Atomic Layer Deposition (ALD) overview

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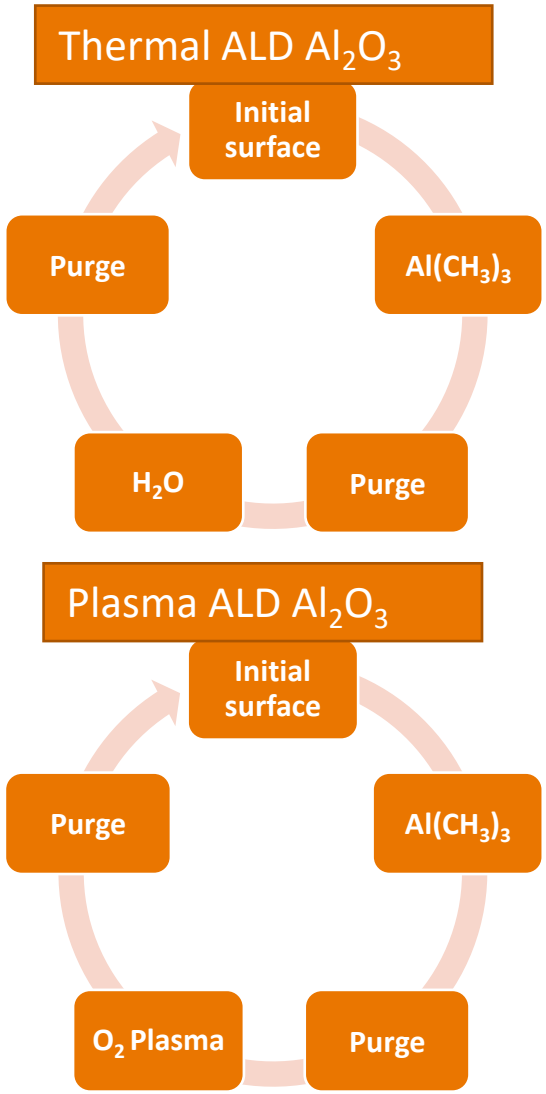
Outline

- **What is ALD?**
- Processes
- System Features
- Application examples
- In situ diagnostics
- Control of ion energy

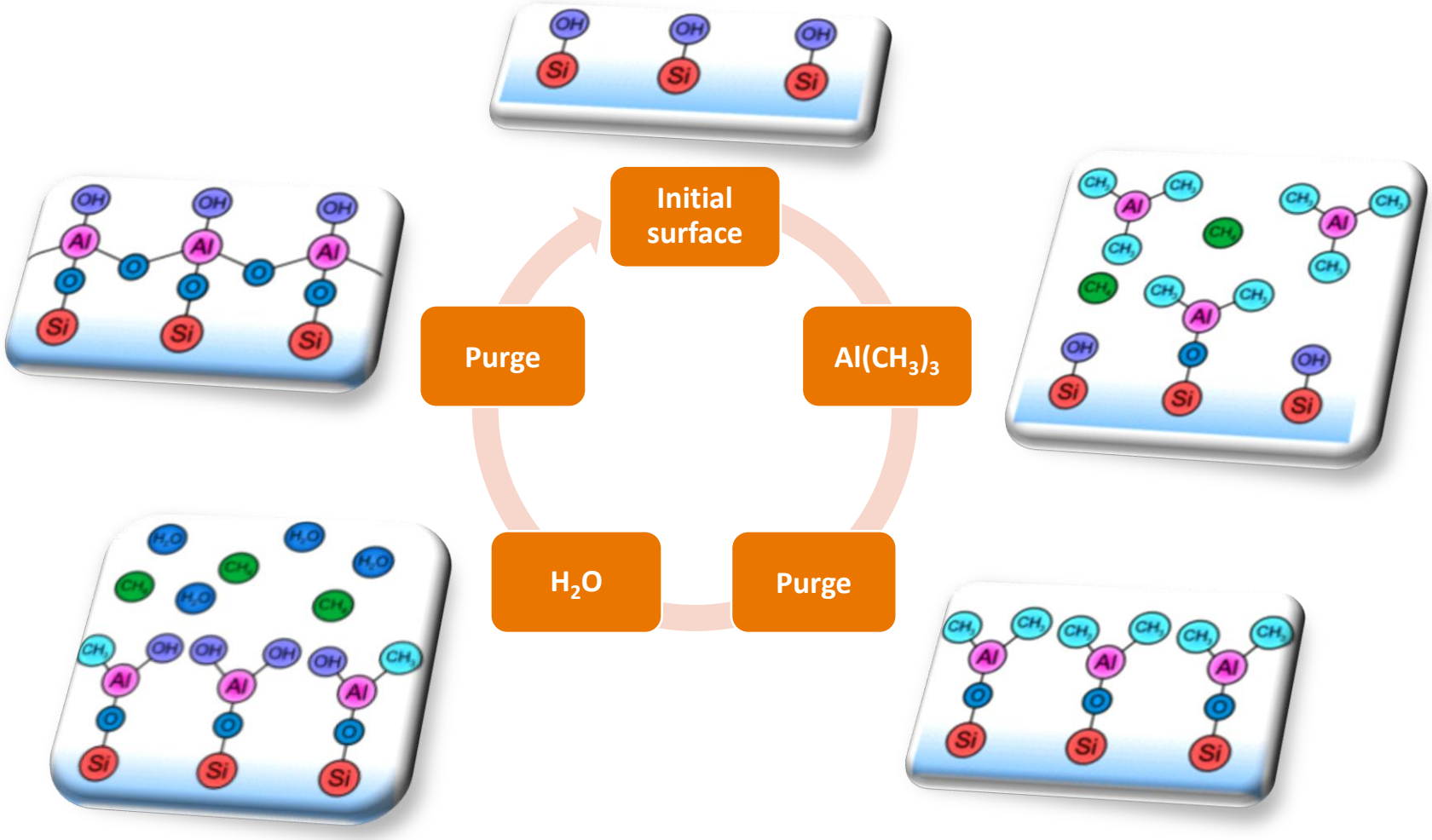
What is Atomic Layer Deposition (ALD)?

ALD is a sequential, self limiting surface reaction, based on two or more reactants

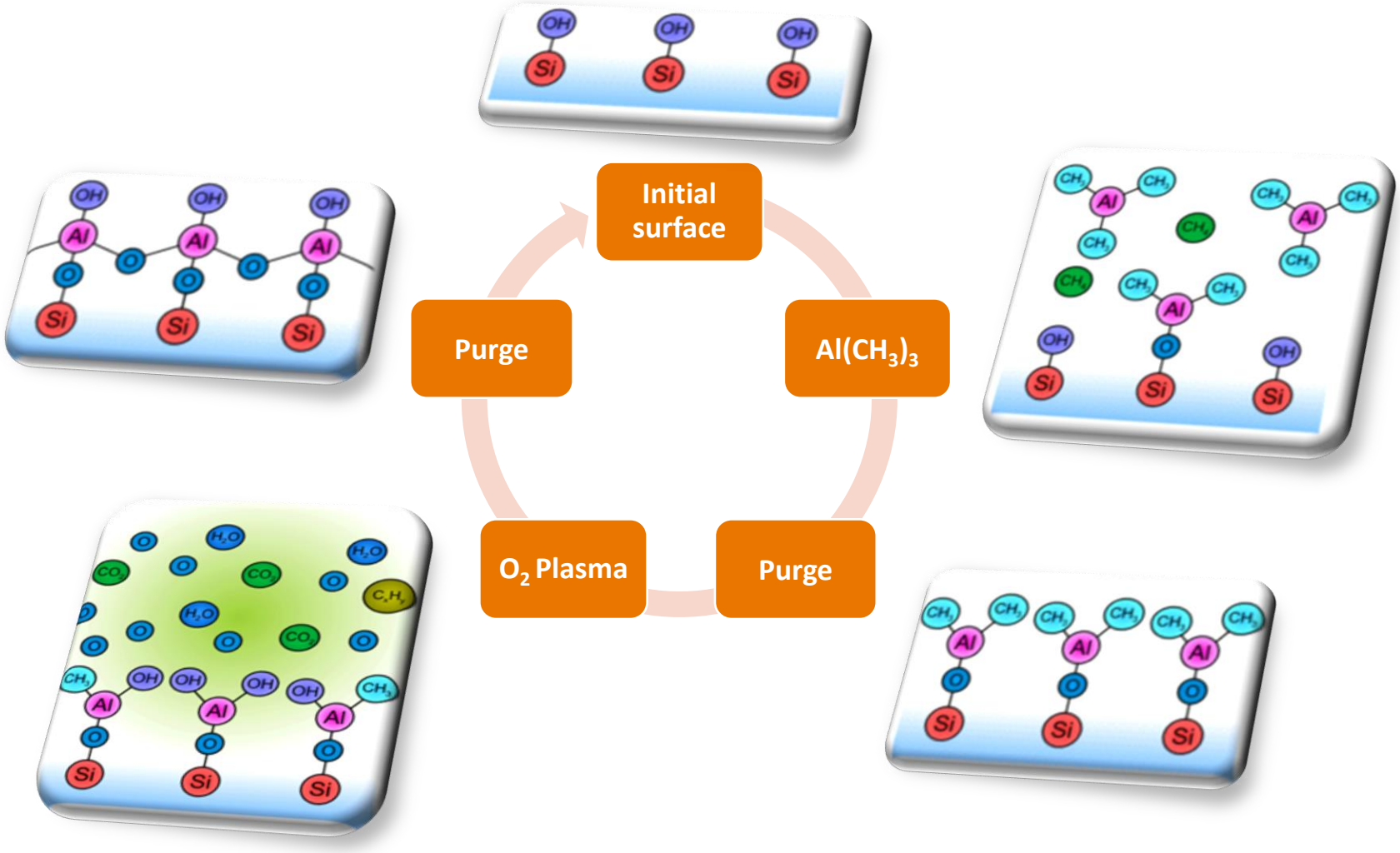
- Precise thickness control
- Growth rate is independent of precursor flux once surfaces are saturated
  - Conformal coating even in high aspect ratio structures
- Low pin hole levels
  - No gas phase reactions generating particles
- Very thin and dense films
  - Low deposition rates, typically 1Å/cycle
- Wide variety of materials possible
  - limited by precursors



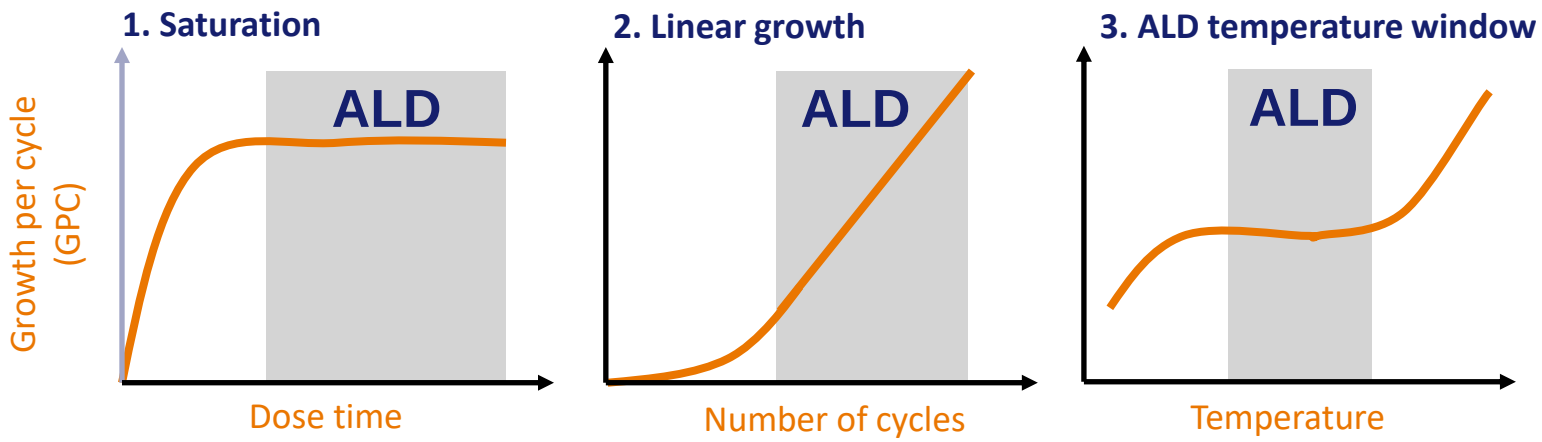
ALD cycle of Al_2O_3 thermal



ALD cycle of Al_2O_3 plasma enhanced



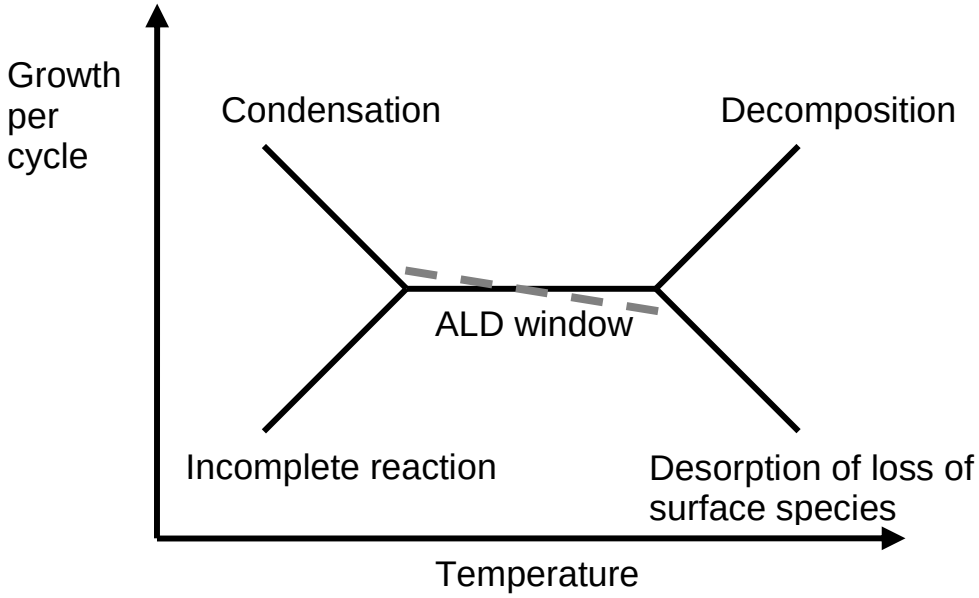
How to identify true ALD growth



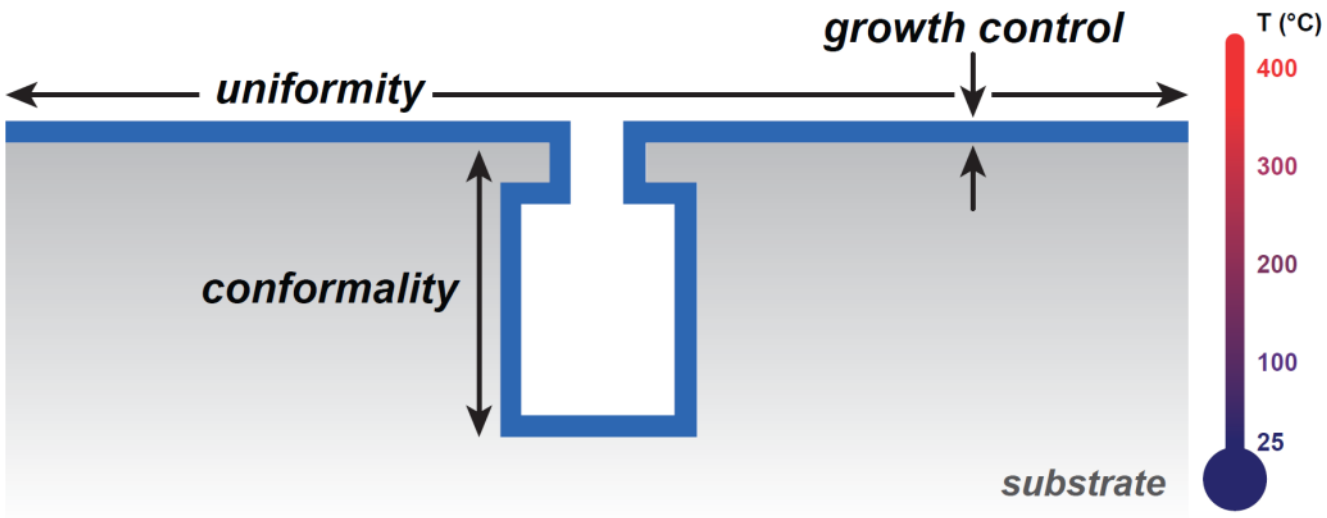
- A plateau in GPC as dose times increase indicates self-limited, ALD. The metal precursor and plasma dose times should follow this trend.
- A linear trend indicates layer-by-layer deposition. Exponential trend indicates under-saturation or CVD.
- Low GPC at low T indicates slow deposition kinetics, i.e. under-saturation, poor nucleation. High GPC at high T indicates precursor decomposition.

Growth per cycle vs temperature

- Differing possibilities depending on reaction mechanism
- ALD temperature window not always flat, since equilibrium density of reactive surface sites (e.g., OH), depends on temperature.



Metrics for film deposition



Knoops et al., *Handbook of Crystal Growth, 2nd edition*, p. 1101–1134 (2015).

Strong points of ALD:

- **Growth control** at the subnanometer level
- **Uniformity** of the films on large substrates
- **Conformality** for complex surface features
- Choice of deposition temperature down to **low substrate temperatures** (using plasma)

Thermal and Plasma

ALD benefits from Plasma

- Improved material properties
  - Film density and composition can be influenced
  - Lower impurities
- Increased choice of precursors and materials
  - Nitrides
  - Metals
- Reduced substrate temperatures
- Surface pre-treatment
  - Surface activation and surface cleaning
- Increased growth rate
- Shorter nucleation periods

Plasma essential for lower oxygen content and lower resistivities.

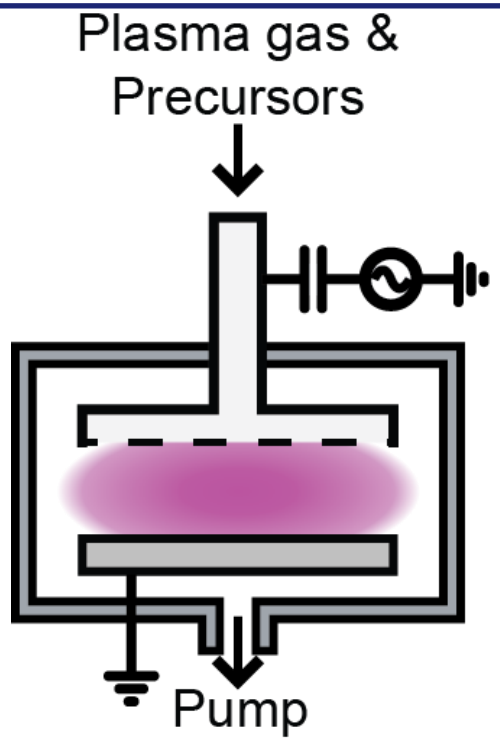
Plasma allows growth often at 100 °C or lower temperatures.

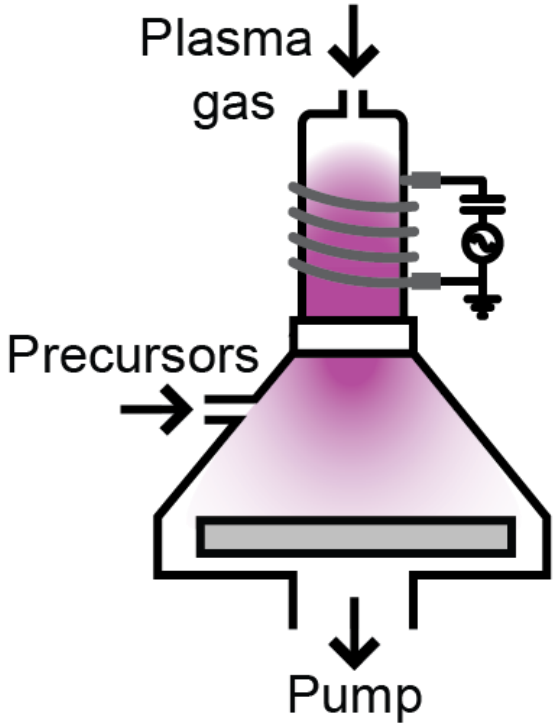
Plasma not recommended for

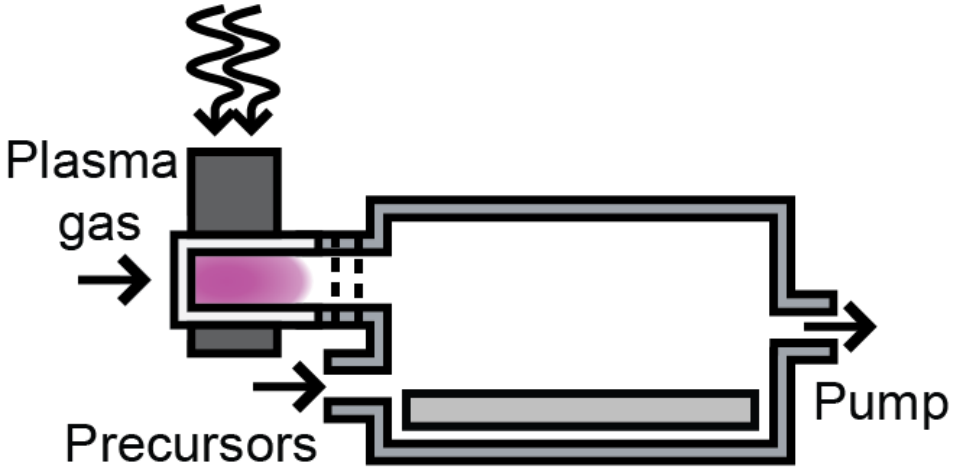
- Aspect ratios above 50:1
- Substrates reactive with plasma

Often soft plasma conditions can be used to minimize damage.

Plasma ALD – reactor types







Direct plasma:
Substrate part of plasma creation zone
Strong ion bombardment
Plasma damage to sensitive devices

Remote plasma:
Substrate "downstream" of plasma creation zone
Mild ion bombardment at low pressure, virtually no ion energy at high pressure
Excellent compromise between direct plasma ALD and radical enhanced

Radical Enhanced:
No plasma above substrate. Often bought in source.
No ions, low radical flux
Poor film quality and uniformity

FlexAL ALD system

- Cutting edge plasma ALD systems with thermal ALD as standard
- Mixed mode operation within a single recipe
  - No hardware changes required to switch mode between plasma and thermal ALD
    - start with thermal Al_2O_3 on sensitive interface but continue with plasma ALD for best material properties
    - for platinum start with plasma to minimise nucleation delay and continue with thermal

FlexAL

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Plasma ALD processing advantages

- Reduced substrate temperatures
  - Advantageous for temperature sensitive substrates such as $LiNbO_3$, $LiTaO_3$, polymers, plastics, etc.
- Improved material properties
  - Film density and composition can be influenced
  - Lower impurity levels
- Increased choice of precursors and materials
  - Nitrides including AlN, Si_3N_4, TiN
  - Metals
- Surface pre-treatment
  - Surface activation and surface cleansing, e.g. GaN
- Shorter nucleation periods, e.g. plasma ALD of metals

Metals
Pt
Ru

Fluorides
AlF_3

Sulphides
MoS_2
WS_2
TiS_2/TiS_3

Oxides	Nitrides
Al_2O_3	AlN
Co_3O_4	
Ga_2O_3	GaN
HfO_2	HfN
In_2O_3	
Li_2CO_3	
MoO_3	
Nb_2O_5	NbN
NiO	
SiO_2	Si_3N_4
SnO_2	
Ta_2O_5	TaN
TiO_2	TiN
WO_3	WN
ZnO	
ZrO_2	

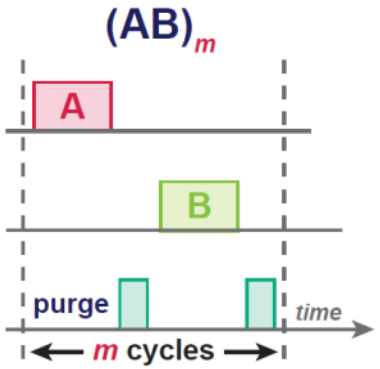
Plasma surface pre-treatments

- Optimal pre-treatment for surface can be integrated in recipe (plasma pressure, power, gas flow).
  - Improved nucleation for certain surfaces (short O_2 plasma on a-Si)
  - Functionalizing graphene, CNTs (O_2 or H_2 plasma)
  - Improving adhesion (H_2 plasma for Pt on TiO_2)
  - In-situ cleaning (TMA pulses to remove oxide, O_2 plasma for carbon)

Pretreatment

plasma, precursor, gas

ALD process

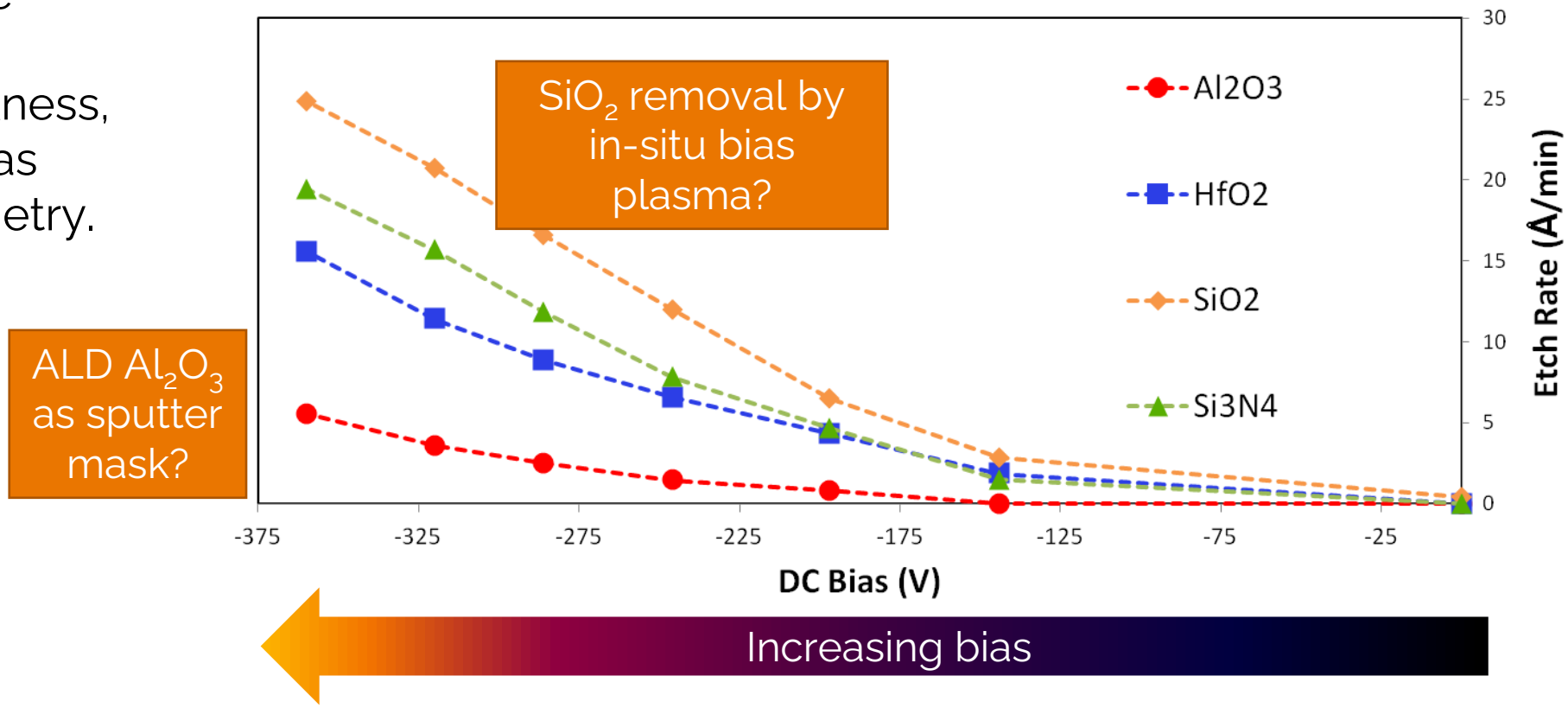


With biasing chemical sputter clean of surfaces (e.g. Ar/H_2 to remove native oxide and carbon)

- Before deposition of dielectrics or metal contact
- Adhesion improvement

Ar sputter etch rates of Al_2O_3, HfO_2, SiO_2 and Si_3N_4

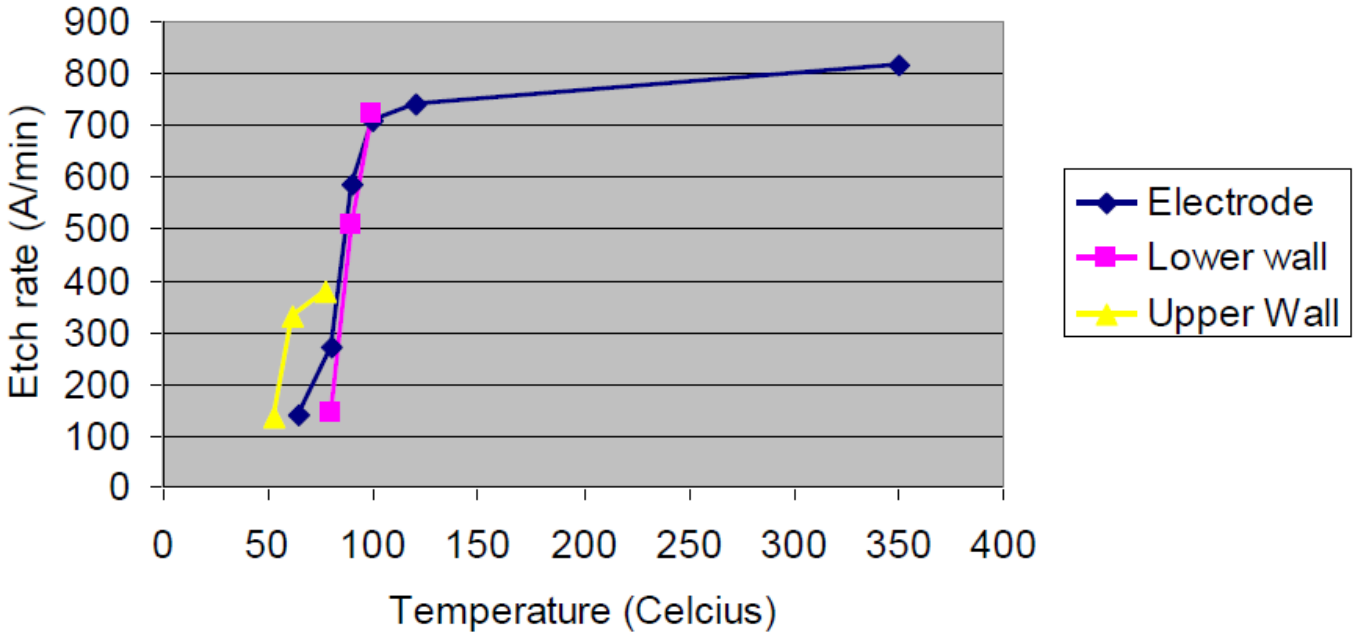
Etch rates (Å/min) under Ar plasma exposure were determined using the difference in film thickness, before and after etch as measured by ellipsometry.



Plasma cleaning by SF_6 for TiN

- Plasma cleaning using SF_6 plasma without bias
- Data available for TiN deposition (should also work for Si, W, Mo, and Ta compounds)
- Expected frequency of cleaning and downtime
  - Clean every >450 nm
  - <10 min plasma clean for TiN

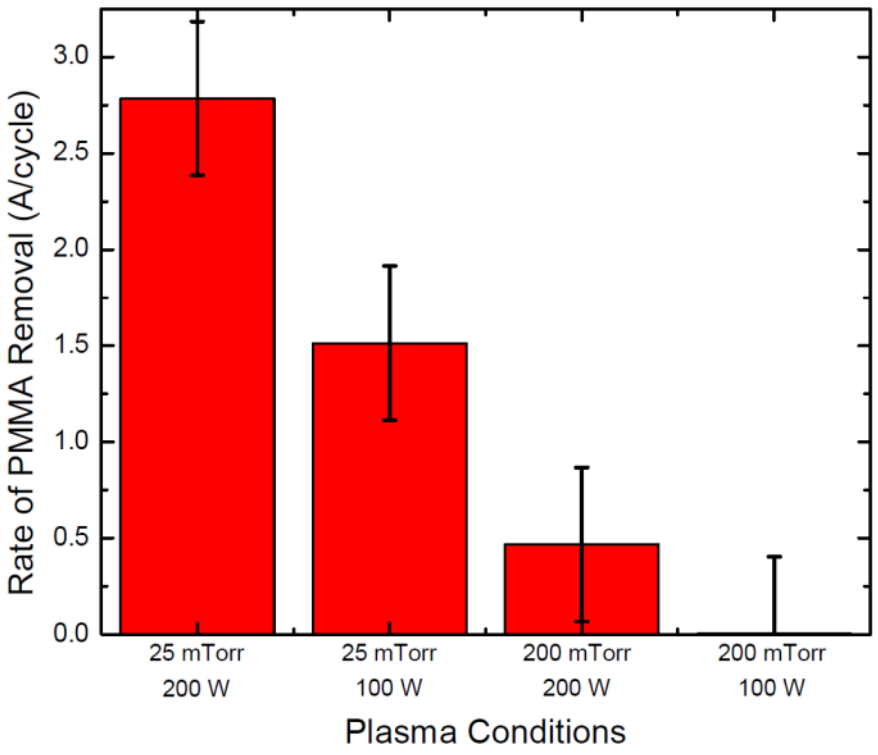
Etch rates of TiN coated on Si test pieces placed at various locations in the system. Effective cleaning for surfaces >100 °C (temperature at which TiF_x becomes volatile).



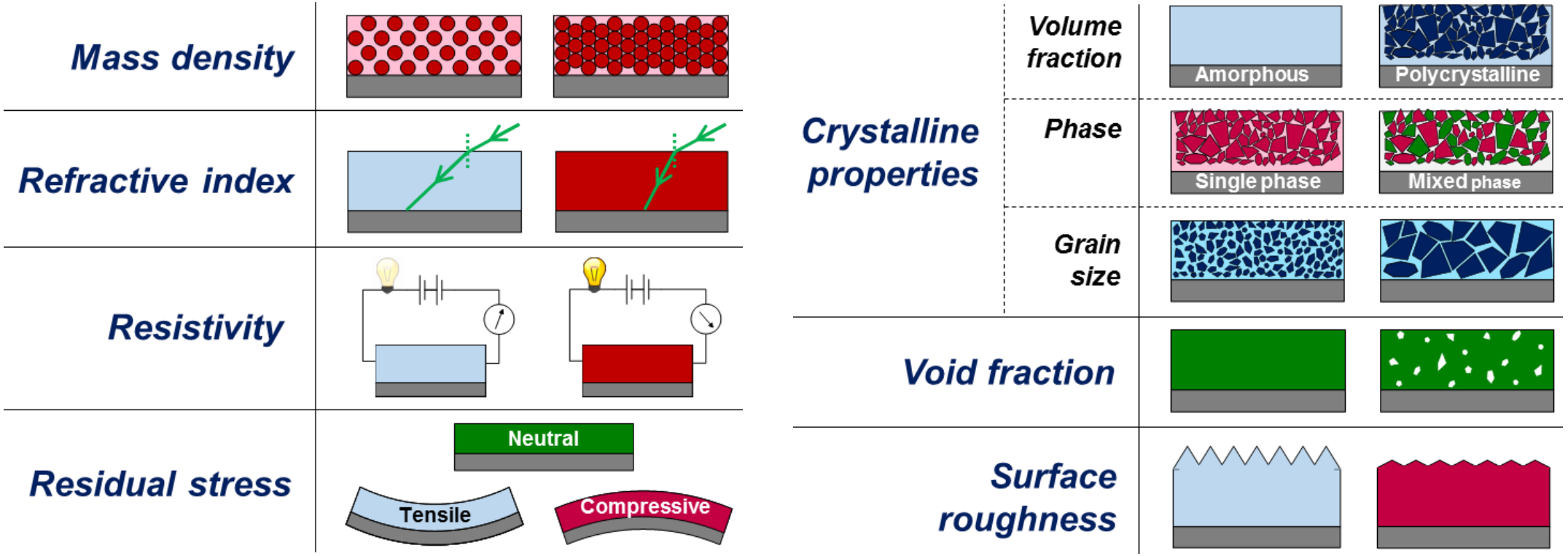
Low damage for depositing on polymers

- To limit etching of a polymer plasma conditions can be set to reduce etching.
- High pressure plasma allows growth on polymers without etching them.
- ALD deposit will also function as protective layer, so generally etching is minimal.

Rate of the resist removal during 50 plasma exposures of 5s each



We enable material property control by substrate biasing



A wide range of properties can be tuned by substrate biasing in ALD

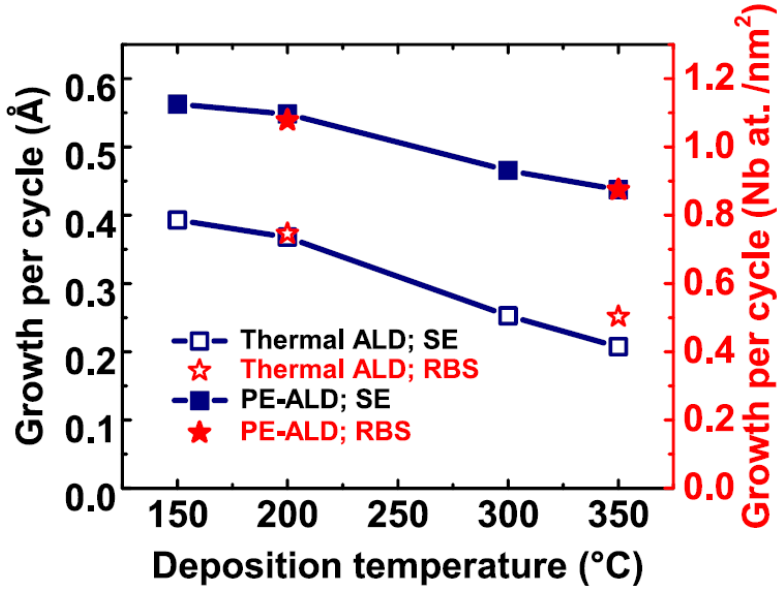
- First to introduce substrate biasing in ALD
- >10 years of plasma ALD experience

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

Deposition of Nb_2O_5

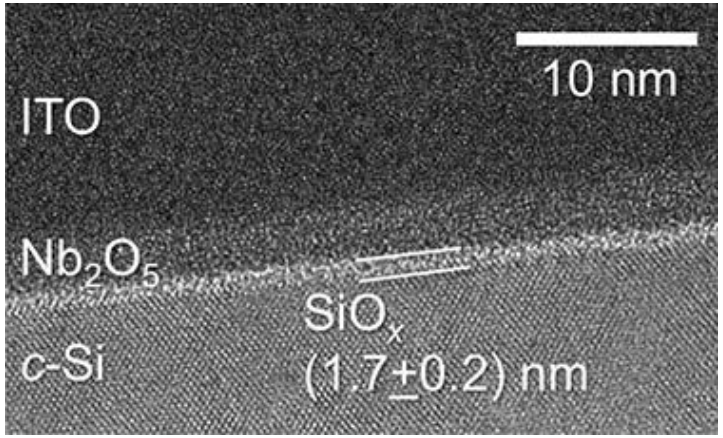
- Plasma and thermal ALD using TBTDEN and O_2 plasma or H_2O.

Wide temperature range for plasma and thermal ALD with higher GPC for plasma process



Basuvalingam et al., *J. Vac. Sci. Technol. A* **36**, 041503 (2018)
Macco et al., *Sol. Energy Mater. Sol. Cells* **184**, 98 (2018)

Material	Nb_2O_5
Precursor	TBTDEN
Co-reactant	O_2 plasma, H_2O thermal
Temperature range	150ºC – 350 °C
Growth per cycle	0.56 Å/cycle (plasma) 0.38 Å/cycle (thermal) @ 200°C
Refractive Index	2.35 – 2.46
Uniformity	± 3-4% over 200mm



Nb_2O_5 on c-Si giving high surface passivation after anneal

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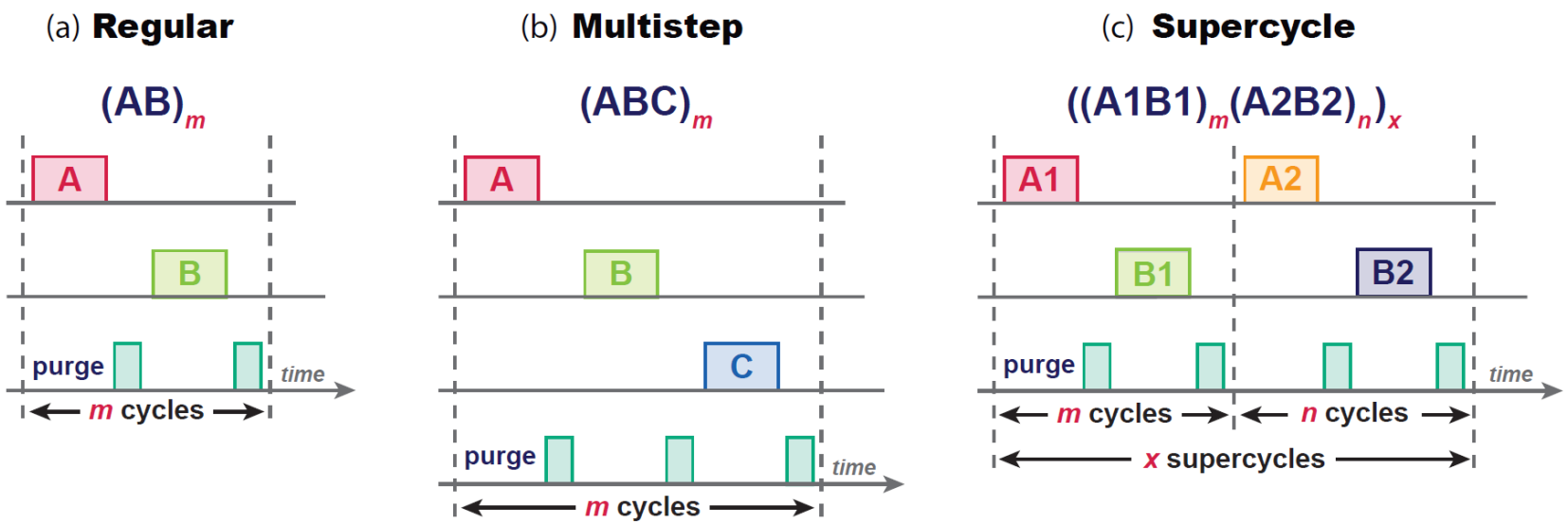
ALD process schemes: multi-component materials

Besides the regular AB process scheme, there are also ABC multistep and ABAB supercycle schemes, which are easily implemented in recipe based software.



e.g. Al_2O_3, TiO_2, Pt

e.g. Pt at low temperature

e.g. ZnO:Al, $HfSiO_x$, $SrTiO_3$

Knoops et al., *Handbook of Crystal Growth, 2nd edition*, p. 1101–1134 (2015).

Conclusions

- Extremely flexible thermal and plasma ALD system
- Wide range of precursors and films
- Low temperature capability for temperature sensitive deposition
- Pretreatments prior to deposition to improve interface and nucleation
- Turbopumping for superior nitride films
- Substrate bias capability for film densification and stress control
- Clusterable with other modules for transfer without vacuum break