growth areas
- It is extremely challenging to obtain area-selective ALD with a high selectivity due to growth initiation at defects and impurities
- **Potential solution: combine area-selective ALD with atomic layer etching (ALE)**

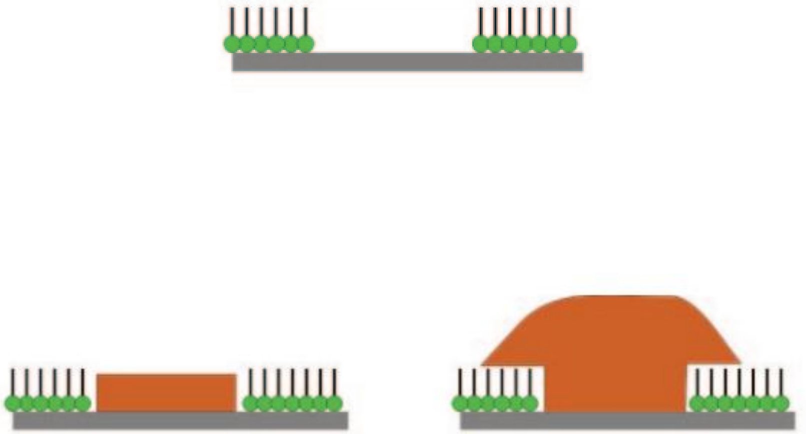
Vallat et al, *J. Vac. Sci. Technol.* A **35**, 01B104 (2017)

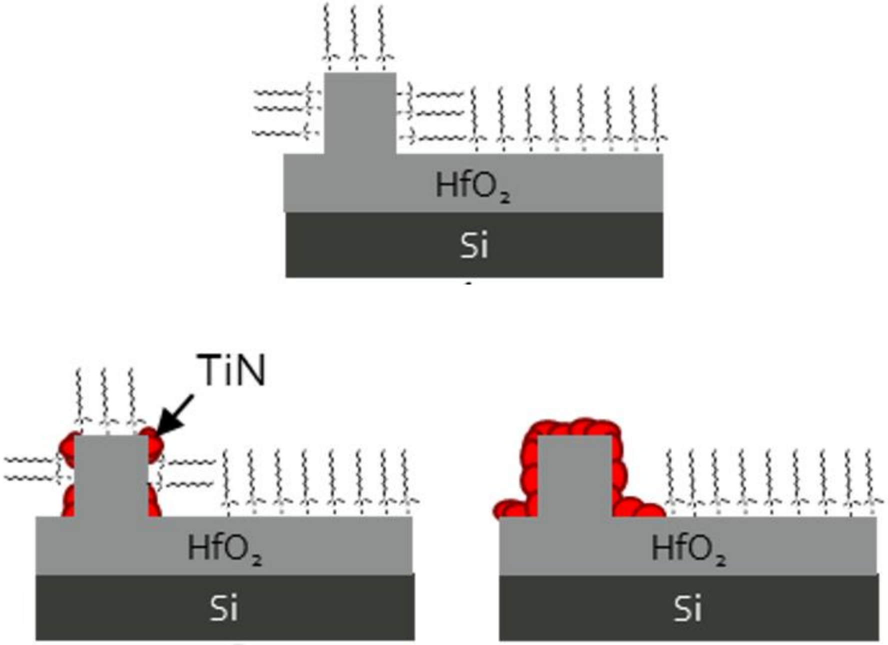
Combination of area-selective ALD and ALE



- Starting point: deposition occurs at a faster rate on the growth area
- ALE is performed to remove any deposited atoms from the non-growth area
- Supercycle is repeated until the desired thickness is reached

Geometrical effects





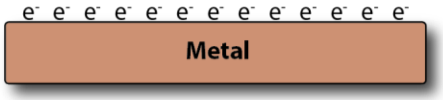
- Mushroom-type growth: Patterns broaden in lateral direction
- SAMs form defects at regions with high curvature

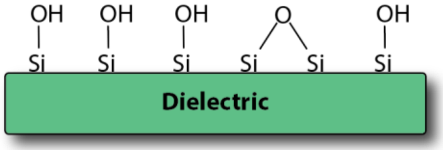
Ras *et al.* JACS **130**, 11252 (2008)
Chopra *et al*, *Chem Mater.* **28**, 4928 (2016)

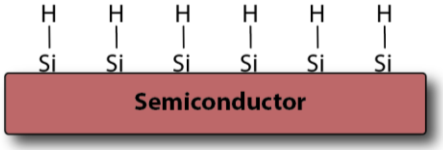
Classes of selectivity

Classes of materials

refers to surface termination







Examples of reported area-selective ALD processes

Metal-on-metal

- Pd on Pt – Cao *et al.*, *Chem. Cat. Chem.* **8**, 326 (2016)

Dielectric-on-dielectric

- HfO_2 on SiO_2 – Guo *et al.*, *ACS Appl. Mater. Interfaces* **8**, 19836 (2016)
- In_2O_3 on SiO_2 – Mameli *et al.*, *Chem. Mater.* **29**, 921 (2017)
- ZnO on SiO_2 – Minaye Hashemi *et al.*, *ACS Appl. Mater. Interfaces* **8**, 33264 (2016)

Semiconductor-on-semiconductor

- WS_2 on Si – Heyne *et al.*, *Nanotechnology* **28**, 04LT01 (2017)

Dielectric-on-semiconductor

- ZnO on Si – Haider *et al.*, *J. Phys. Chem. C* **120**, 26393 (2016)

Metal-on-semiconductor

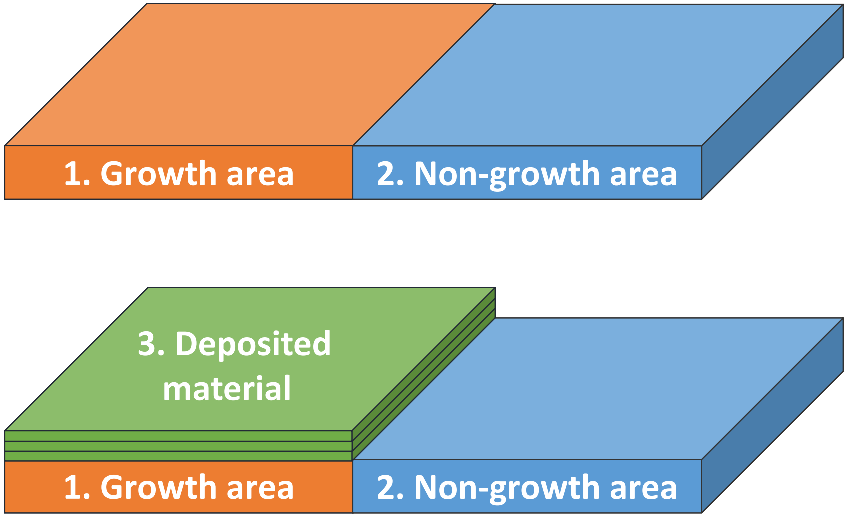
- W on Si – Lemaire *et al.*, *J. Chem. Phys.* **146**, 052811 (2017)

Metal-on-dielectric ?

Dielectric-on-metal ?

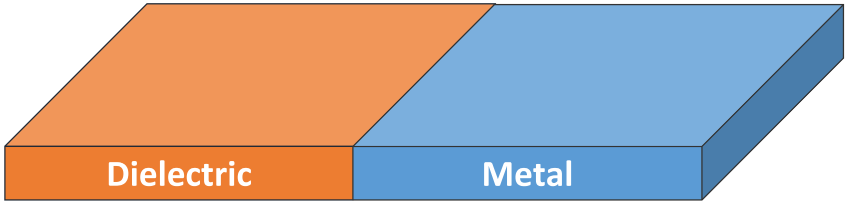
Mayberry, 15th ALD conference (ALD 2015)
Delabie *et al.*, 2nd Area Selective Deposition workshop (ASD 2017)

Surfaces to take into account



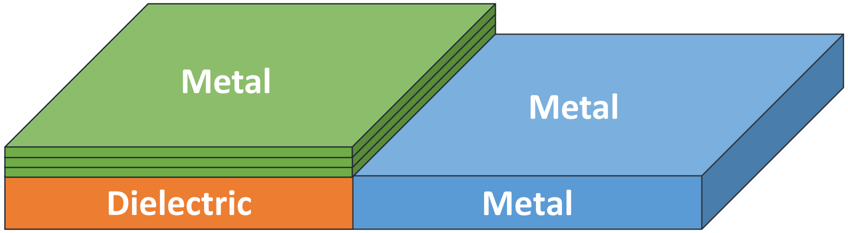
Surfaces to take into account

Example: metal-on-dielectric with metal non-growth area



Starting point:

- Dielectric growth area
- Metal non-growth area



After covering dielectric growth area:

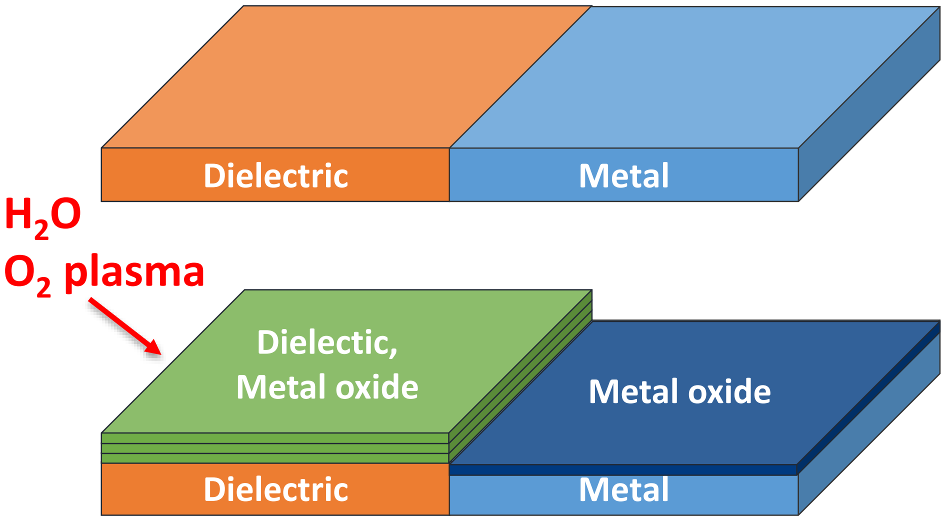
- Two metal surfaces

Difficult classes:

- Metal-on-dielectric with metal non-growth area
- Dielectric-on-metal with dielectric non-growth area

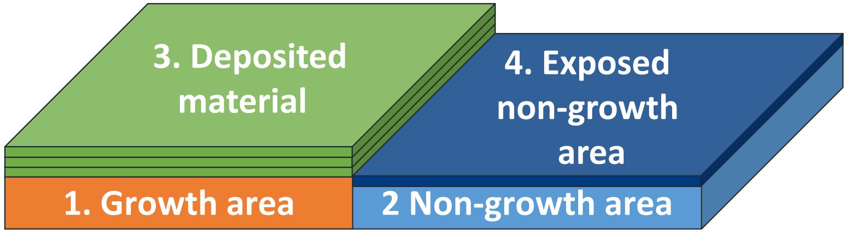
Modification of non-growth area

Example: dielectric-on-dielectric with metal non-growth area



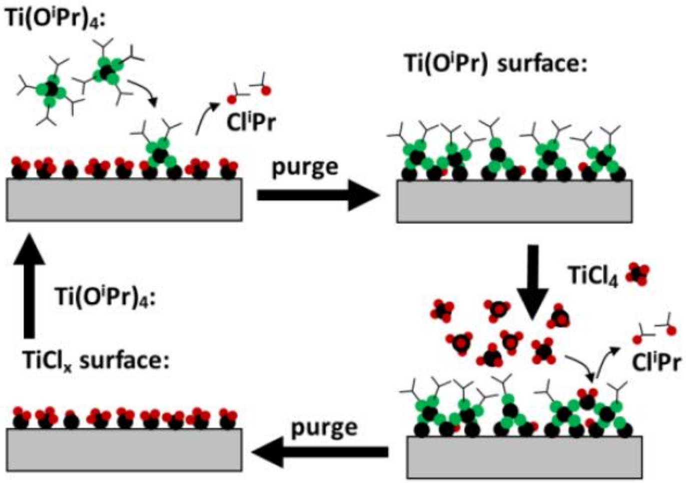
Character of the non-growth area changes due to exposure to precursor/co-reactant

Modification of non-growth area

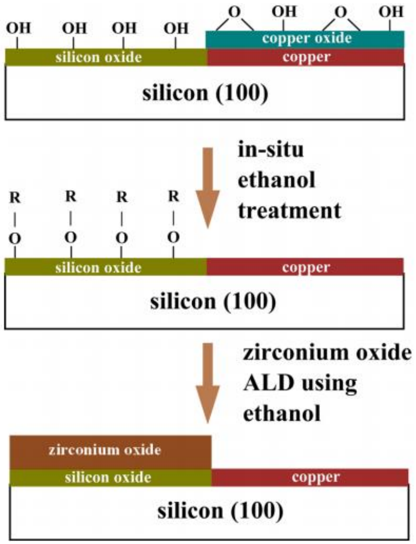


Character of the non-growth area changes due to exposure to precursor/co-reactant

TiO_2 from $TiCl_4$ and $Ti(O^iPr)_4$

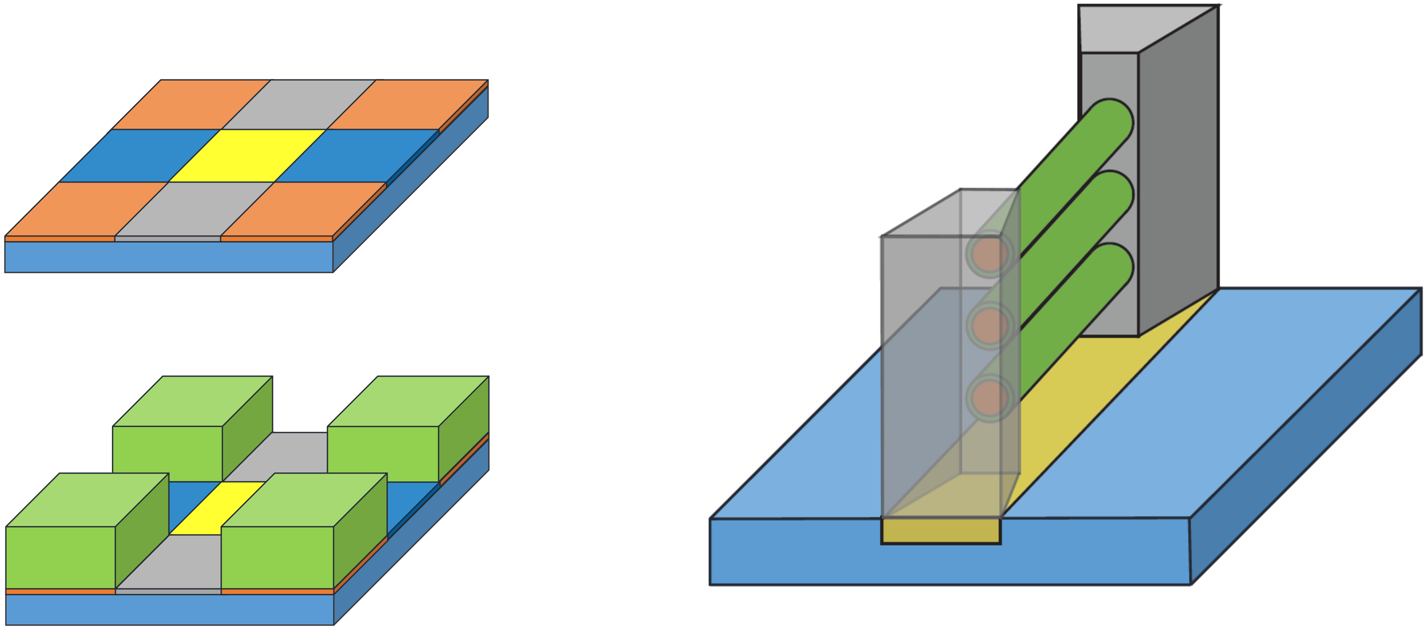


ZrO_2 ALD using ethanol as co-reactant



Atanasov *et al.* *JVSTA* **34**, 01A148 (2016)
Selvaraj *et al*, *JVSTA* **32**, 010601 (2014)

Area-selective ALD on a device structure



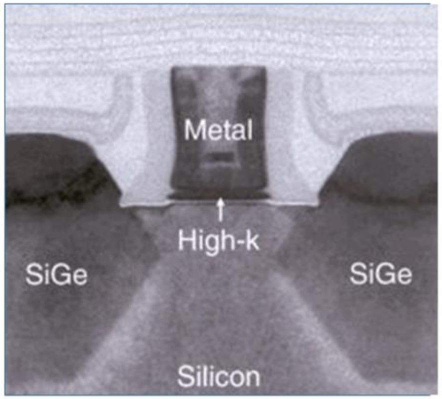
- A device structure consists of many more materials

Carver *et al.*, ECS JSST 4, N5005 (2016)

ALD for semiconductor fabrication

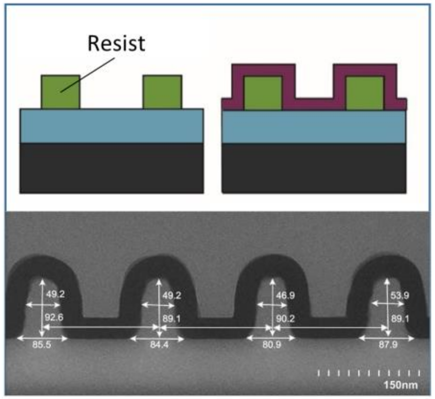
Key ALD-enabled innovations in semiconductor fabrication

2007
45 nm node



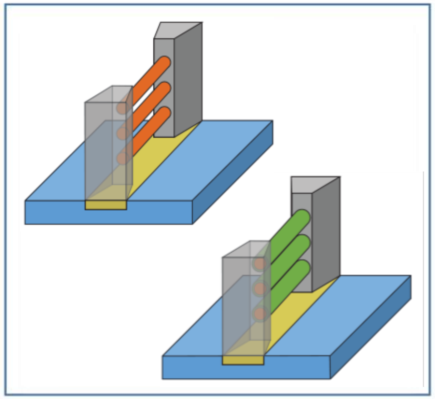
High-κ dielectric

2014
14 nm node



Double patterning

2021?
5 nm node?



Area-selective ALD

Scaling

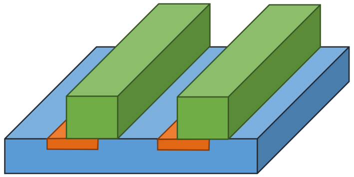
Self-aligned fabrication

Area-selective ALD for self-aligned fabrication has the potential to become the next ALD-enabled innovation in semiconductor fabrication

Summary

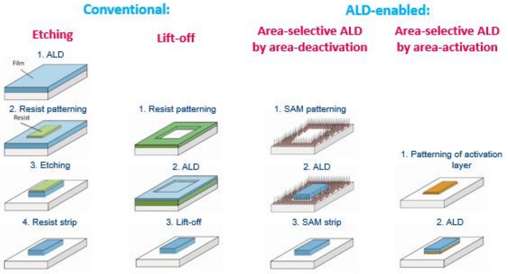
Motivation for area-selective ALD

- Elimination of compatibility issues
- Enable self-aligned fabrication
- Controlled synthesis of complex nanostructures



Patterning of ALD-grown films

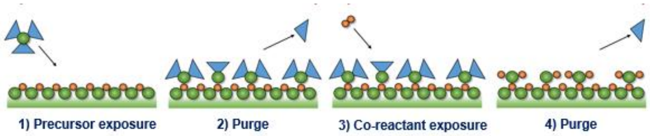
1. Area-selective ALD by area-deactivation
2. Area-selective ALD by area-activation



Review paper: *The use of ALD in advanced nanopatterning*
Mackus *et al.*, *Nanoscale* **6**, 10941 (2014)

Main approaches for area-selective ALD

1a. Selective precursor adsorption
1b. Precursor blocking prior to deposition
1c. Precursor blocking during deposition
2a. Catalytic activation of the co-reactant



Challenges for area-selective ALD

- Achieve sufficiently high selectivity
- Eliminate lateral broadening