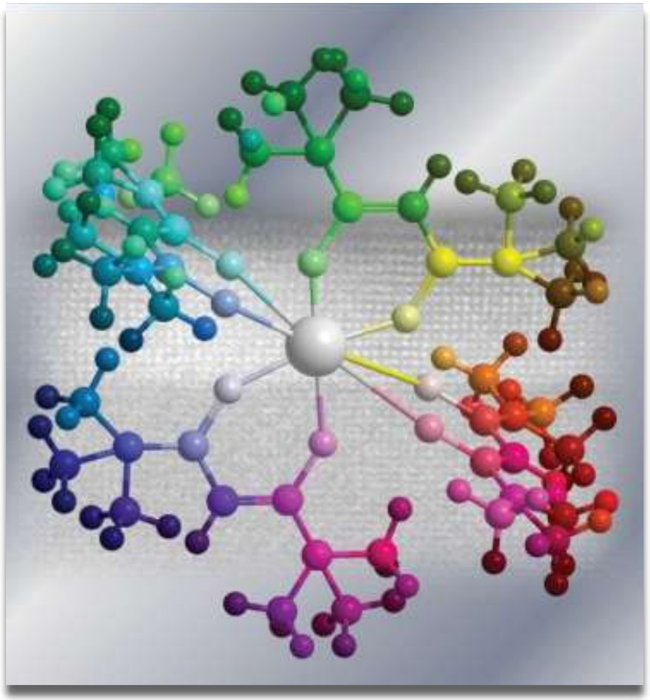
Introduction to chemical deposition methods to prepare functional oxide thin films



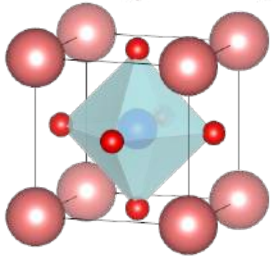
Mariona Coll
Institut de Ciència de Materials de Barcelona
mcoll@icmab.es

ISOE2023 August 29- September 8

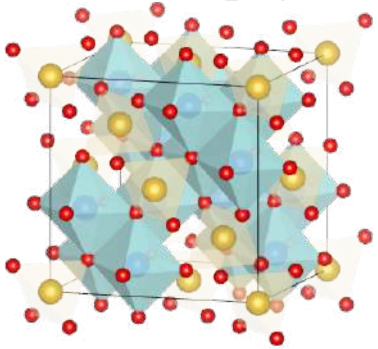
Complex oxides

- ✓ Broad variety of structures
- ✓ Composition versatility
- ✓ (chemical, thermal, mechanical) stability
- ✓ Unique physical properties

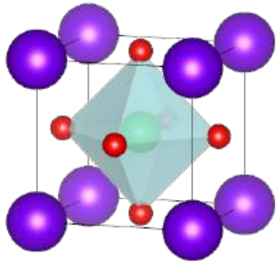
$BiFeO_3$, $SrTiO_3$



$CoFe_2O_4$



$La_{0.7}Sr_{0.3}MnO_3$



Photovoltaic

Ferroelectricity

Magnetism

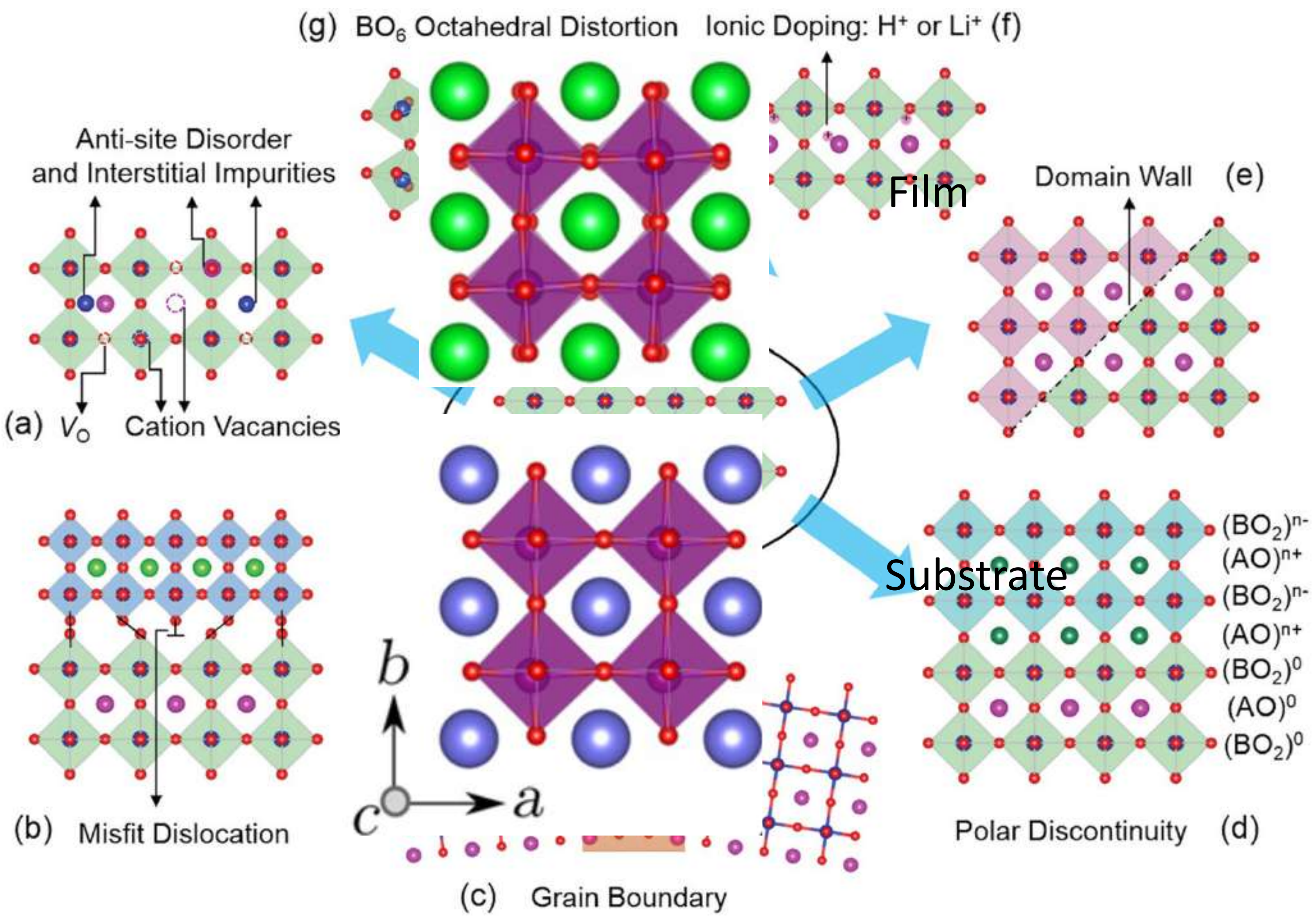
Superconductivity

Metal-insulator transitions

…

Examples of defects in perovskites

Epitaxy

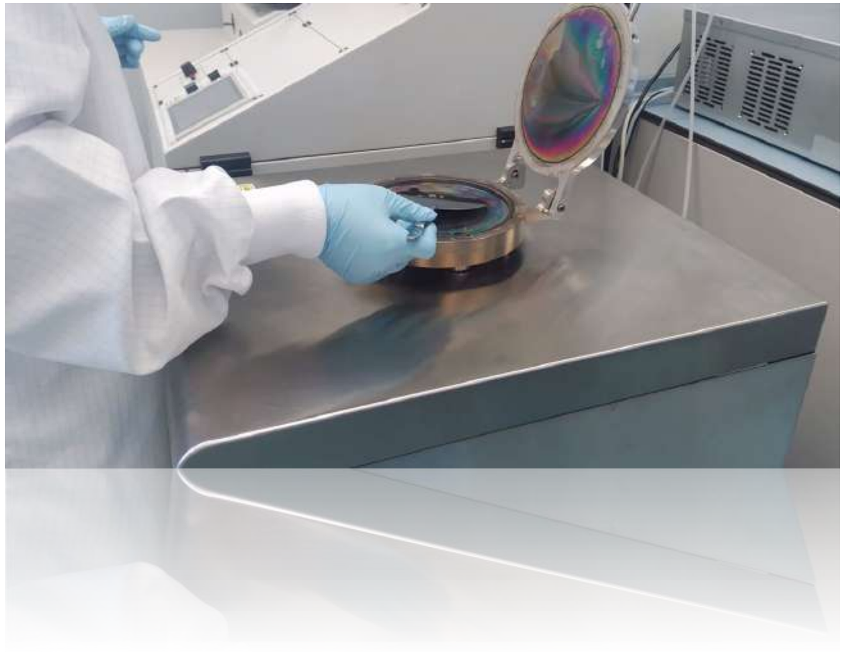


Appl. Surf. Sci., ***482***:1–93, 2019 Roadmap Towards Oxide Electronics

Mater. Horiz., 2020,***7***, 2832-2859

Chemical Deposition Methods

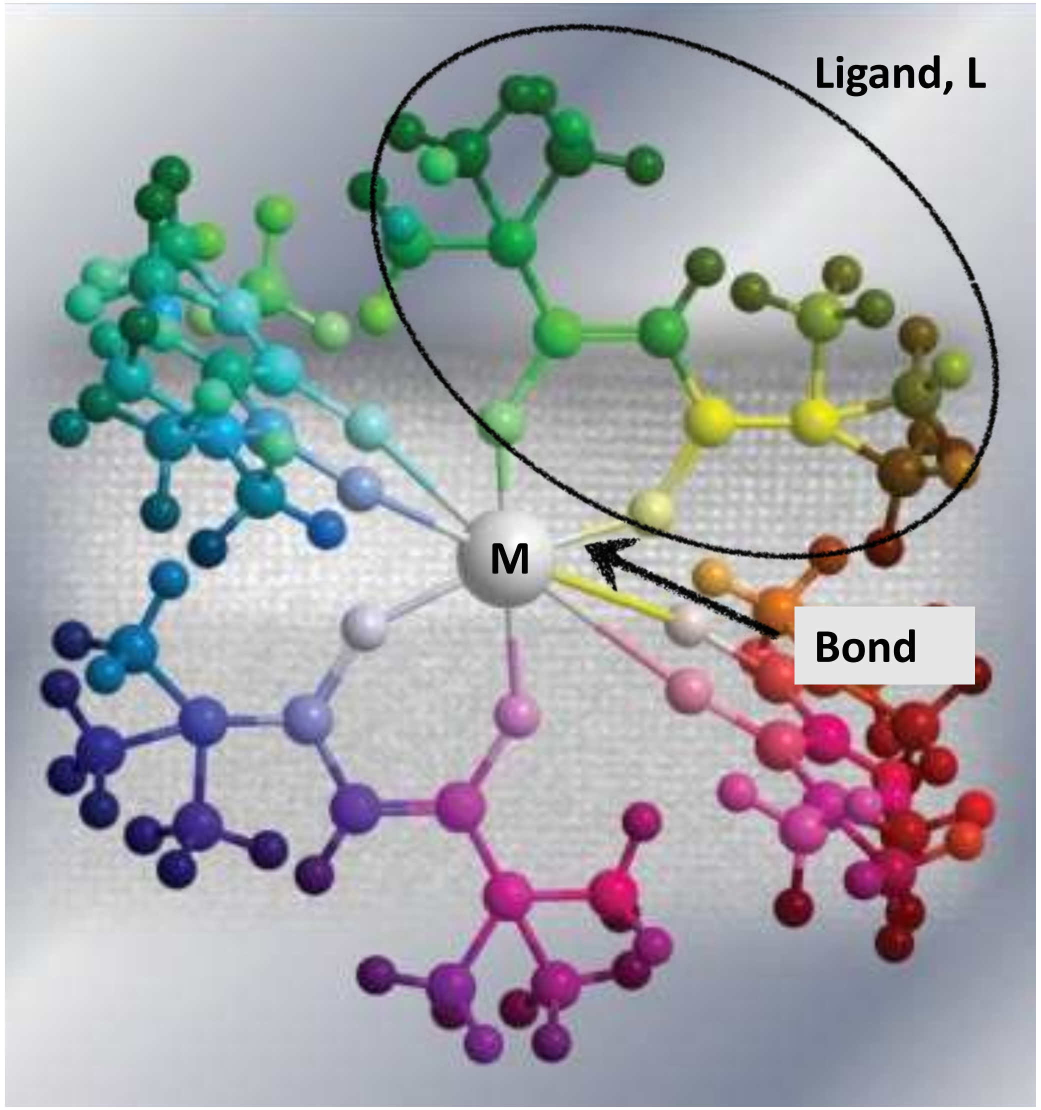
Atomic Layer Deposition



Chemical Solution Deposition

precise growth and cost-effective, potentially scalable

Chemical Precursor:



Metal

Ligand

Bond

undergo chemical reactions
P, T, t, flow

Film

Outline

1) **PART I Chemical solution deposition CSD**

2) **PART II Atomic layer deposition ALD**

Fundamentals
Opportunities/
Challenges

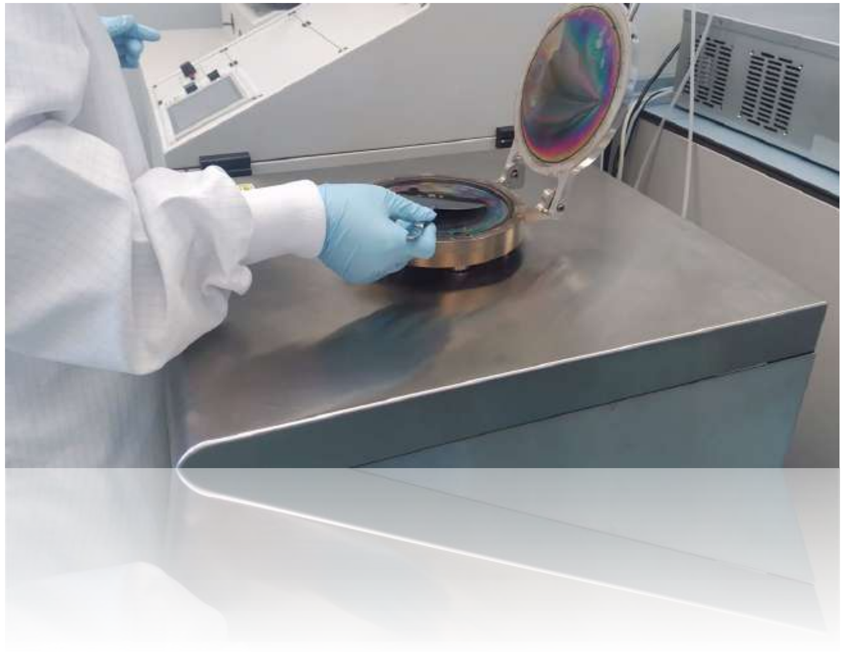
Key examples

3) **Wrapping up: 1 slide Comparison**

Chemical Deposition Methods

Chemical Solution Deposition (CSD)

Atomic Layer Deposition (ALD)



precise growth and cost-effective, potentially scalable

Chemical Solution Deposition (CSD) Timeline

silica gel

1850 ish

SiO_2
TiO_2
ZrO_2
Al_2O_3

Optical coatings on industrial scale

1950s

Transparent conducting oxides for heat-reflecting windows (Philips)

1970s

PZT

FERAM
high- k

1980

Superconductivity and coated conductors
Fuel cells
Electron and ion conductors
…

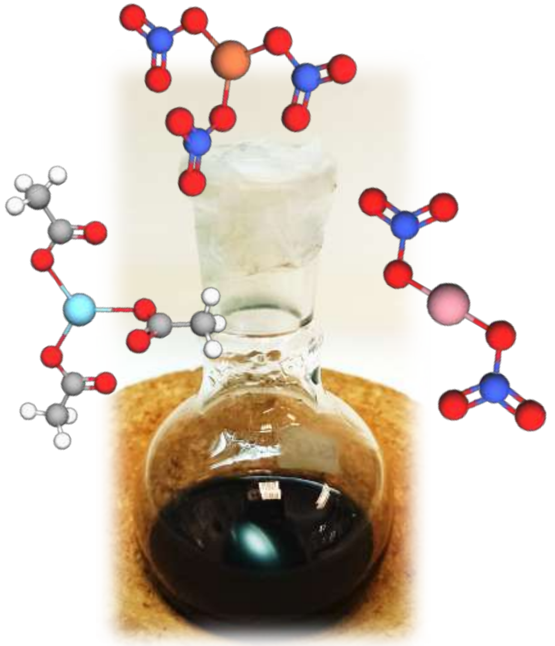
Chemical solution deposition of functional oxide thin films, T. Schneller, M. Kosec, D. Payne, Springer, 2013

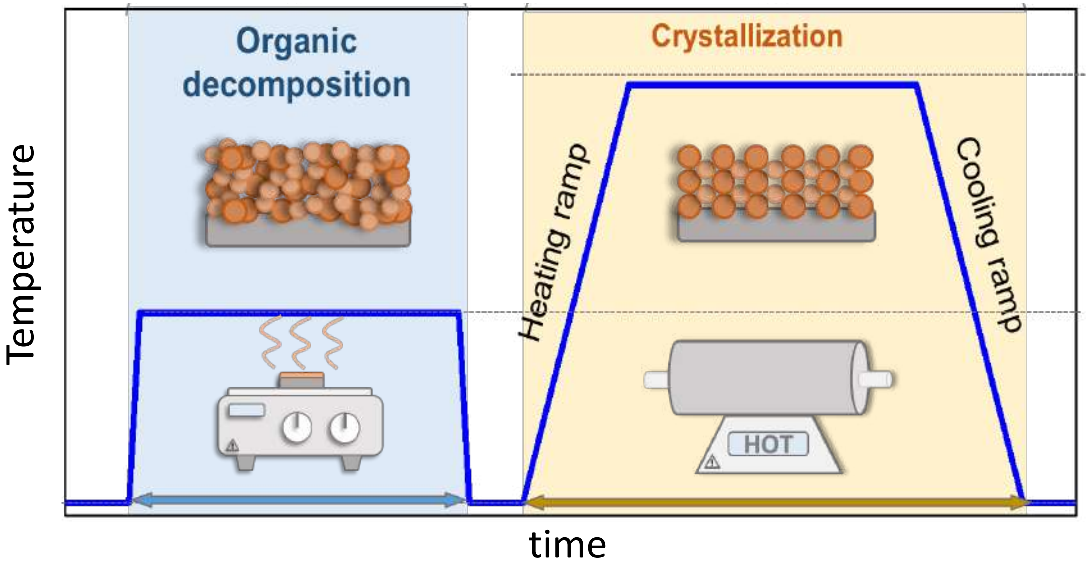
Chemical Solution Deposition (CSD): Process overview

1 Solution design

2 Deposition

3 Thermal Treatment





RT- 300-400ºC

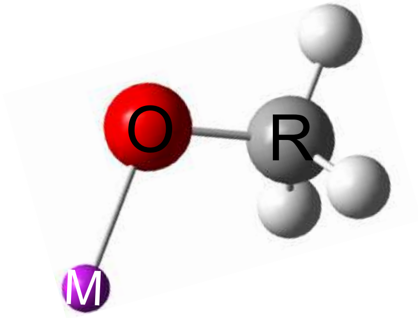
400-900 ºC

low investment

Chemical Solution Deposition (CSD): Reactivity

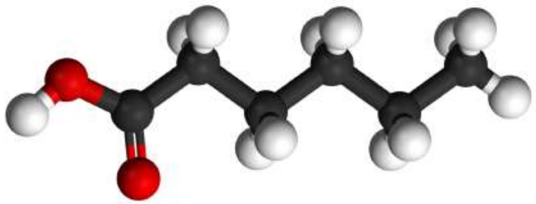
1 Solution chemistry

Alkoxides

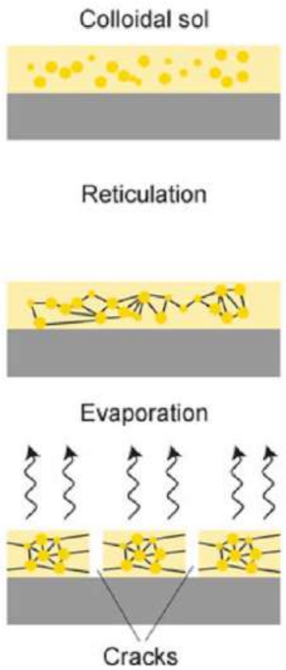


High solubility in organic solvents
High reactivity
Hydrolysis+condensation: difficult to control
Organic part can be tuned to desgin reactivity (i.e UV- sensitive)

Carboxylate



Alkoxides



- Compatible precursor, solvent and additive chemistry, concentration, stoichiometry

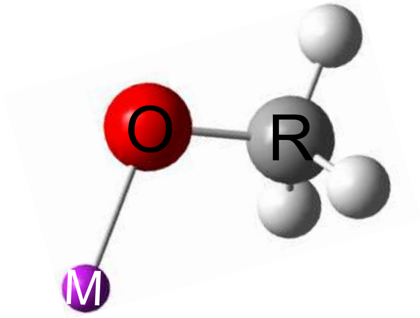
Homogeneity, stability, viscosity

Solubility: Like dissolves like

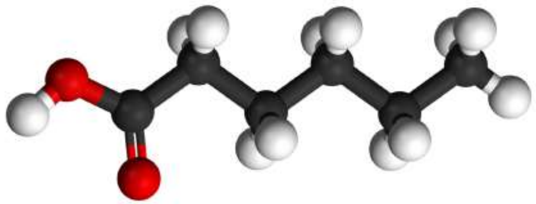
Chemical Solution Deposition (CSD): Reactivity

1 Solution chemistry

Alkoxides



Carboxylate



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High reactivity
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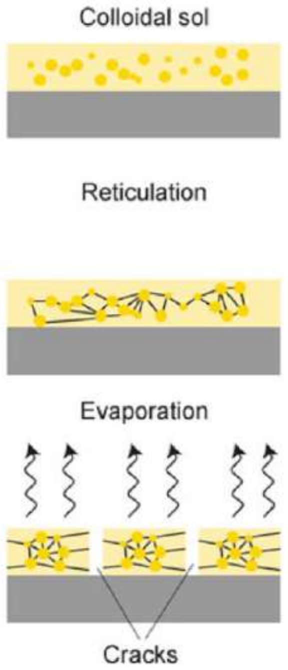
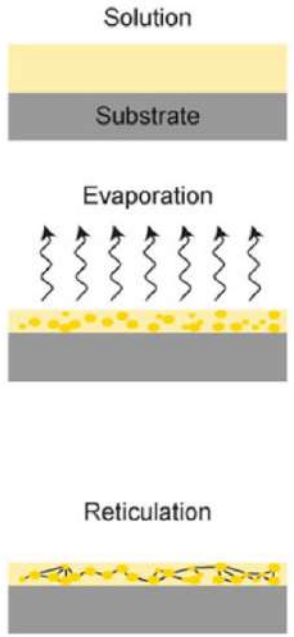
Alkoxides



Carboxylate (PZT, BTO, YBCO...)

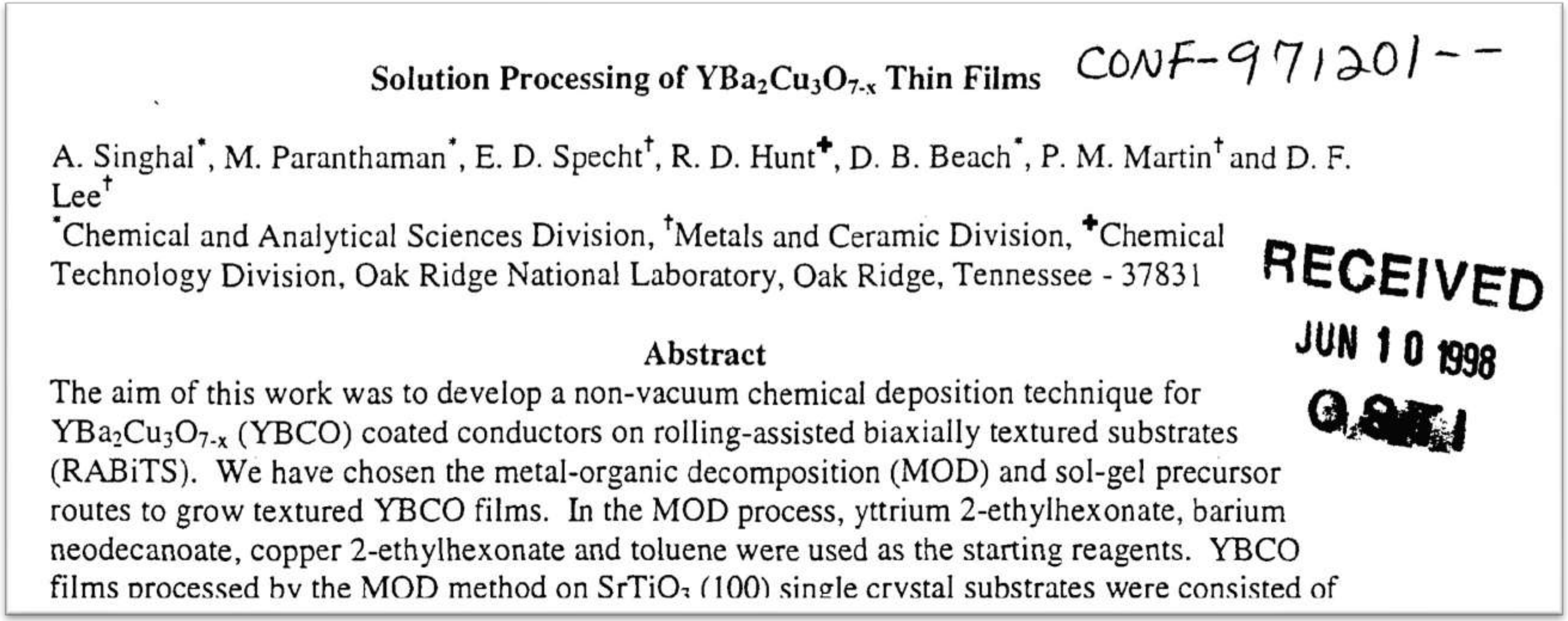


- Compatible precursor, solvent and additive chemistry, concentration, stoichiometry

Homogeneity, stability, viscosity

Solubility: Like dissolves like

higher stability against premature hydrolysis and condensation



Solution Processing of $YBa_2Cu_3O_{7-x}$ Thin Films

CONF-971201--

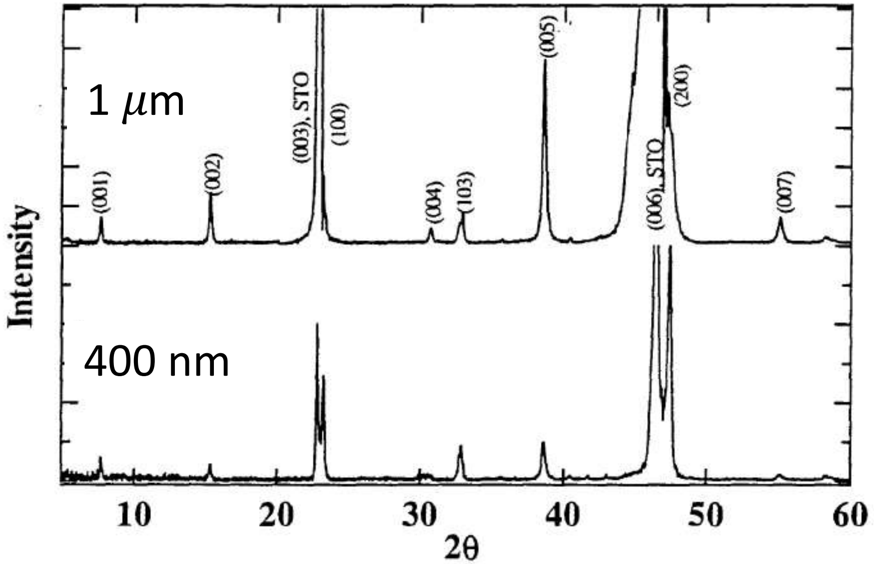
A. Singhal[*], M. Paranthaman[*], E. D. Specht[†], R. D. Hunt[✚], D. B. Beach[*], P. M. Martin[†] and D. F. Lee[†]
[*]Chemical and Analytical Sciences Division, [†]Metals and Ceramic Division, [✚]Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee - 37831

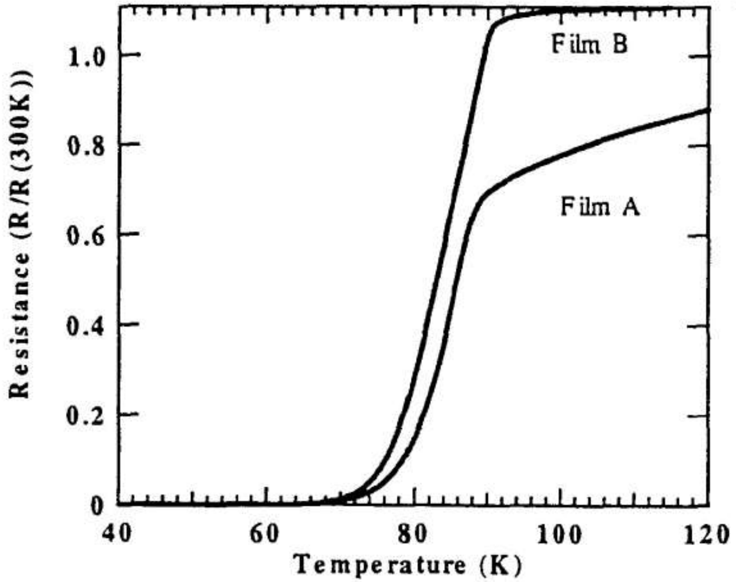
Abstract

The aim of this work was to develop a non-vacuum chemical deposition technique for $YBa_2Cu_3O_{7-x}$ (YBCO) coated conductors on rolling-assisted biaxially textured substrates (RABiTS). We have chosen the metal-organic decomposition (MOD) and sol-gel precursor routes to grow textured YBCO films. In the MOD process, yttrium 2-ethylhexonate, barium neodecanoate, copper 2-ethylhexonate and toluene were used as the starting reagents. YBCO films processed by the MOD method on $SrTiO_3$ (100) single crystal substrates were consisted of

Epitaxial YBCO films

T_c 89 K

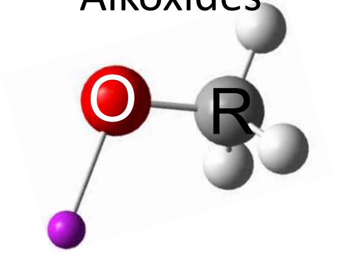




Chemical Solution Deposition (CSD): Reactivity

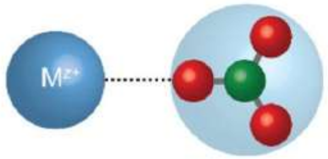
1 Solution chemistry

Alkoxides



High solubility in organic solvents
High reactivity
Hydrolysis+condensation: difficult to control
Organic part can be tuned to desgin reactivity (carboxylates, UV- sensitive...)

Nitrates



Soluble in water and decompose at lower T than carboxylates...
but sometimes very exothermic

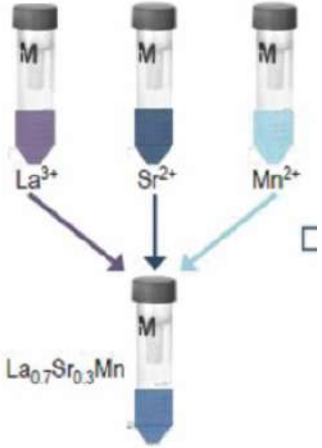
J. Mater. Chem. A, 2019,**7**, 24124-24149

Polymer assisted (PAD)

Entrap stable metal ion chelate complex in a polymer network
Stable independent cations, easy to mix and design new stoichiometries.

PAD: Li DQ, Jia QX (2003) United Sates Patent No. 6,589,457

J. Mater. Chem. C, 2018, 6, 3834



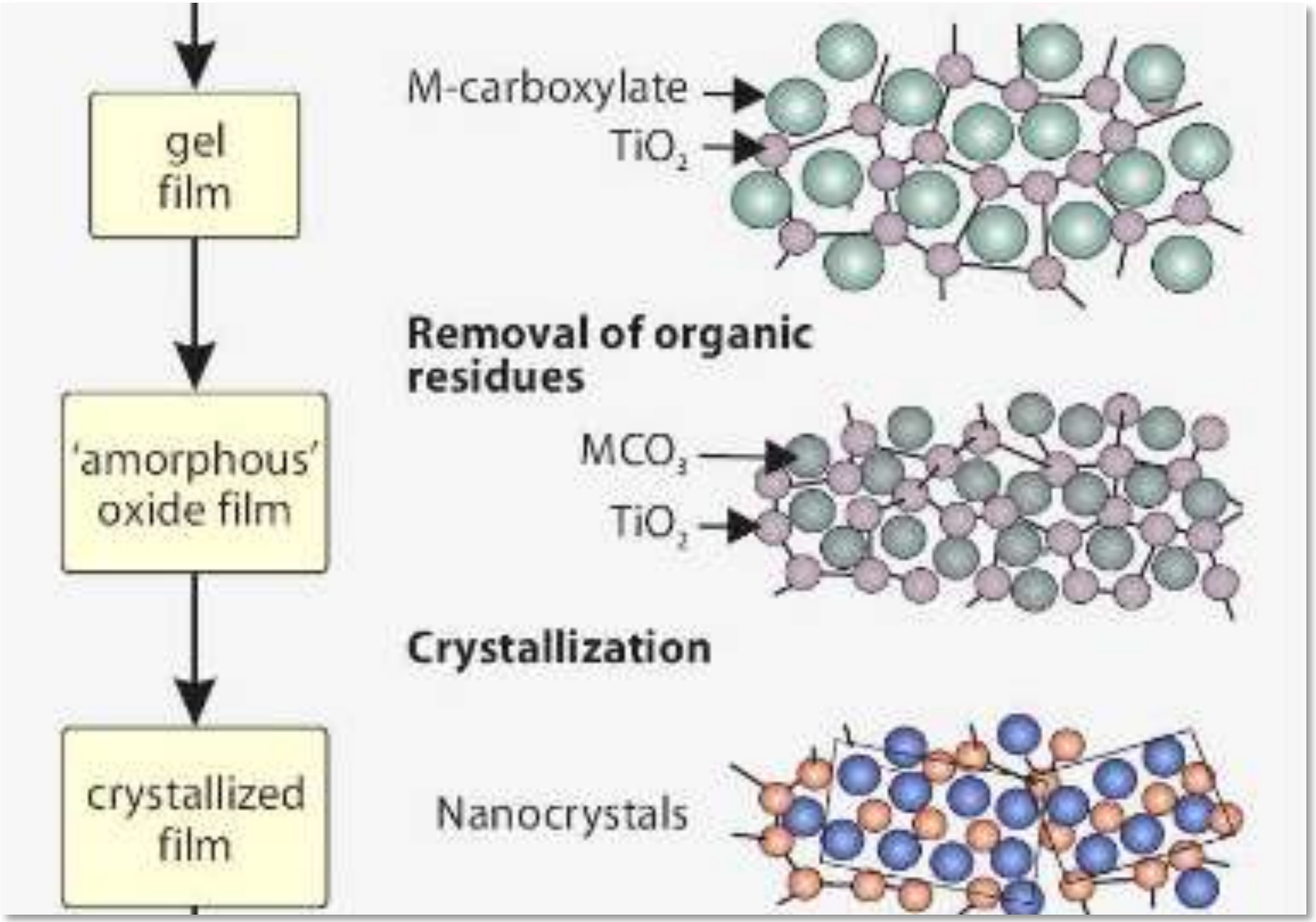
Chemical Solution Deposition (CSD): Deposition

2 Deposition

- All material deposited on the substrate from the start
- Volume, acceleration, rate...

Coverage, homogeneity

Conversion precursors to oxides. From where do we start?

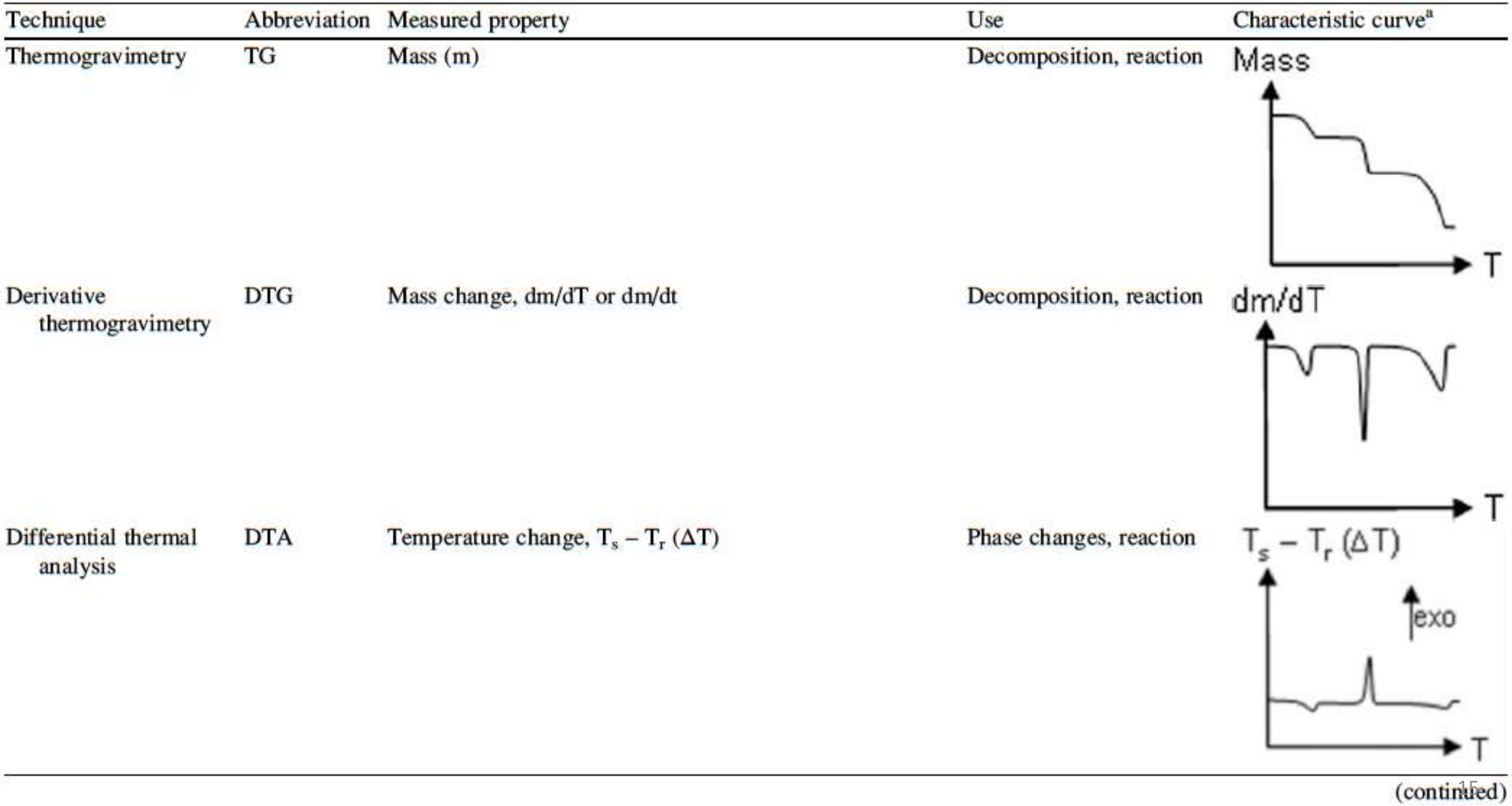


Aimed to leave solely the cations (and oxygen)

Decomposition: no organic residue, no phase separation....

Conversion precursors to oxides. From where do we start?

Thermogravimetric analysis



Technique	Abbreviation	Measured property	Use	Characteristic curve[a]
Thermogravimetry	TG	Mass (m)	Decomposition, reaction	Mass / T
Derivative thermogravimetry	DTG	Mass change, dm/dT or dm/dt	Decomposition, reaction	dm/dT / T
Differential thermal analysis	DTA	Temperature change, $T_s - T_r$ (ΔT)	Phase changes, reaction	$T_s - T_r$ (ΔT) / exo / T

(continued)

Chemical solution deposition of functional oxide thin films, T. Schneller, M. Kosec, D. Payne, Springer, 2013

Conversion precursors to oxides. From where do we start?

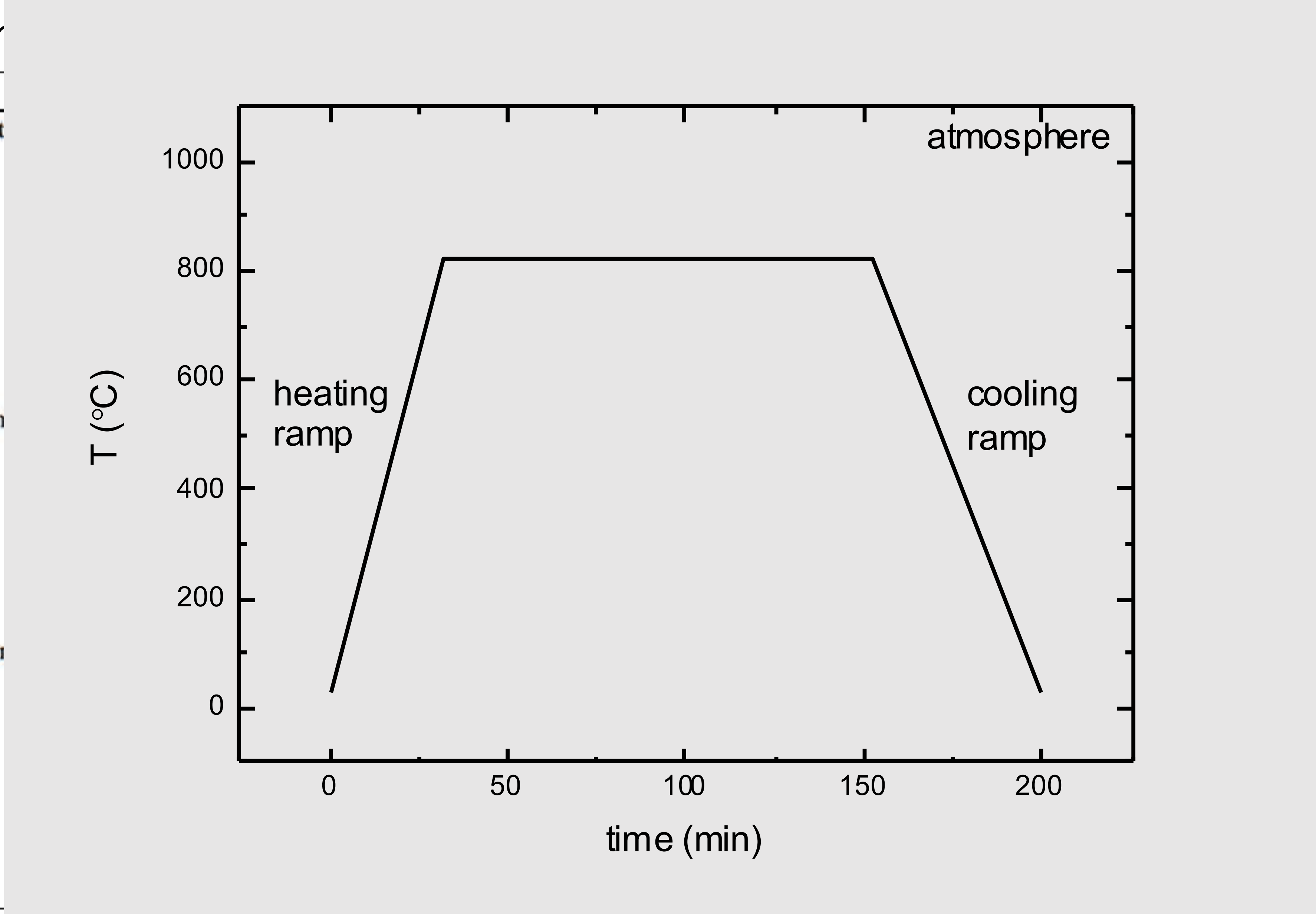
Thermogravimetr

Technique

Thermogravimet

Derivative thermogravin

Differential ther analysis



curve^a

T

T

T)

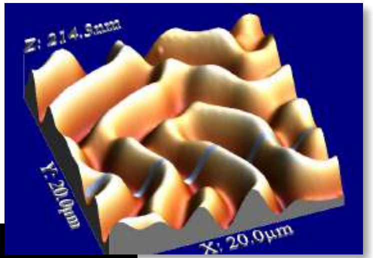
exo

T

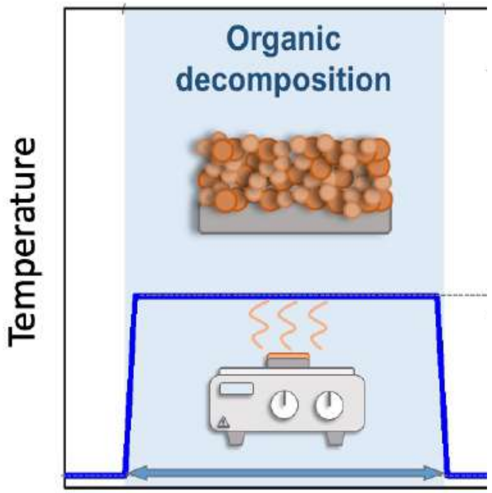
(continued)

Chemical solution deposition of functional oxide thin films, T. Schneller, M. Kosec, D. Payne, Springer, 2013

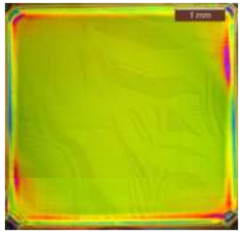
Precursor Decomposition: Example 1: $YBa_2Cu_3O_7$ thin films

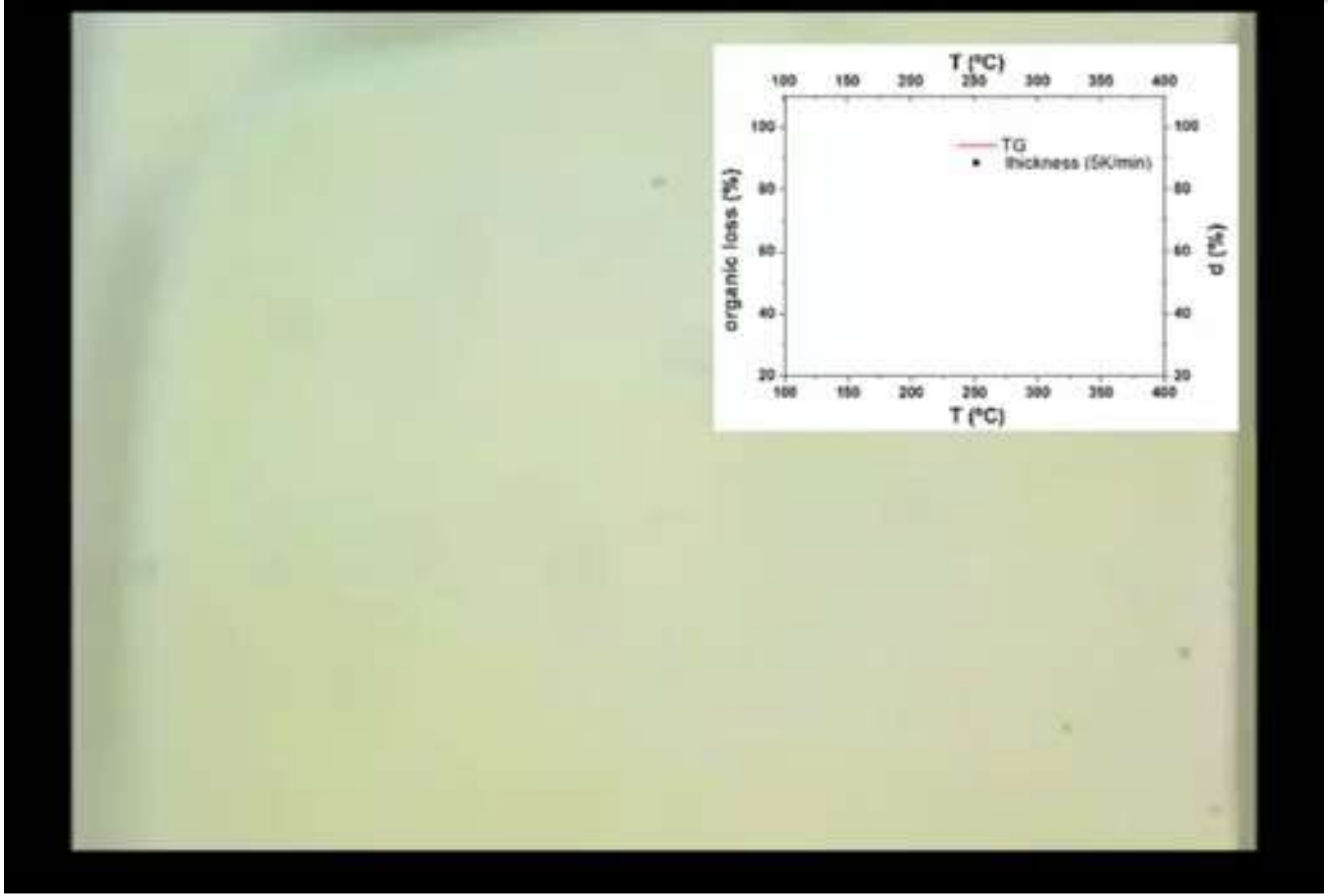


Temperature
Weight loss
Thickness/density



RT- 300-400ºC

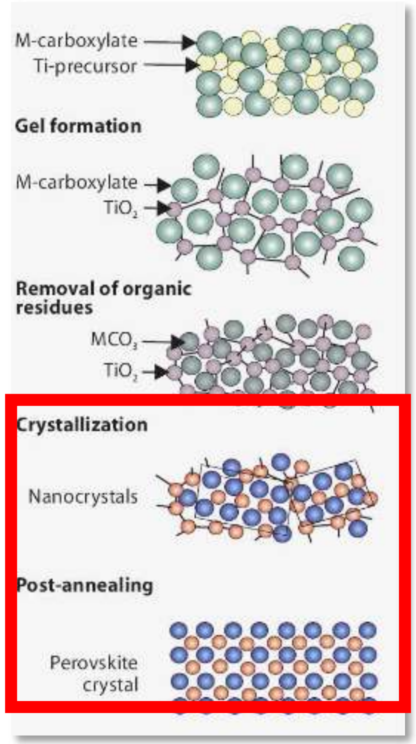


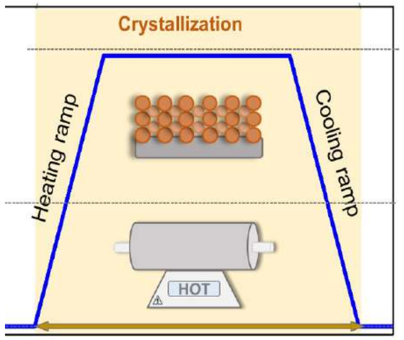


Courtesy of B. Villarejo

Chemical Solution Deposition (CSD): Reactivity

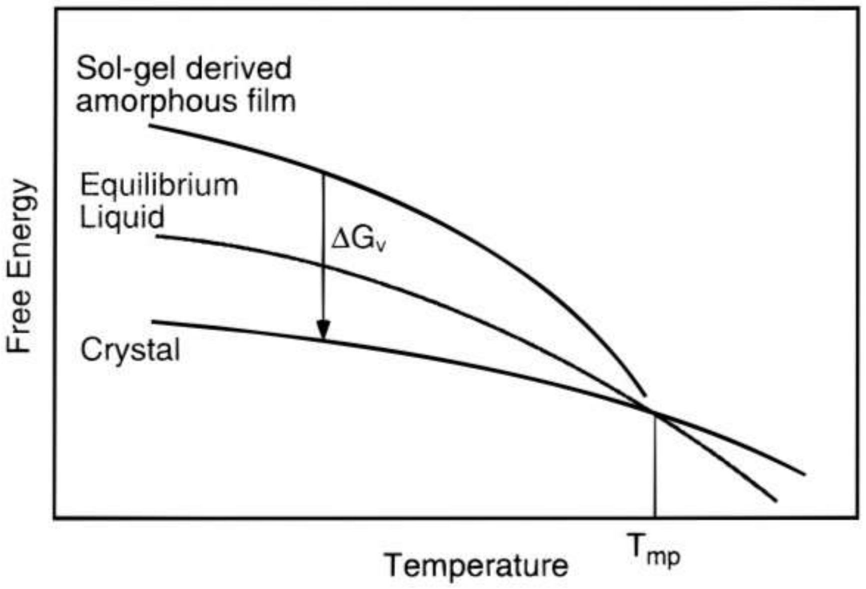
Role of thermodynamic factors on the transformation process





time

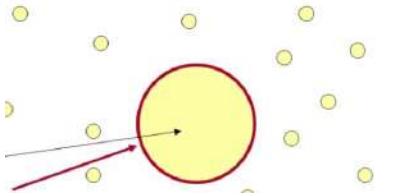
400-900 ºC



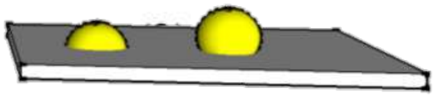
Gibbs Free Energy:

ΔG = Δ H - T Δ S

$$\Delta G^*_{homo} = 16\pi\gamma^3/3(\Delta G_v)^2$$



$$\Delta G^*_{hetero} = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} f(\theta)$$



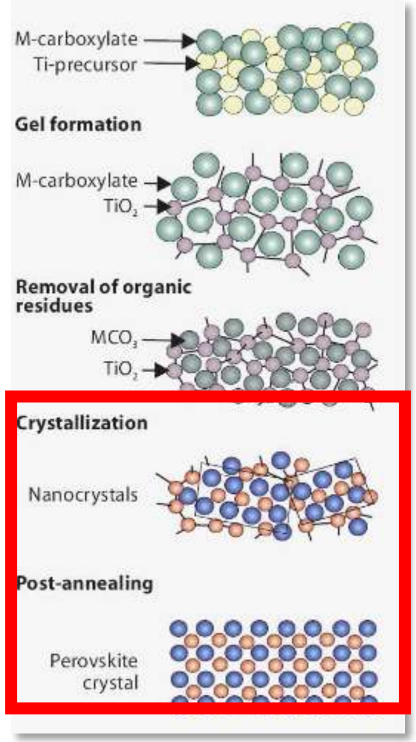
$$f(\theta) = (2 - 3\cos\theta + \cos^3\theta)/4$$

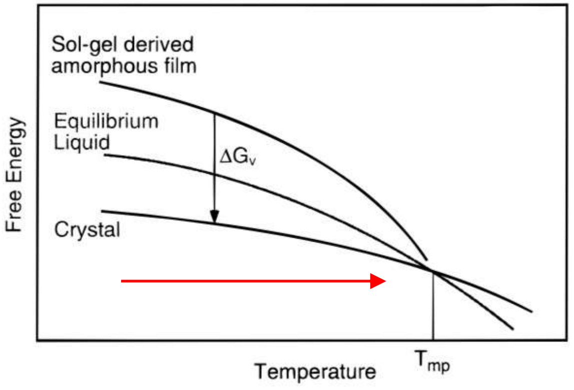
ΔG_v= driving force for crystallization
γ= Interfacial energy
θ= Related to contact angle

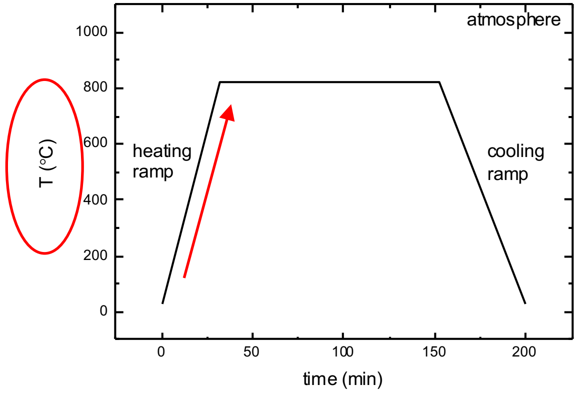
structure/mismatch

Chem. Mater., Vol. 9, No. 11, 1997 2333

Role of thermodynamic factors on the transformation process





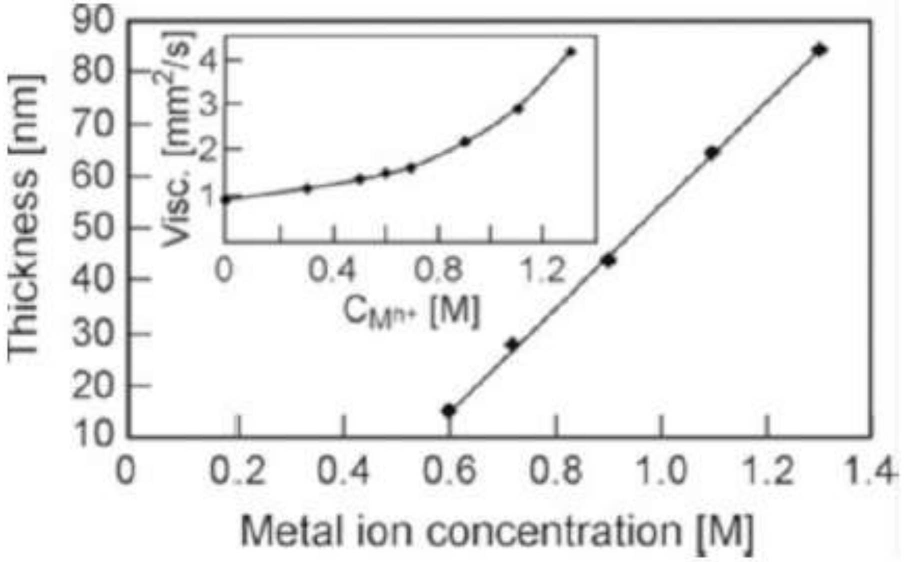


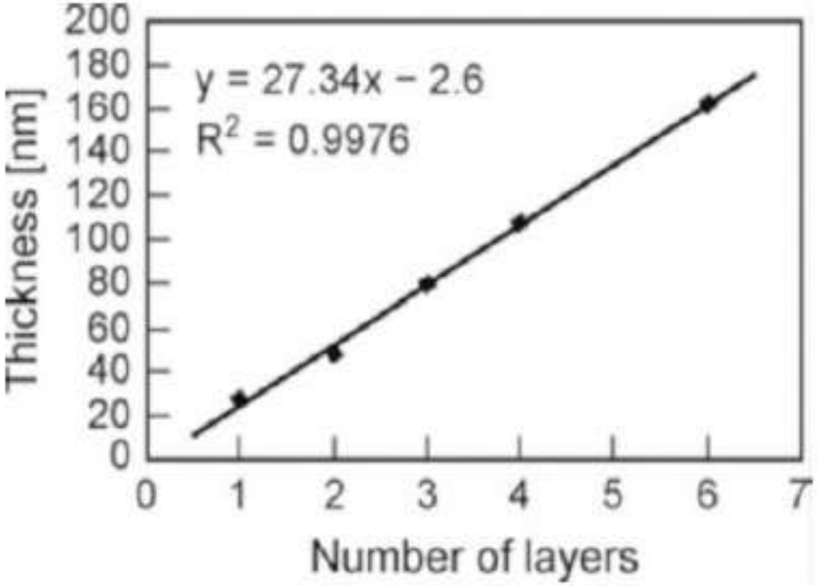
(1) Crystallization at **higher temperatures** results in lower driving forces, and due to the $f(\theta)$ term, lower energy **heterogeneous nucleation** events become **more important**.

(2) Unless **rapid thermal processing** techniques are used, film crystallization usually begins during heating to the anneal temperature. Therefore, as the temperature of the sample increases, more energy becomes available to surmount the barriers for nucleation events in addition to the energetically most favorable nucleation event. This can lead to film microstructures defined by nucleation and growth processes associated with **more than one nucleation event**.

Film thickness

PZT films

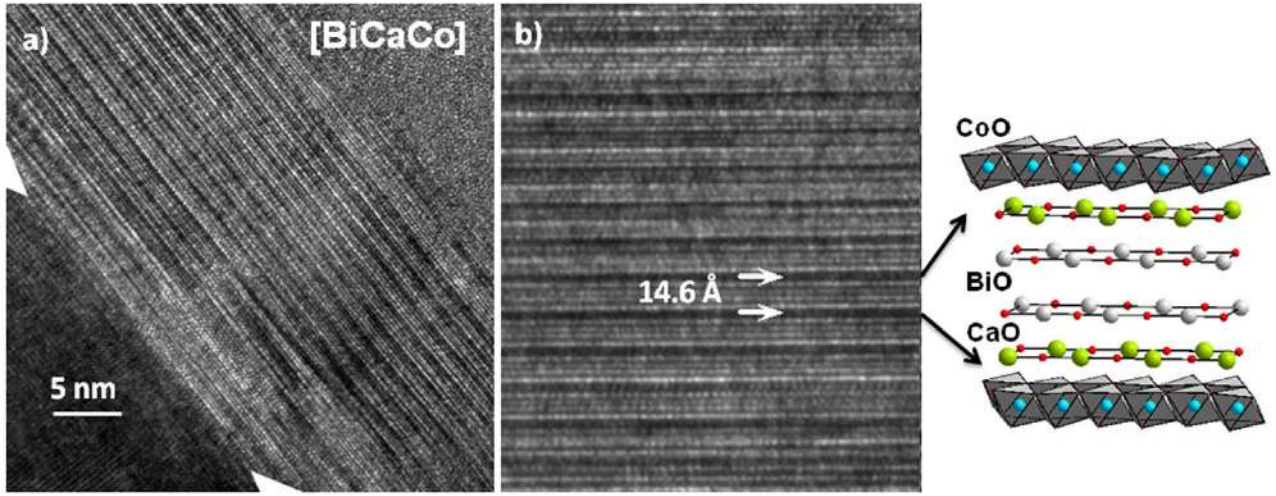




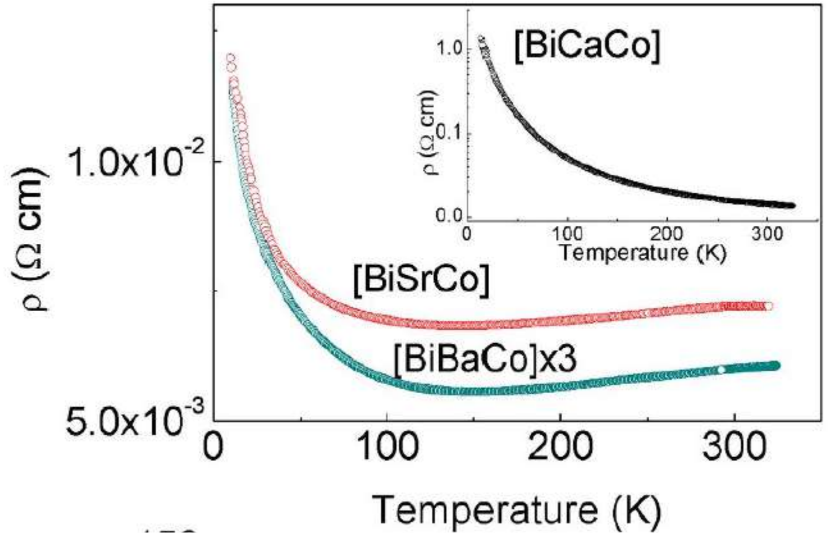
Van Genechten D (2005). Pb(Zr$_{0.3}$Ti$_{0.7}$)O$_3$ films. PhD Thesis, University of Hasselt

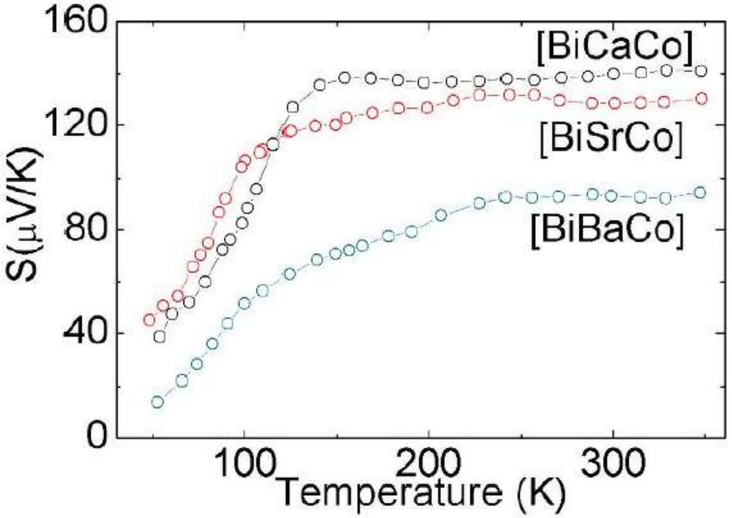
Thermoelectric materials- misfit cobaltates Bi-Ca-Co-O

Challenging to fabricate by high vacuum deposition techniques : difficult to control stoichiometry → Cations coordinated to EDTA and PEI + H_2O



Epitaxial matching ($LaAlO_3$)
Clean interfaces



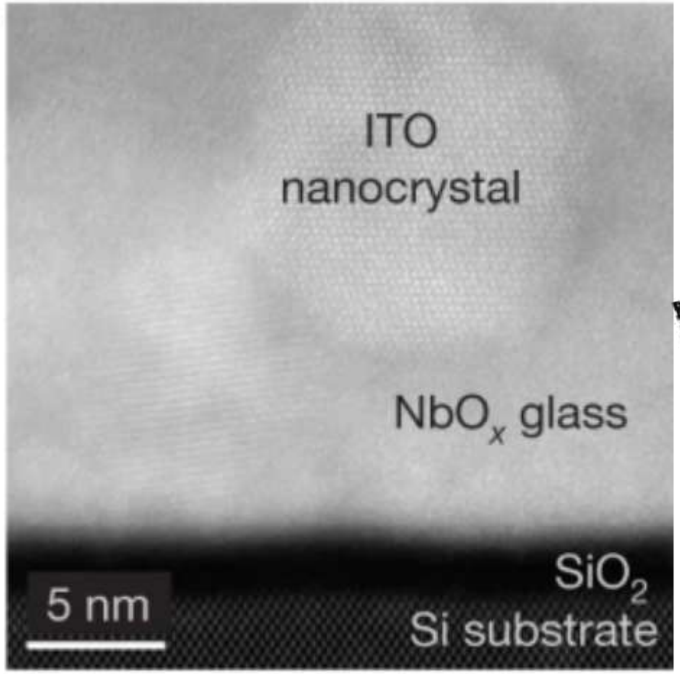


comparable to single cyrstals

Beatriz Rivas-Murias, Rivadulla et al, Scientific Reports I 5:11889 I DOI: 10.1038/srep11889

Chemical coating to control the sunglight passing through the windows

Crystal-glass interfaces: difficult to control experimentally by traditional methods



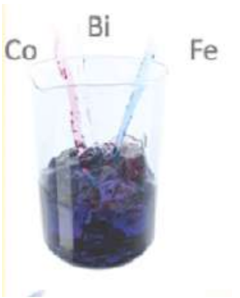
polyoxometalate clusters

$Nb(OEt)_5$
$N(CH_3)_4OH \cdot 5H_2O$
ITO nanocrystal

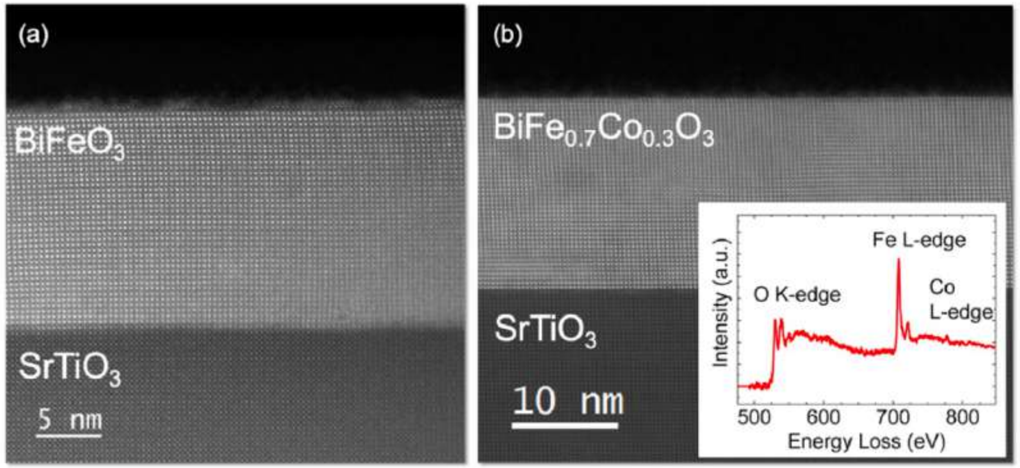
NbOx glass-covalent linkage to ITO crystal: changes in optical properties f(V) (transmittance spectra)

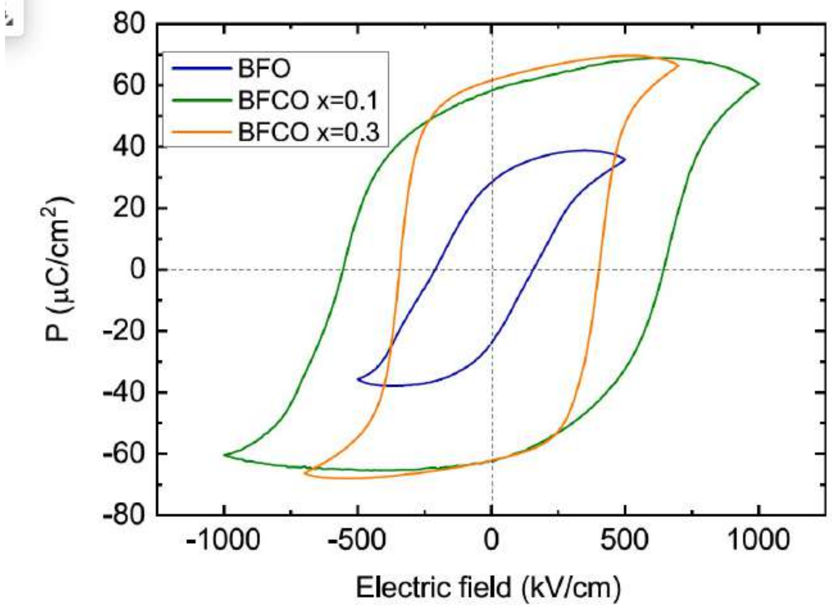
A. Llordés et al. Nature, 500, pages 323–326 (2013)

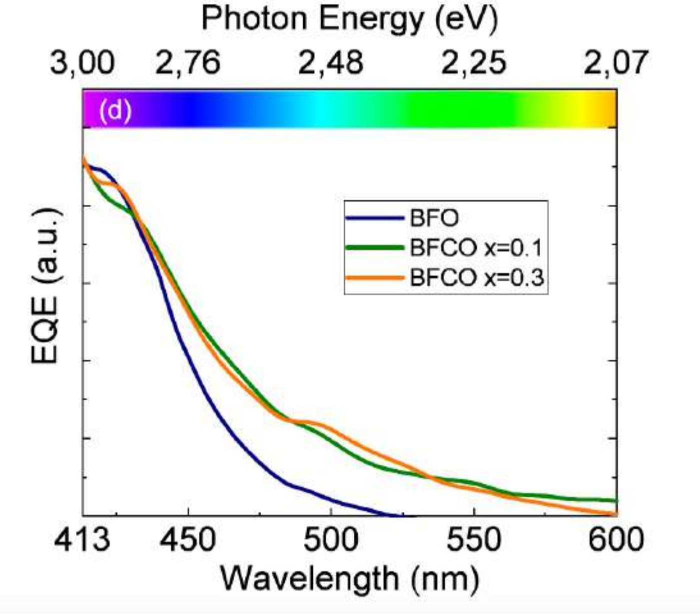
Ferroelectric and photovoltaic $BiFe_{1-x}Co_xO_3$



nitrates
acetic acid
methoxyethanol







Doping
Epitaxy
Ferroelectric
Photovoltaic

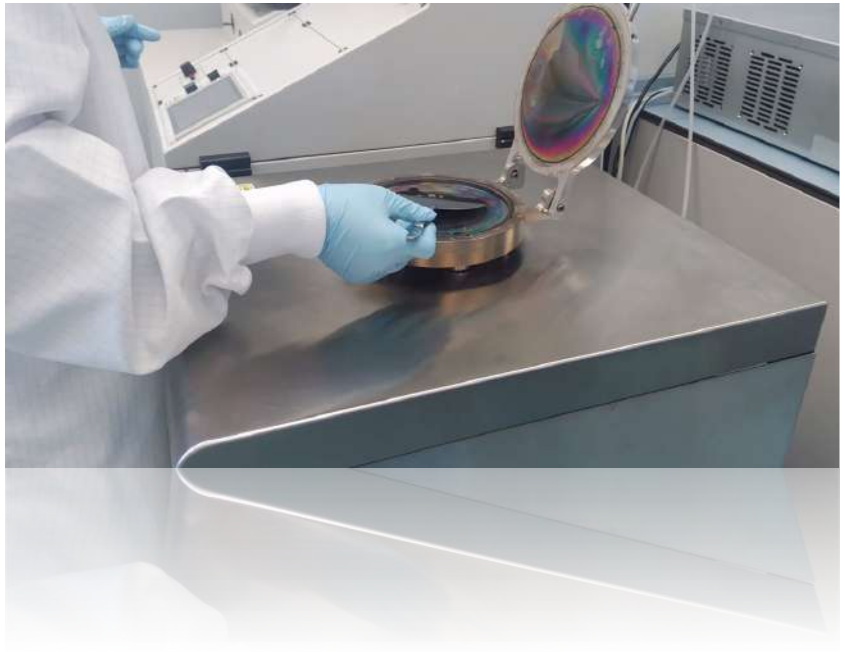
P. Machado et al. Chem. Mater. 2019, 31, 3, 947−954

CSD
Precursor solution deposited all at once
Stoichiometry and composition determined from precise precursor weighing
Use of solvents and additives / PAD
Large availability of precursors less restrict environment manipulation
Thickness controlled by solution concentration/ multideposition
Epitaxy
hybrid films: thin films and nanoparticles;
low initial investment, no vacuum
Compatible with semiconductor fabrication techniques

Chemical Deposition Methods

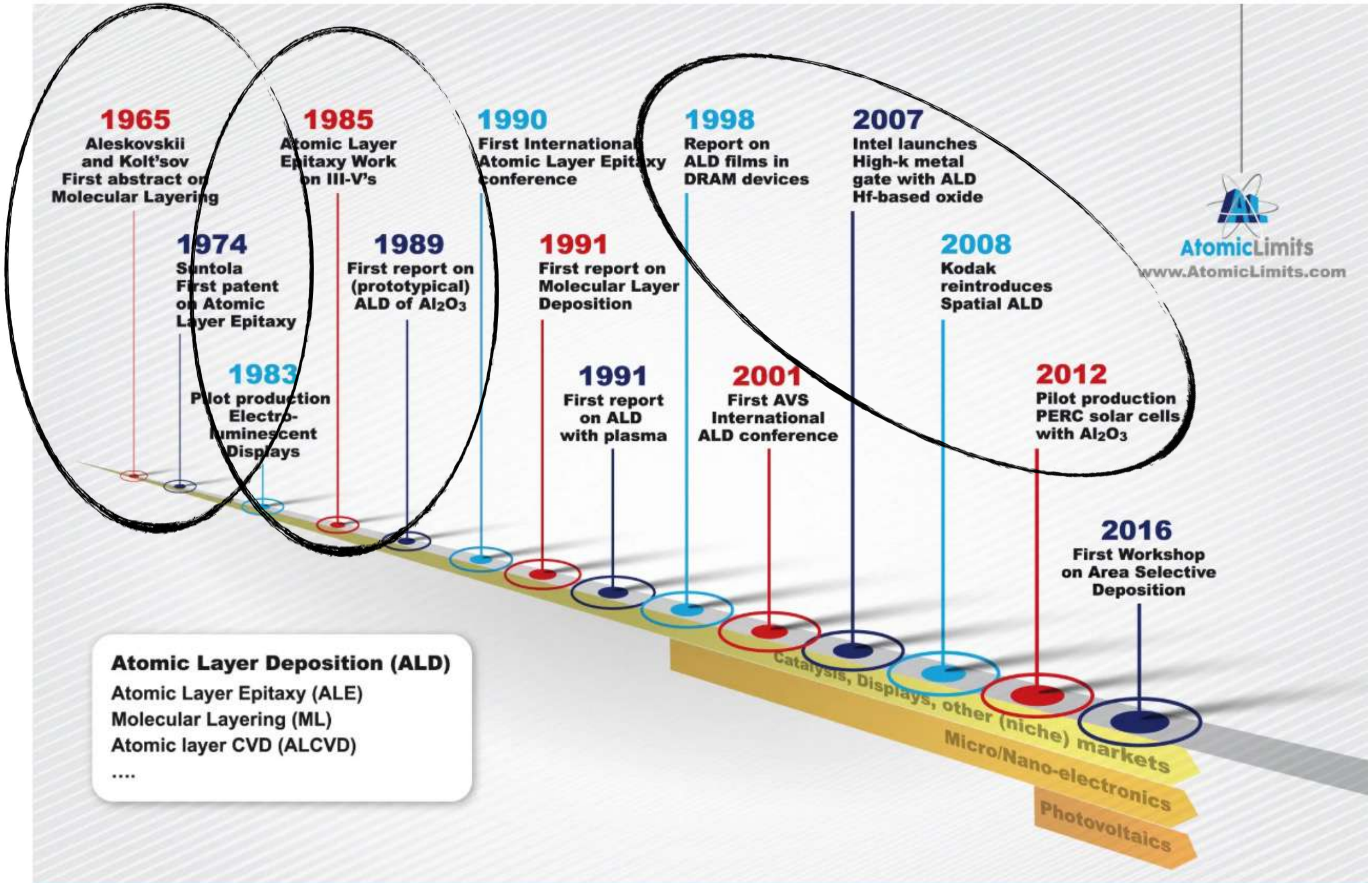
Chemical Solution Deposition (CSD)

Atomic Layer Deposition (ALD)



precise growth and cost-effective, potentially scalable

ALD timeline

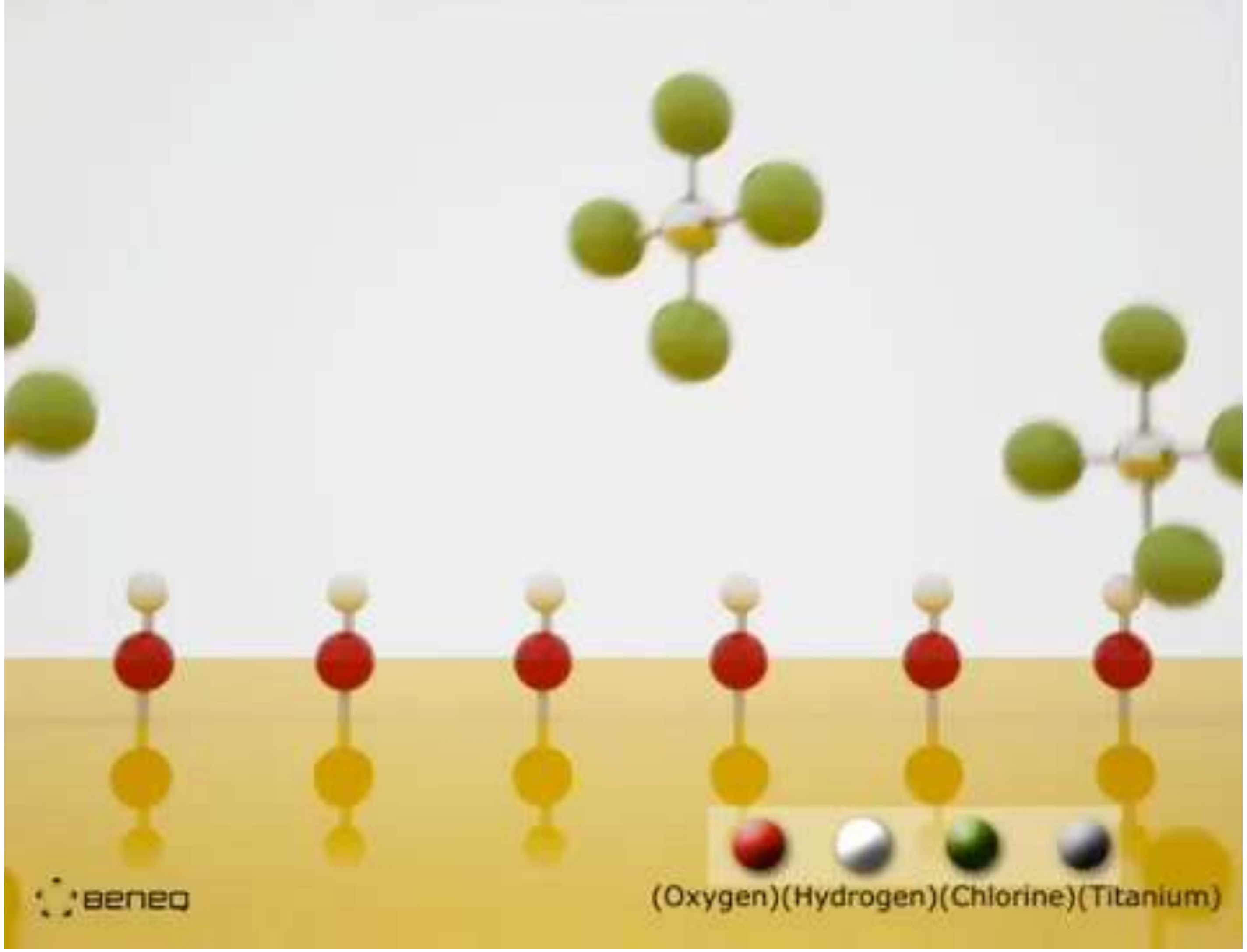


ALD Timeline

Erwin Kessels, ALD turns 45: the history of ALD in a timeline and an animated version of the ALD periodic table, Atomic Limits blog (2019)

https://www.atomiclimits.com/

Overview of Atomic Layer Deposition



Transport of reactants to substrate surface (gas phase)

Chemical reaction of reactants on surface (self-limiting surface reaction)

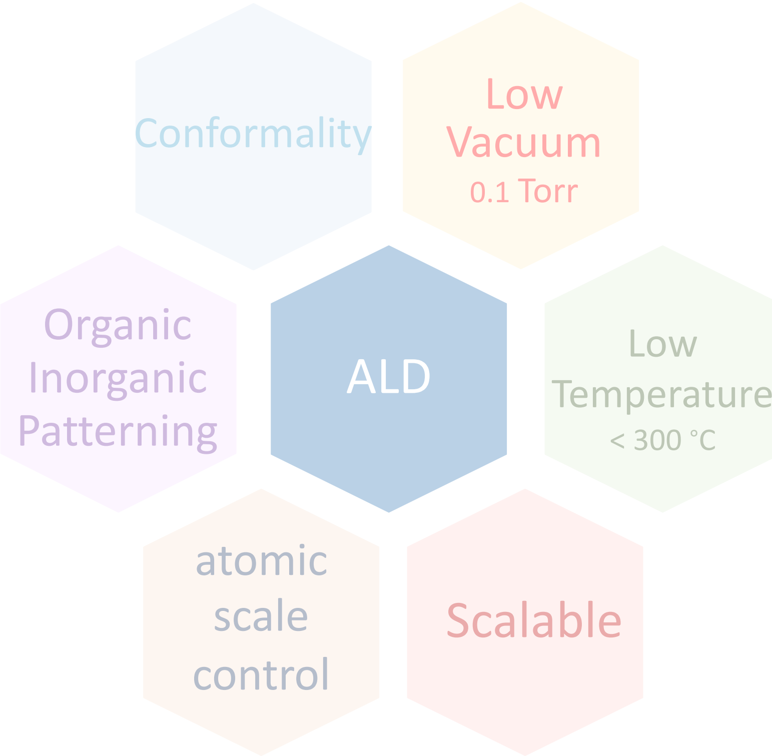
Desorption of by-products

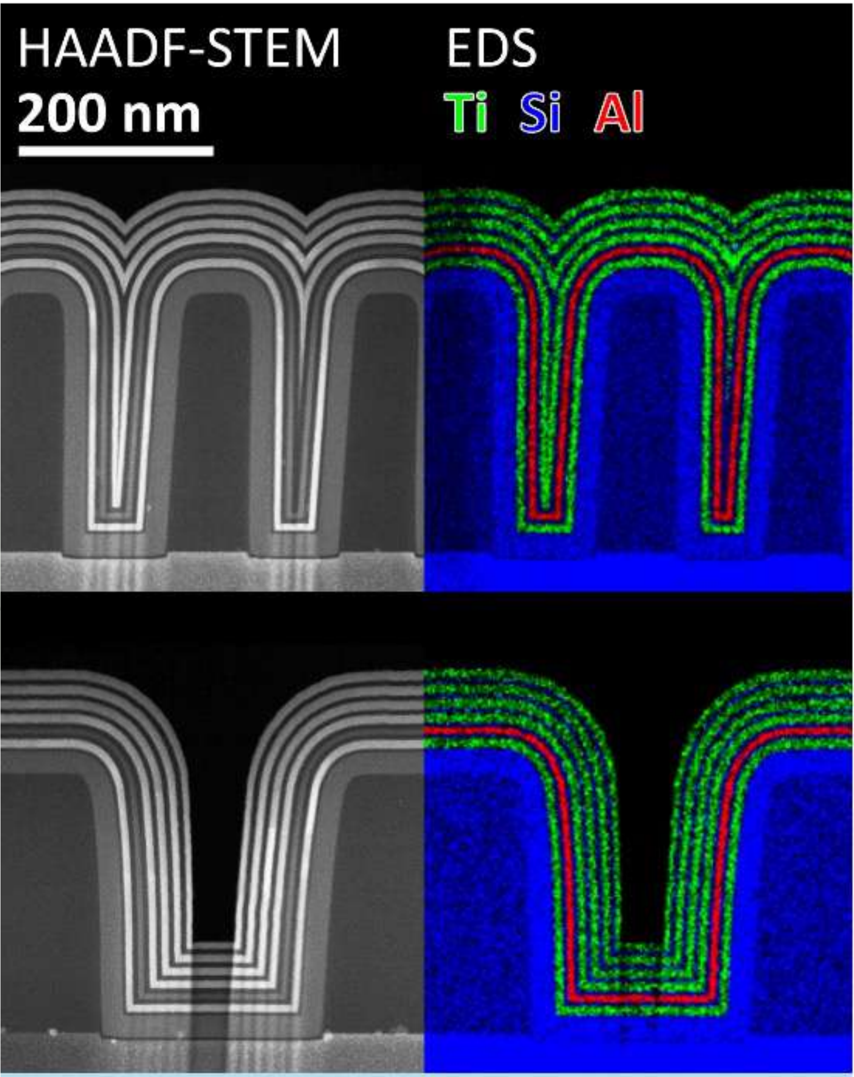
Transport of by-products and excess reactant into the gas stream

layer-by-layer

Overview of Atomic Layer Deposition

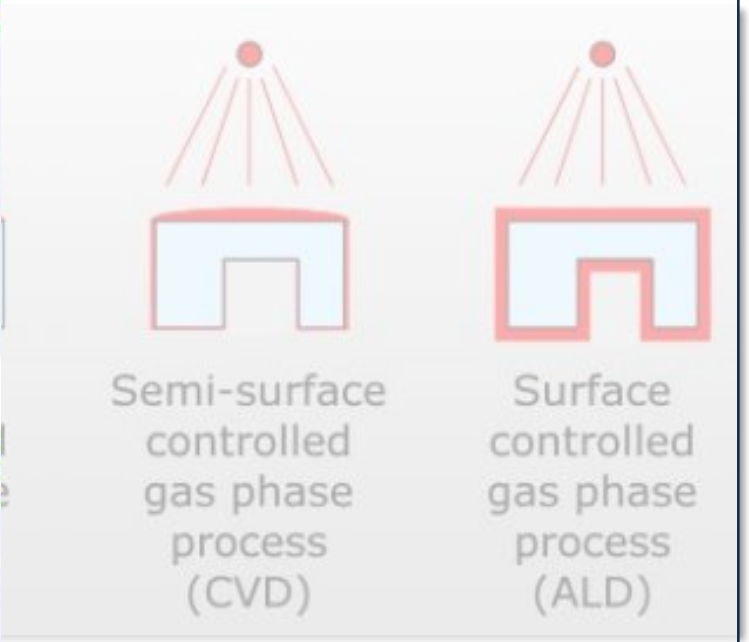
...self-limiting reactions



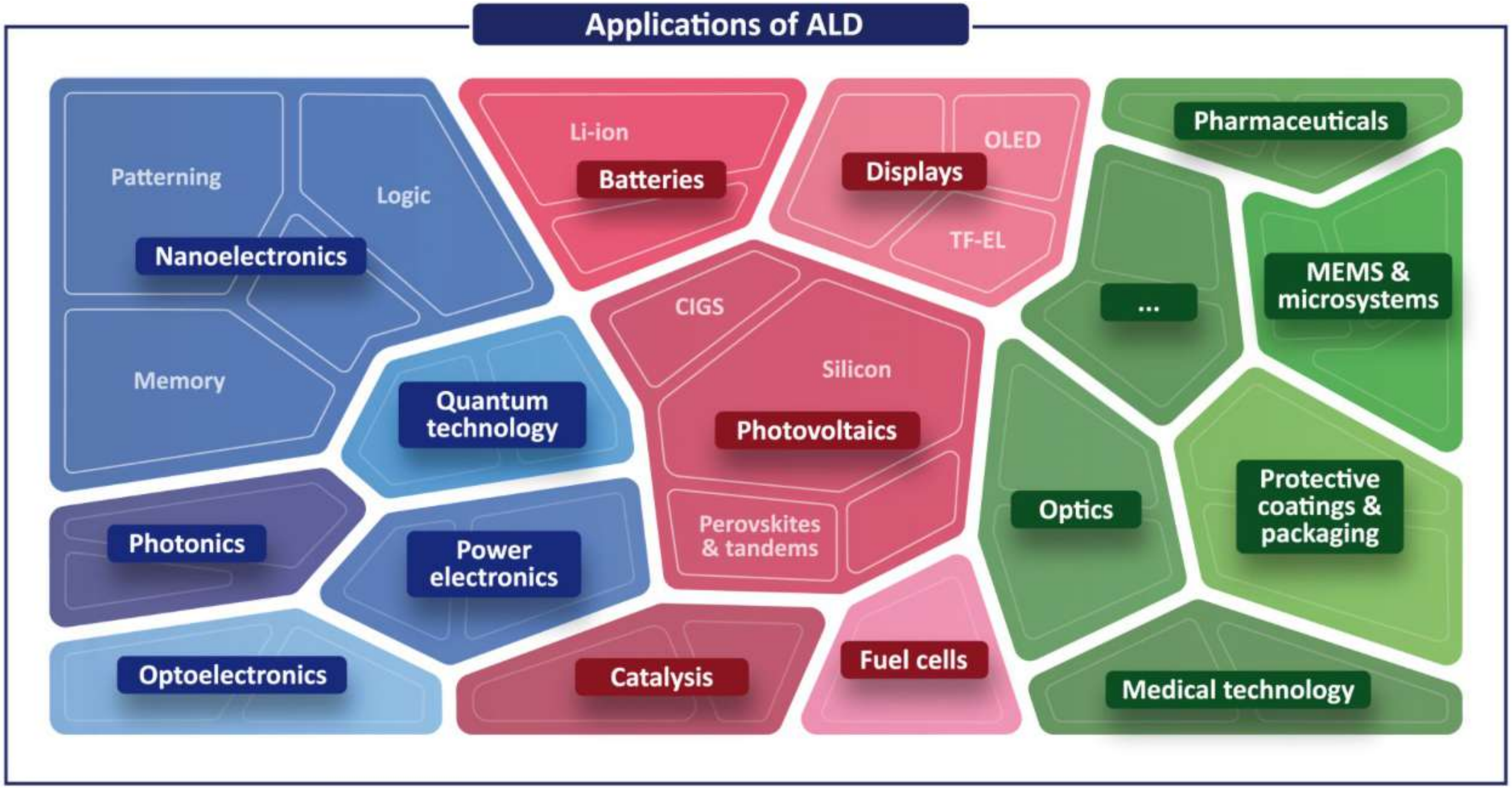


Conformal Deposition Of SiO2, TiO2 And Al2O3 By Plasma ALD (HAADF-STEM And EDS)

K. Arts, M.A. Verheijen, W.M.M. Kessels and H.C.M Knoops (CC BY 4.0 license), image library a
www.AtomicLimits.com, 2021. Corresponding paper DOI: 10.1021/acs.chemmater.1c00781

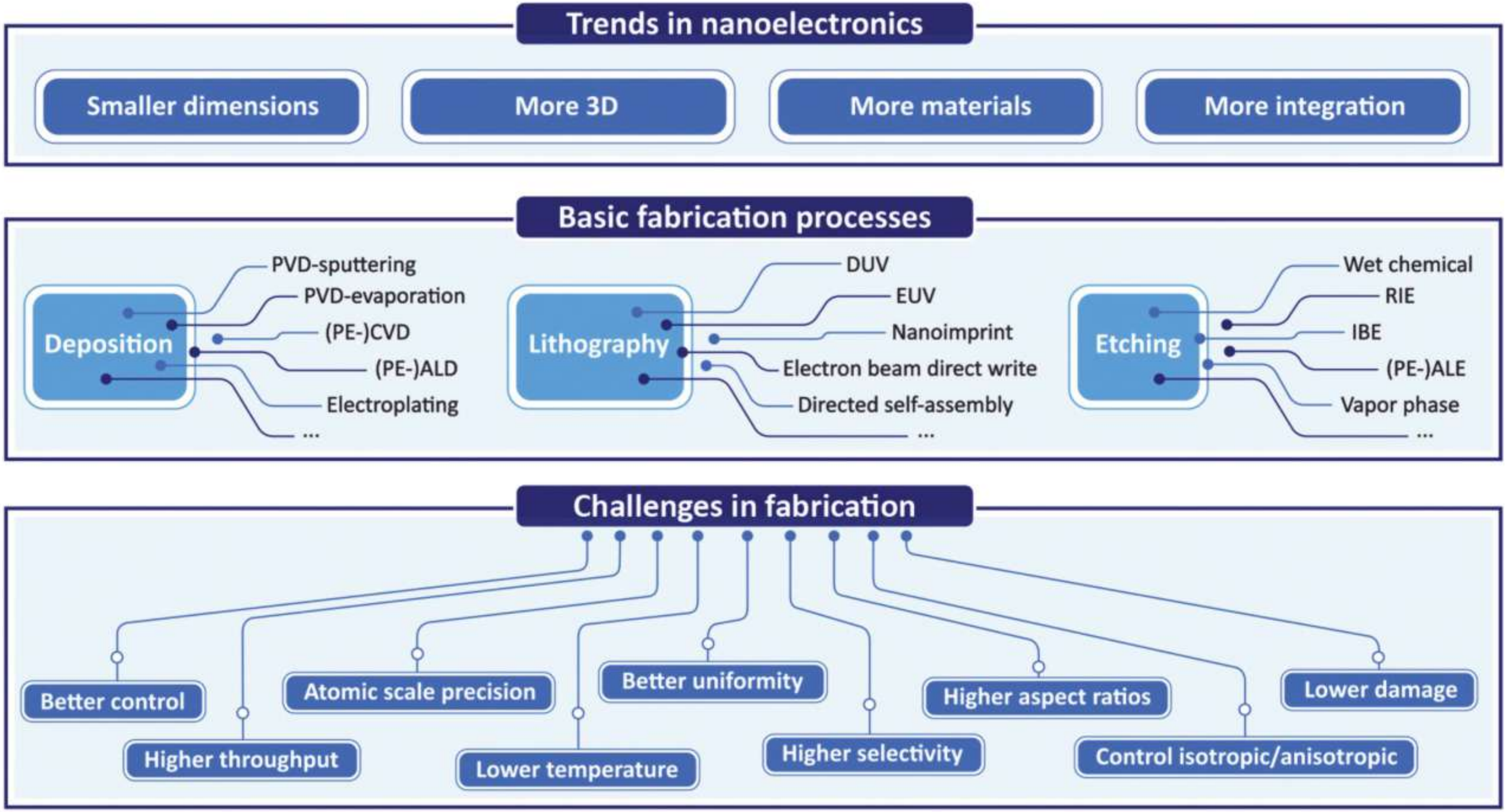


Arts, Kessels, Knoops et al, Chem. Mater. 2021, 33, 13, 5002−5009



Erwin Kessels, ALD From An Application Perspective, AtomicLimits (2022)

https://www.atomiclimits.com/



Trends in nanoelectronics

- Smaller dimensions
- More 3D
- More materials
- More integration

Basic fabrication processes

- Deposition
  - PVD-sputtering
  - PVD-evaporation
  - (PE-)CVD
  - (PE-)ALD
  - Electroplating
  - ...
- Lithography
  - DUV
  - EUV
  - Nanoimprint
  - Electron beam direct write
  - Directed self-assembly
  - ...
- Etching
  - Wet chemical
  - RIE
  - IBE
  - (PE-)ALE
  - Vapor phase
  - ...

Challenges in fabrication

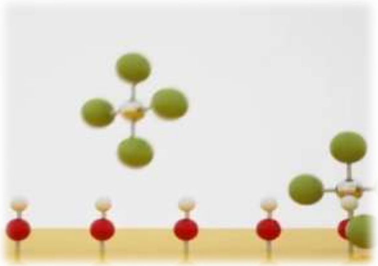
- Better control
- Higher throughput
- Atomic scale precision
- Lower temperature
- Better uniformity
- Higher selectivity
- Higher aspect ratios
- Control isotropic/anisotropic
- Lower damage

Trends And Challenges In The Fabrication Of Present-Day Nanoeletronics.

Karsten Arts et al, Foundations of atomic-level plasma processing in nanoelectronics, Plasma Sources Sci. Technol. 31 103002 (2022), DOI 10.1088/1361-6595/ac95bc

https://www.atomiclimits.com/

PRECURSOR AND CO-REACTANT CHEMISTRY



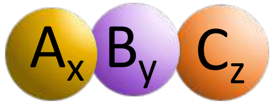
ALD precursor

- High volatility
- Low cost
- Low toxicity
- Suitable size
- Clean decomposition
- High reactivity
- Moderate thermal stability

$M_{\alpha}X_{\beta}$

Gordon, R. G., ALD Precursors and Reaction Mechanisms. In *Atomic Layer Deposition for Semiconductors, C., H., Ed. Springer: Boston, MA, 2014; pp 15-46.*

PRECURSOR CHEMISTRY



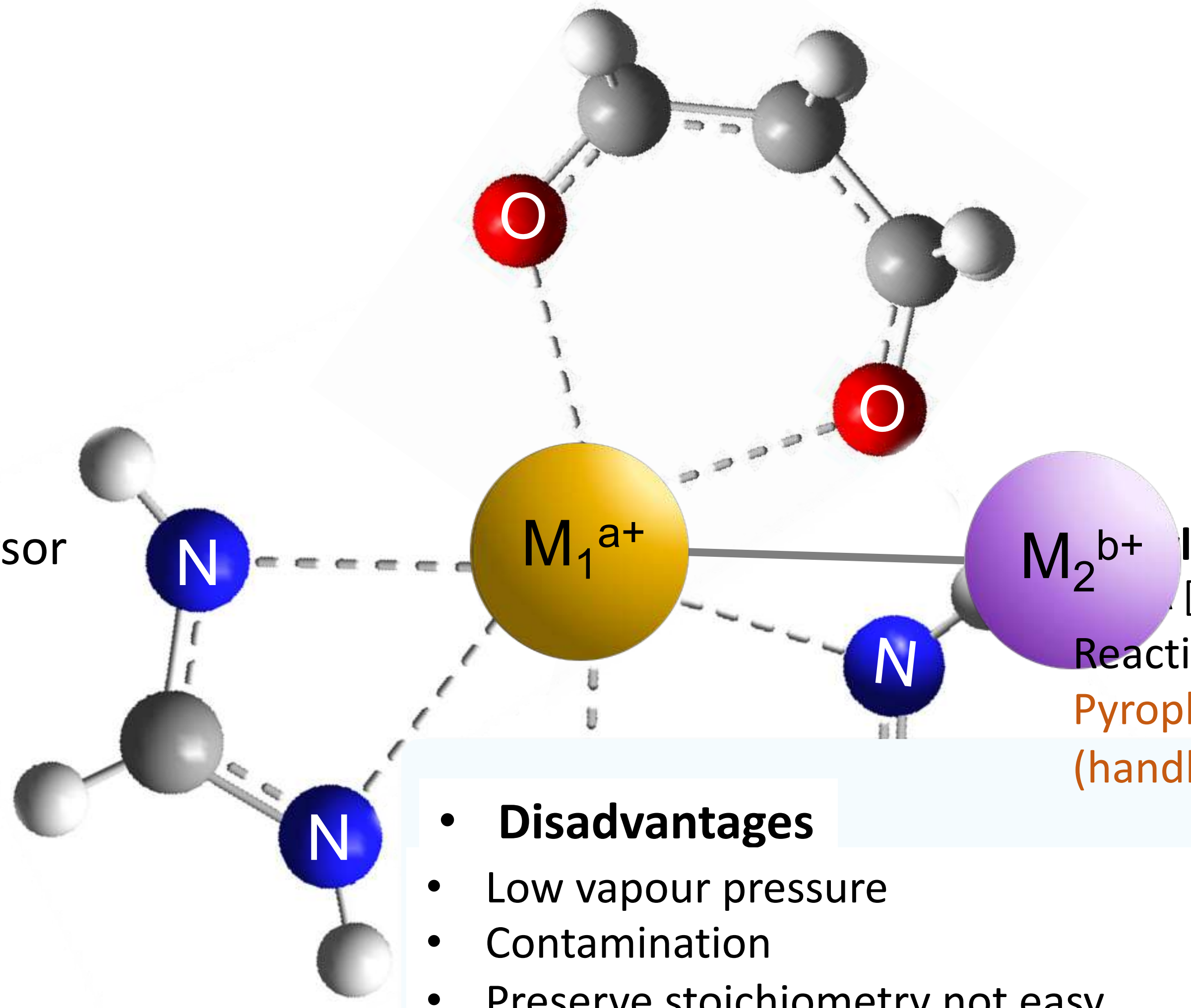
more research on synthesis of precursors is required

Rich precursor chemistry

- M-X (F, Cl, I)
- M-C
- M-Cp
- M-O-C
- M-N-C

Chances to develop improved precursor by tuning precursor chemistry

- Bidentate structure
- Mixture of functionalities
  - O stability
  - N reactivity
- Heterometallic precursor



ls

[(CH$_3$)$_3$Al]

Reactivity

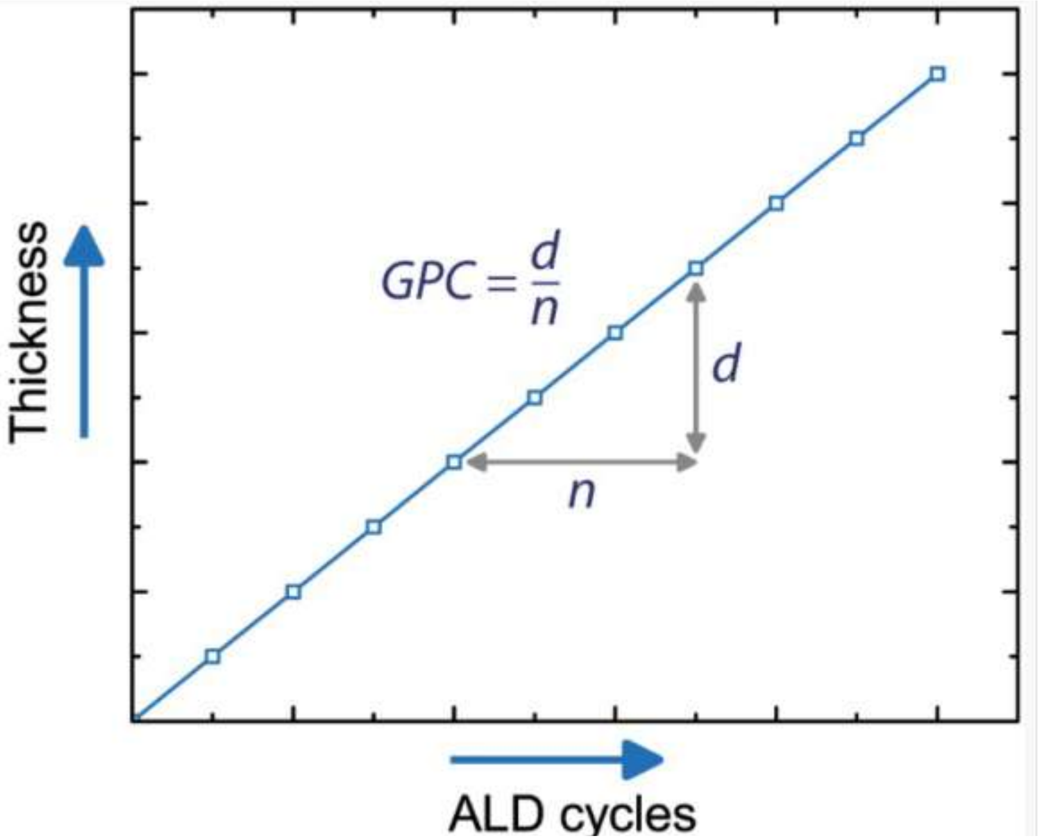
Pyrophoric behavior (handling, storage)

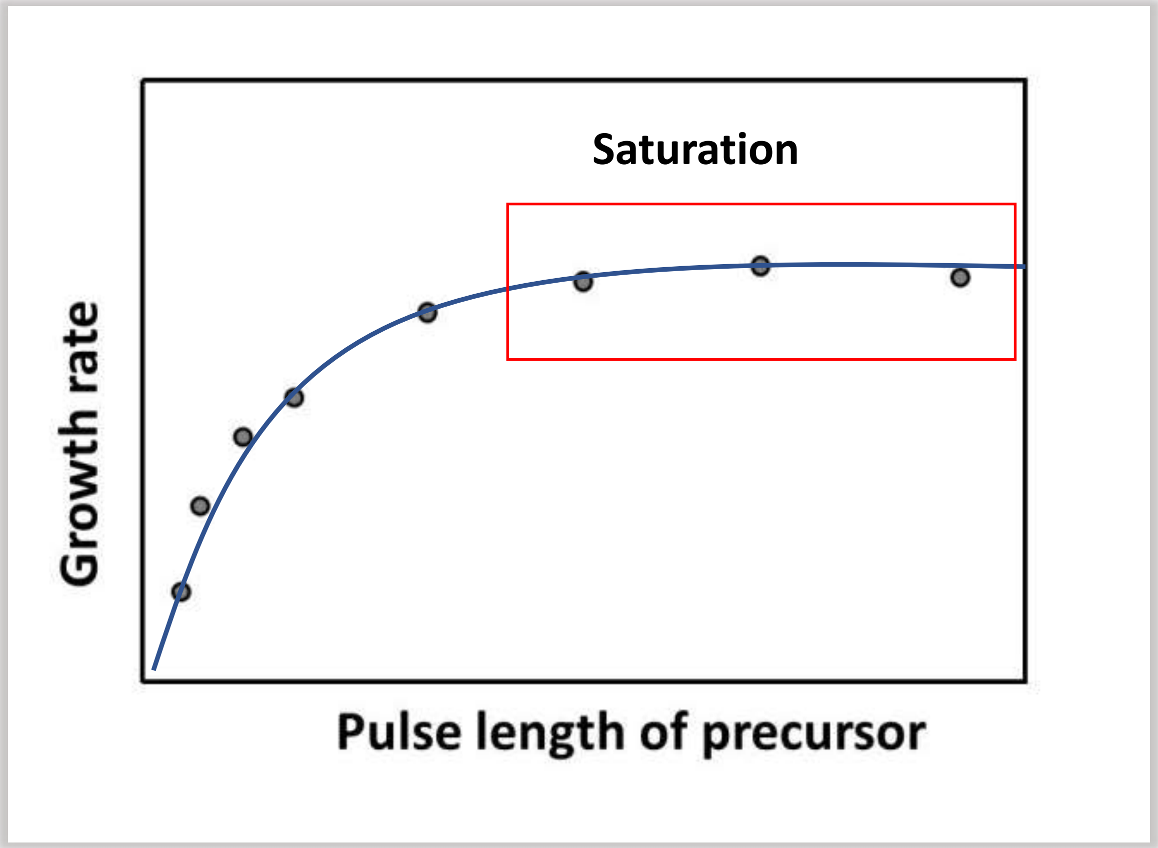
- **Disadvantages**
- Low vapour pressure
- Contamination
- Preserve stoichiometry not easy

Carbon contamination

Gordon, R. G., ALD Precursors and Reaction Mechanisms. In *Atomic Layer Deposition for Semiconductors, C., H., Ed. Springer: Boston, MA, 2014; pp 15-*

Thickness control & Saturation to confirm self-limited growth



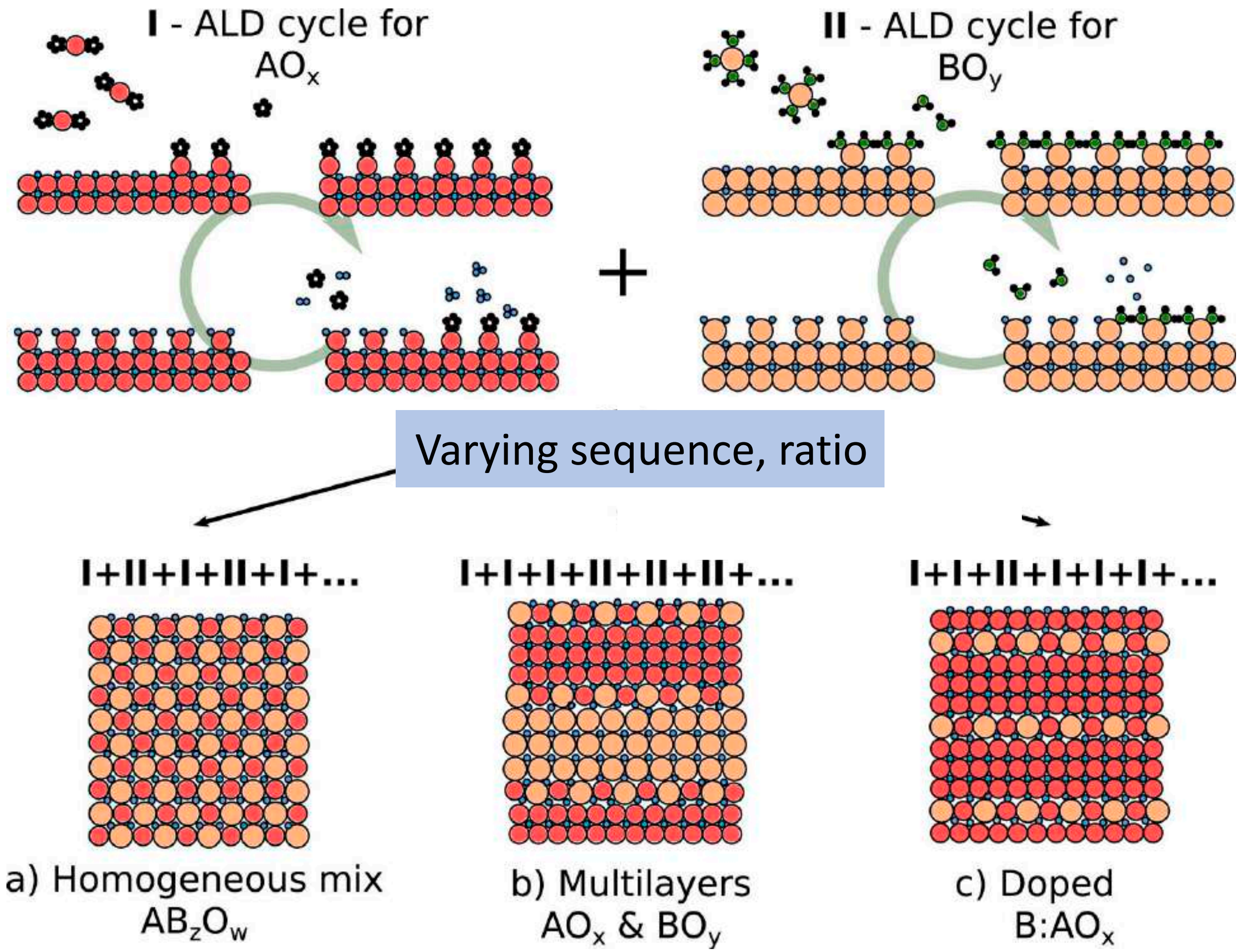


GPC: Growth Per Cycle

COMPLEXITY IN ALD MULTICOMPONENT OXIDE PROCESSES

Supercycle approach

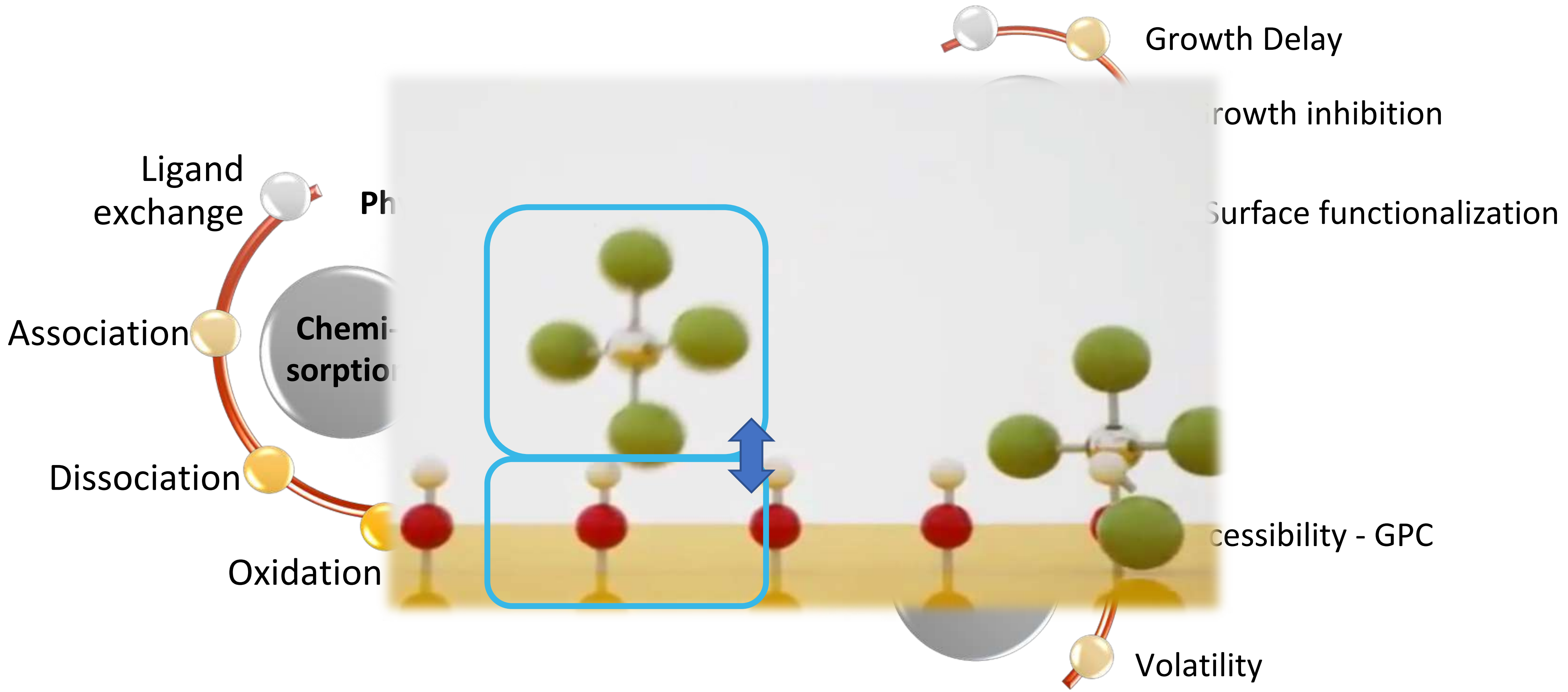
Combination of binary process
(A-O, B-O subcycles)



M.Coll and M. Napari, *APL Materials*, **2019, 7(11), 110901.**

IMPORTANT PARAMETERS IN NUCLEATION AND GROWTH

Surface-precursor interactions



Growth acceleration

Growth Delay

rowth inhibition

urface functionalization

cessibility - GPC

Volatility

Ligand exchange

Ph

Association

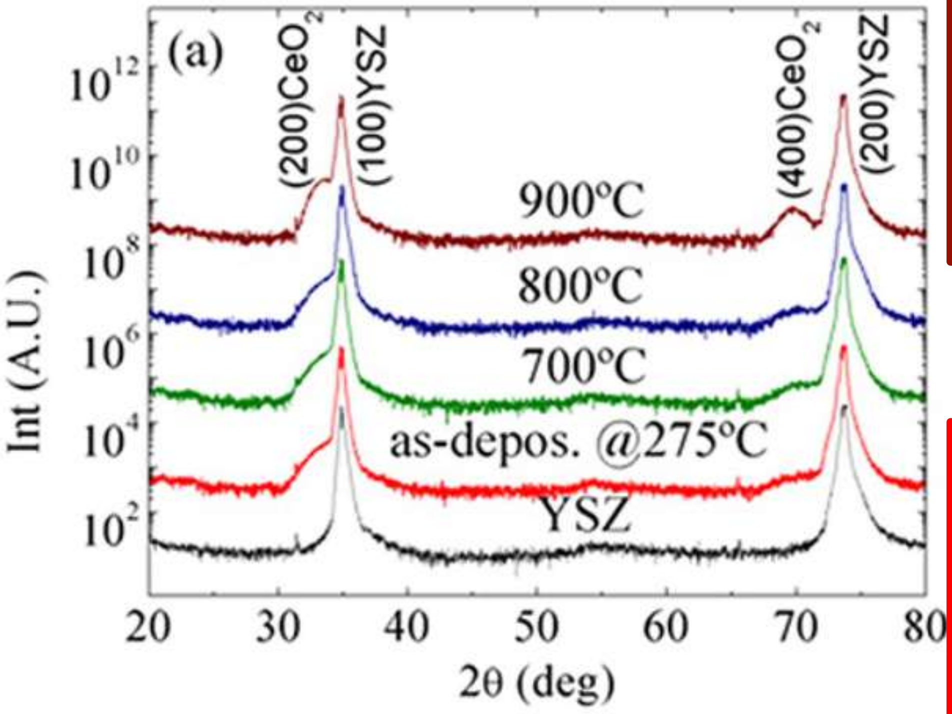
Chemi- sorptio

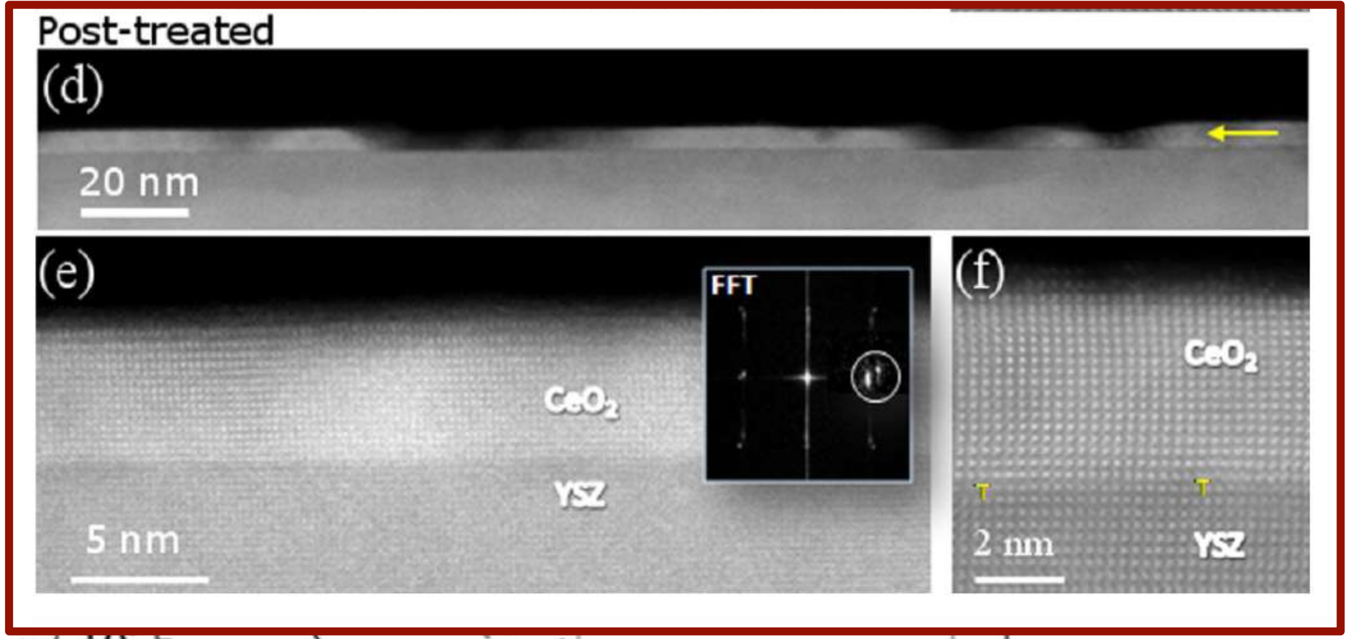
Dissociation

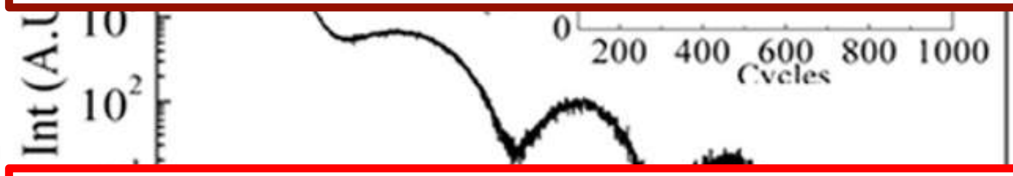
Oxidation

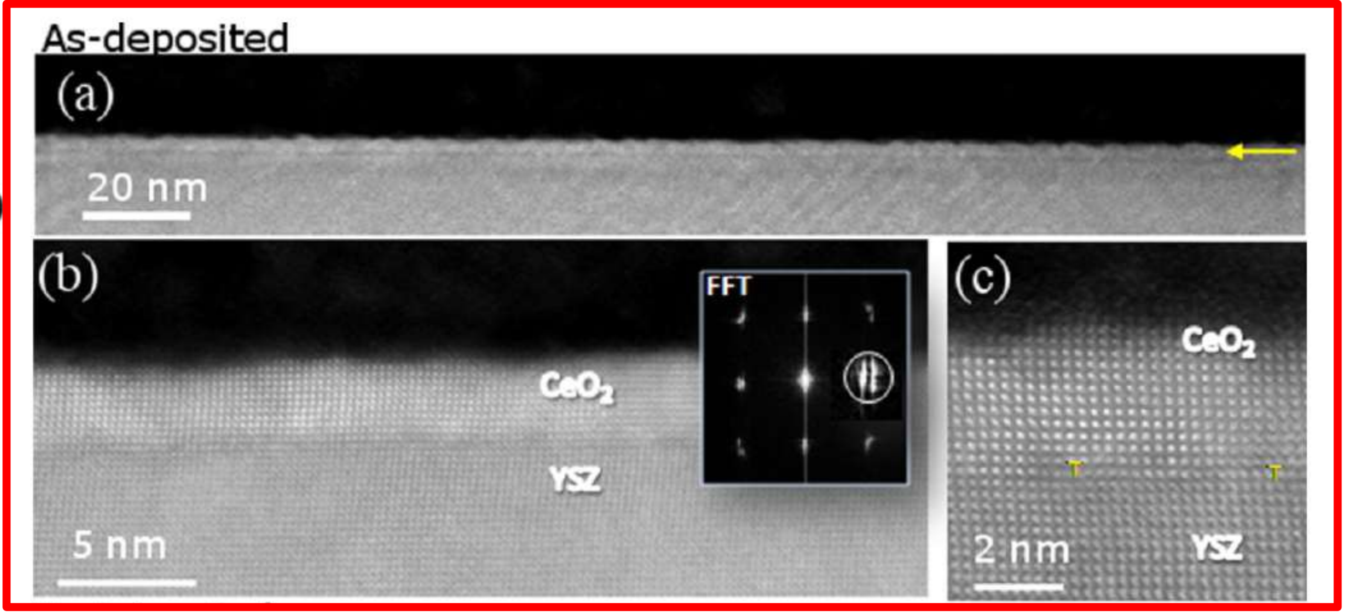
Epitaxy at low T : CeO_2

$(Ce(thd)_4 + O_3)$









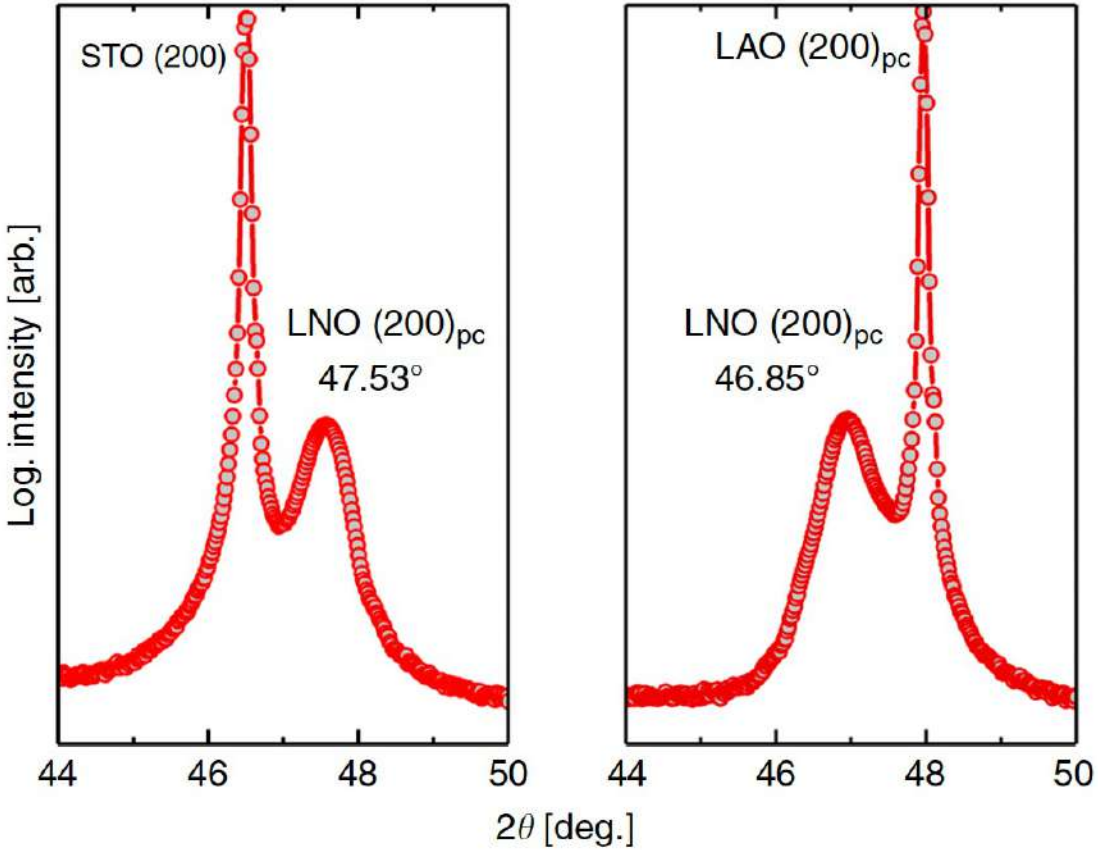
Chem. Mater. 2012, 24, 19, 3732–3737

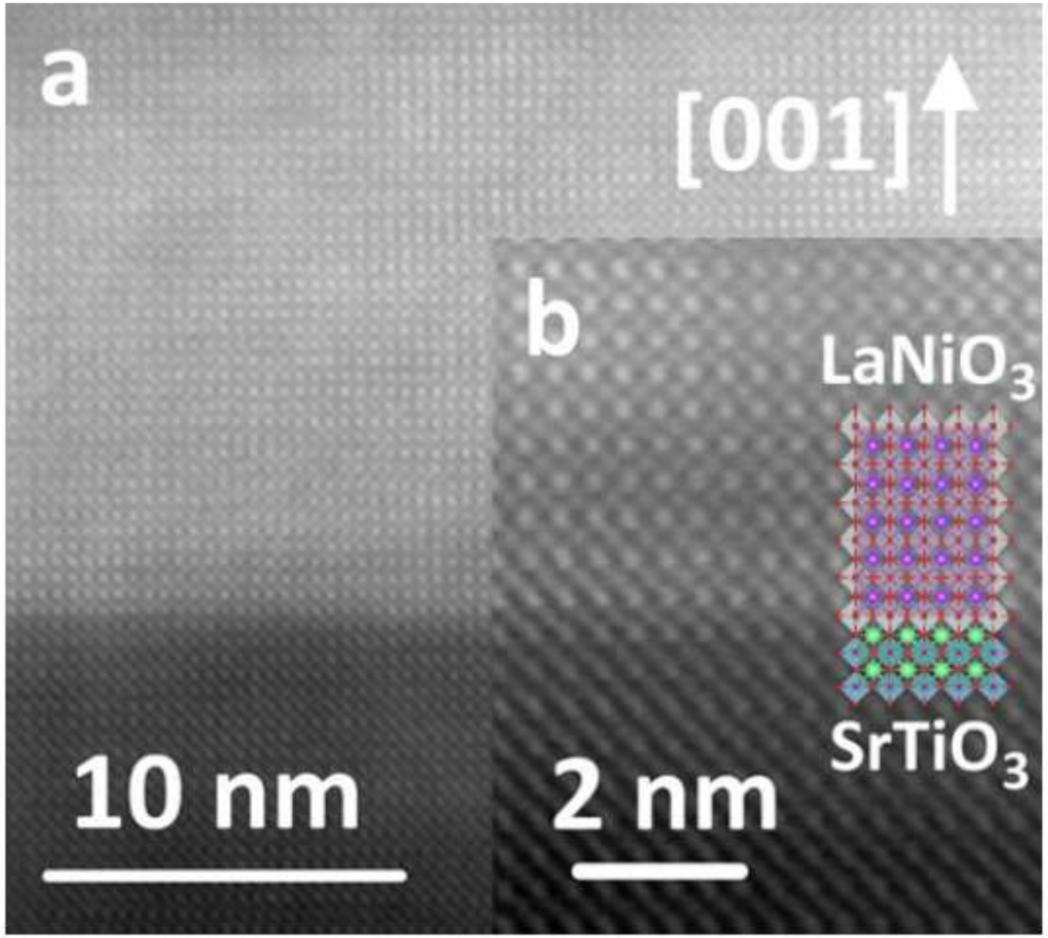
Epitaxy at low T : $LaNiO_3$ towards integration in Silicon Tech

($La(thd)_3 + O_3$)

($Ni(acac)_2 + O_3$)

@ 225 °C





Nature communications, ***volume 11***, *2872 (2020)*

$Hf_xZr_{1-x}O_2$ Mixed Oxides:

$Hf[N(CH_3)(C_2H_5)]_4$ and $CpZr[N(CH_3)_2]_3$
Ozone (O_3) @ 280 °C

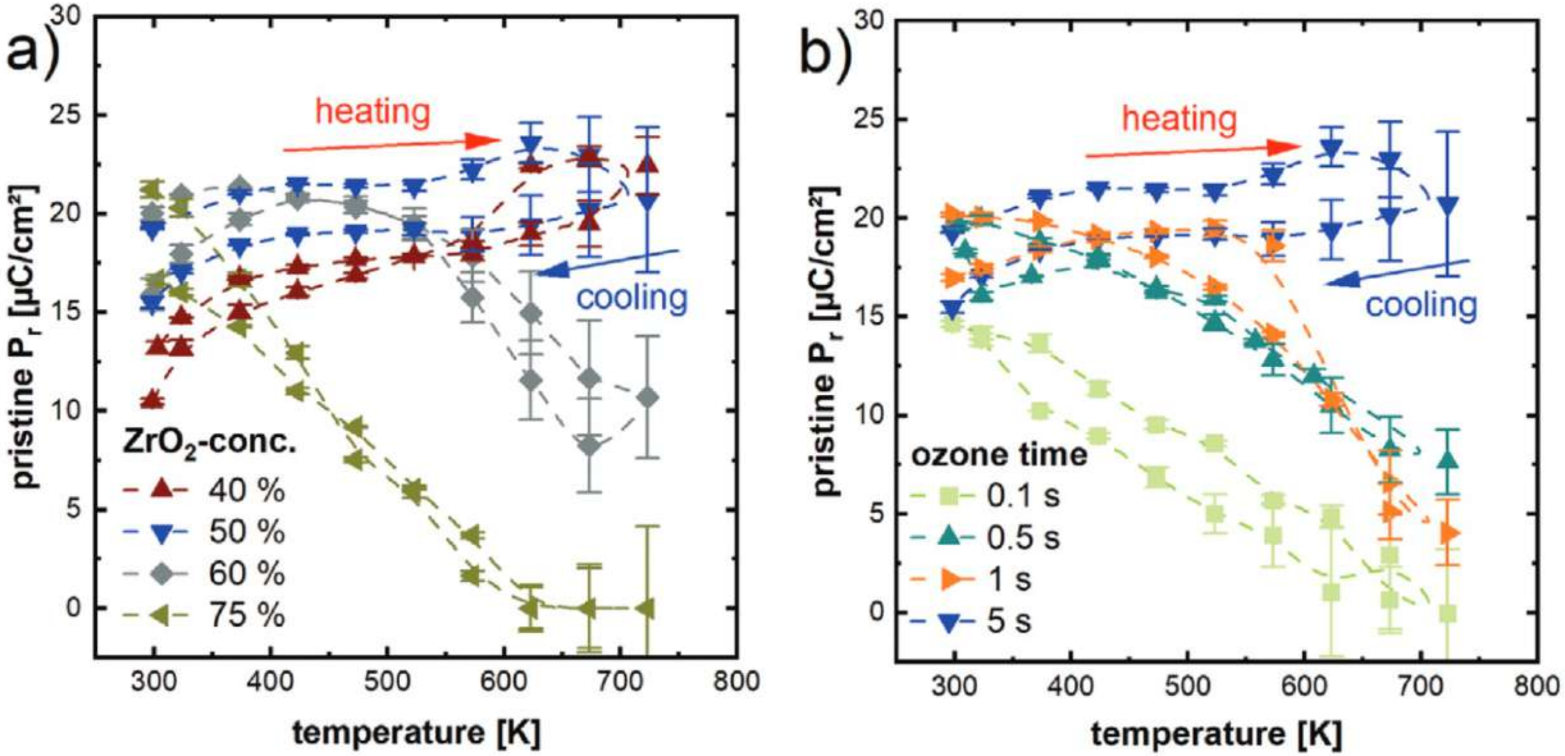
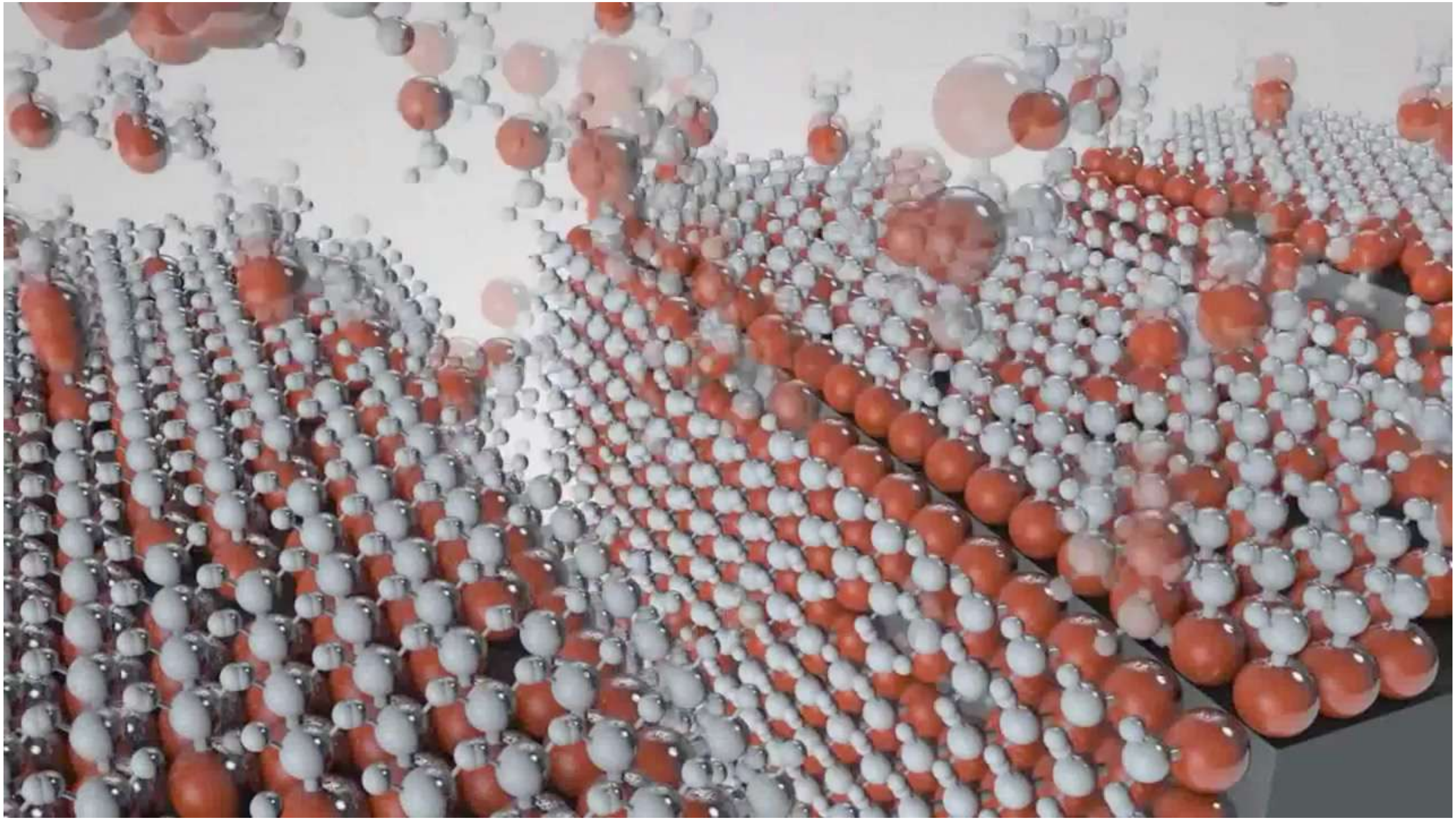


Figure 3. Temperature hysteresis of the remanent polarization. a) Remanent polarization as a function of temperature during heating and cooling for $Hf_xZr_{1-x}O_2$ with different ZrO_2 content and 5 s ozone dose time. b) Remanent polarization as a function of temperature for $Hf_{0.5}Zr_{0.5}O_2$ and different O_3 dose times. The dashed lines are guidelines for the eyes.

U. Schröder et al. Adv. Electron.Mater. 2022, 8, 2200265

Conformality: Step coverage in ALD



Step coverage in ALD

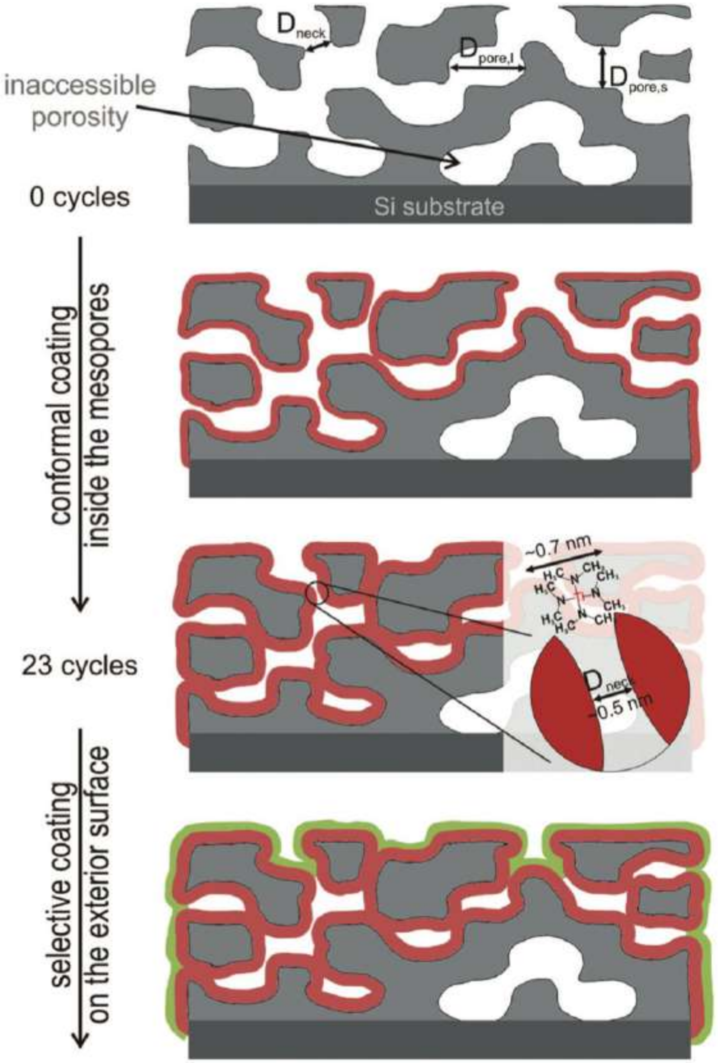


Fig. 9 Schematic representation of the mesoporous titania film and the pore filling by ALD of TiO_2.

Reactants must undergo self-limiting reaction
Reactants with proper doses must be present on the entrance of the holes for a long time so that the reactants get sufficient time to diffuse and react with the interior of the hole

Parameters that affect step coverage:

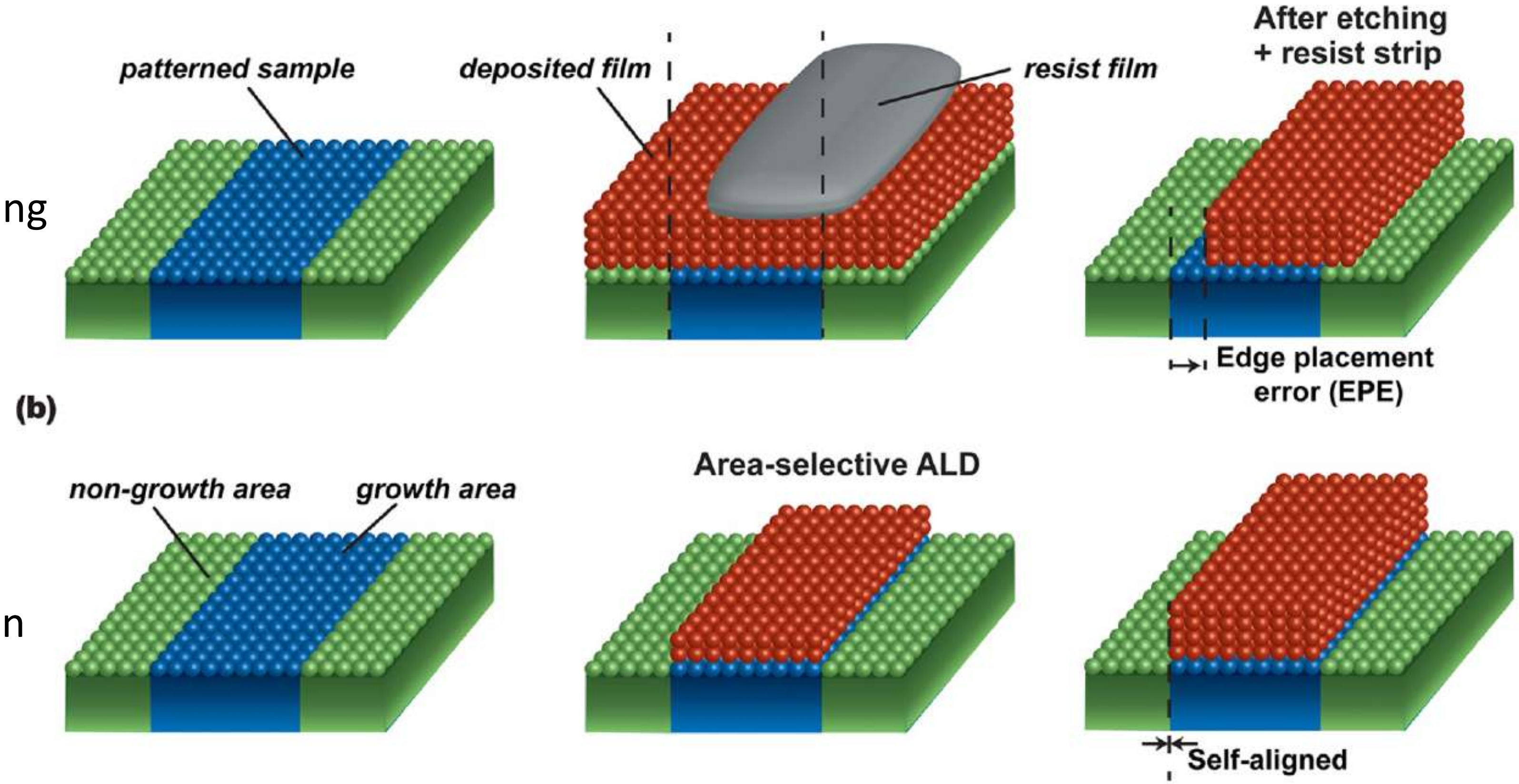
- Dose of the reactants
- Partial pressure of the reactants (P)
- Exposure time or pulse duration (t)
- Molecular mass (m)
- Temperature during exposure (T)
- Aspect ratio of the features (a)

Atomic layer deposition of nanostructured materials 2012 Wiley-VCH Verlag GmbH.
Nanoscale, 2014, 6, 14991–14998

Area Selective Deposition (ASD) for sub 5 nm scale feature

Conventional patterning

Self-aligned fabrication

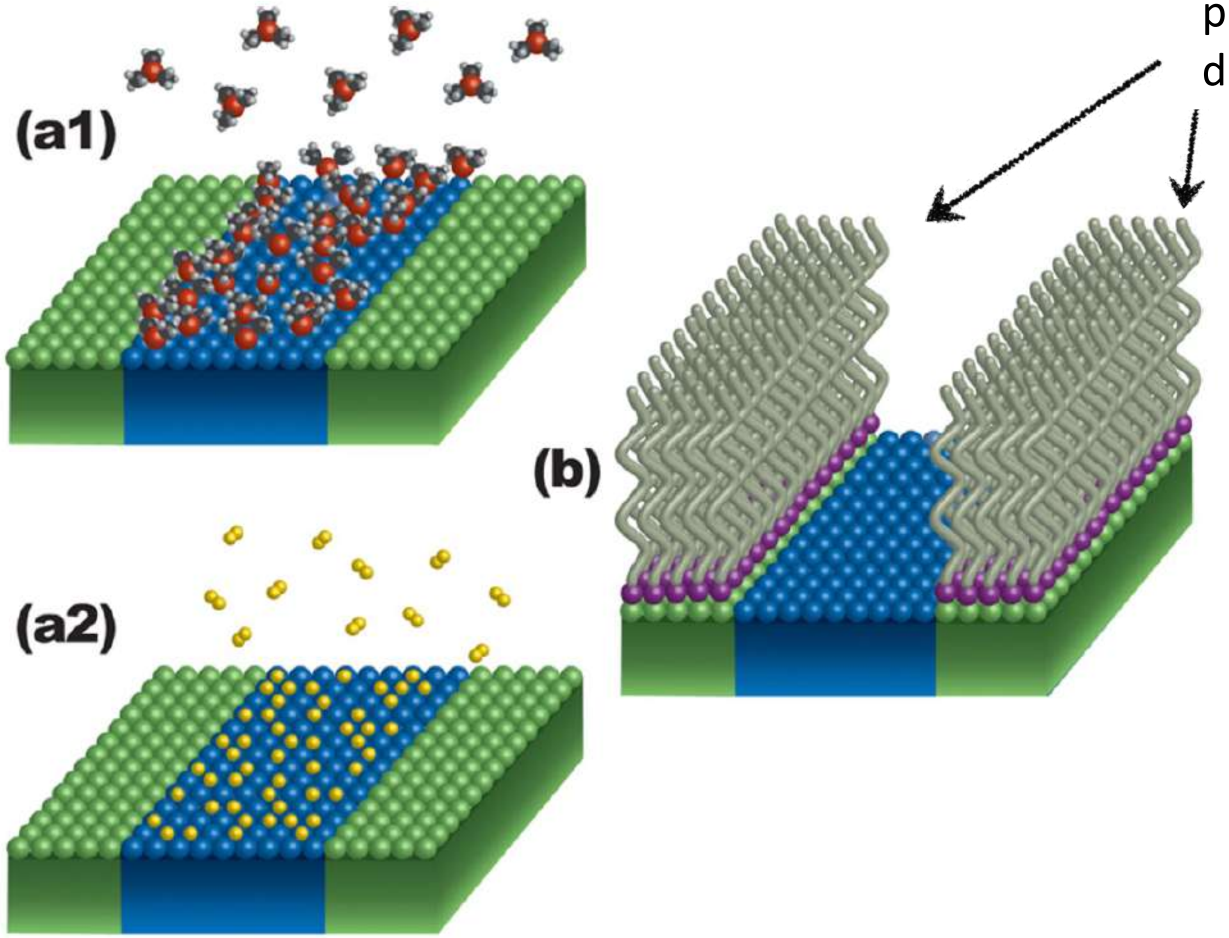


Challenging to
align the features

Deposition only
on the surface of
specific material
Alignment step
eliminated

Chem Mater. *2019 Jan 8; 31(1): 2–12*

Area Selective Deposition (ASD)

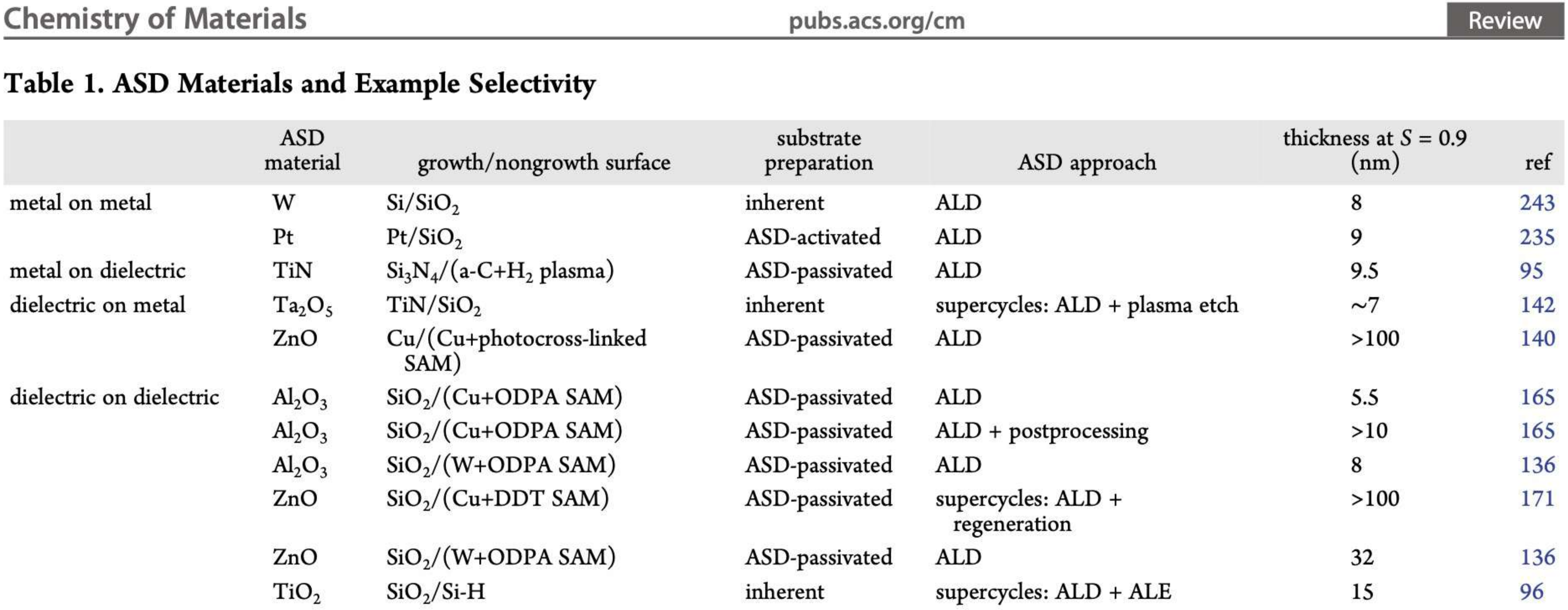


selective
precursor
adsorption

selective
co-reactant
adsorption

Surface selectively functionalized
prior to the deposition to
deactivate the ALD growth

Chem Mater. 2019 Jan 8; 31(1): 2–12



Chemistry of Materials pubs.acs.org/cm Review

Table 1. ASD Materials and Example Selectivity

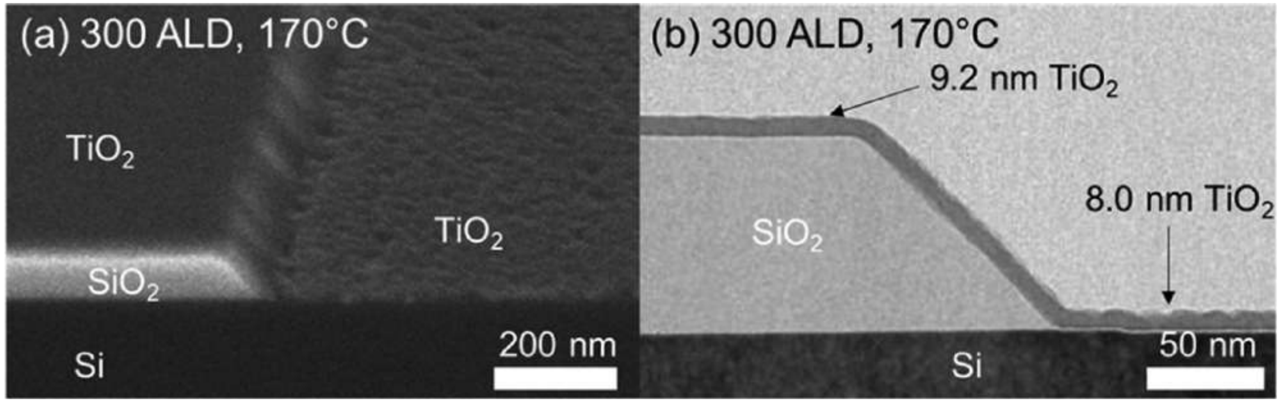
	ASD material	growth/nongrowth surface	substrate preparation	ASD approach	thickness at $S = 0.9$ (nm)	ref
metal on metal	W	Si/SiO_2	inherent	ALD	8	243
	Pt	Pt/SiO_2	ASD-activated	ALD	9	235
metal on dielectric	TiN	Si_3N_4/(a-C+H_2 plasma)	ASD-passivated	ALD	9.5	95
dielectric on metal	Ta_2O_5	TiN/SiO_2	inherent	supercycles: ALD + plasma etch	~7	142
	ZnO	Cu/(Cu+photocross-linked SAM)	ASD-passivated	ALD	>100	140
dielectric on dielectric	Al_2O_3	SiO_2/(Cu+ODPA SAM)	ASD-passivated	ALD	5.5	165
	Al_2O_3	SiO_2/(Cu+ODPA SAM)	ASD-passivated	ALD + postprocessing	>10	165
	Al_2O_3	SiO_2/(W+ODPA SAM)	ASD-passivated	ALD	8	136
	ZnO	SiO_2/(Cu+DDT SAM)	ASD-passivated	supercycles: ALD + regeneration	>100	171
	ZnO	SiO_2/(W+ODPA SAM)	ASD-passivated	ALD	32	136
	TiO_2	SiO_2/Si-H	inherent	supercycles: ALD + ALE	15	96

Chem. Mater. 2020, 32, 12, 4920–4953

Atomic Layer Etching (ALE)

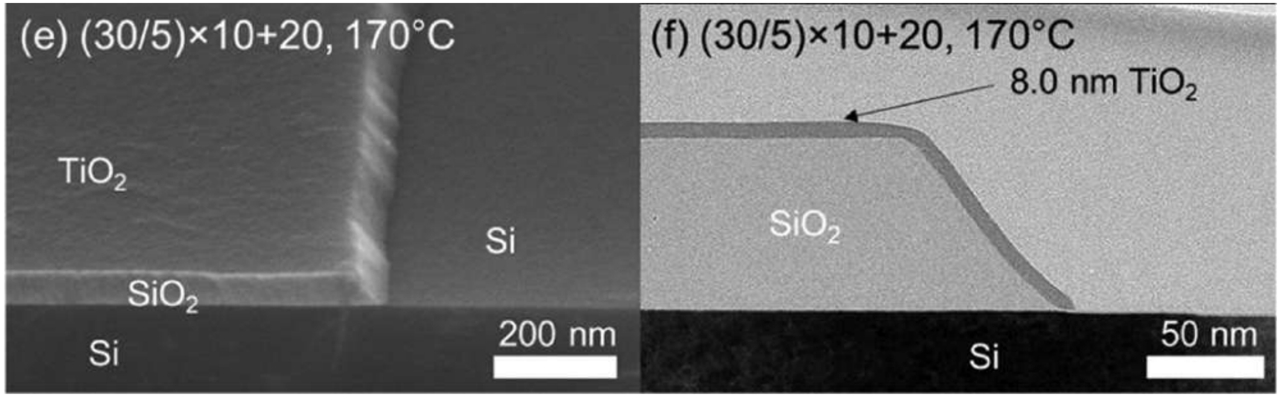
SiO_2 vs H-Si

$TiCl_4 + H_2O$



ALD

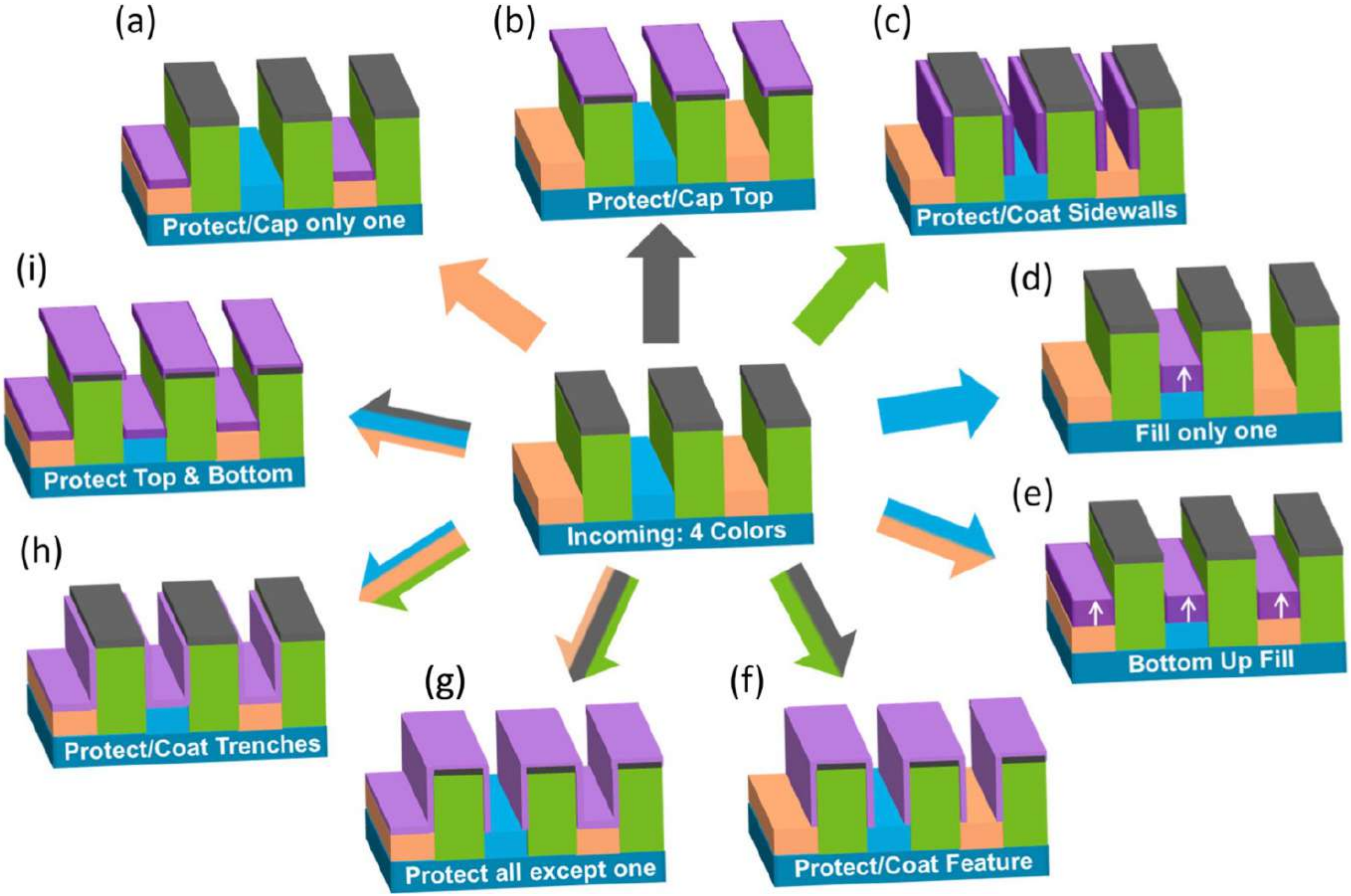
$TiCl_4 + H_2O$
$WF_6/N_2/BCl_3/N_2$



ALD+ ALE

Chem. Mater.2 019, 31, 4793−4804

Selective deposition tool-box



Chem. Mater. 2020, 32, 12, 4920–4953

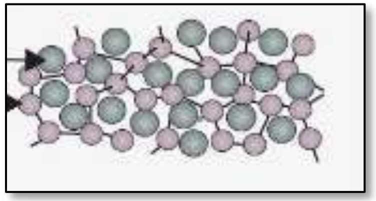
ALD AND CSD COMPARISON

Chemical precursor

CSD

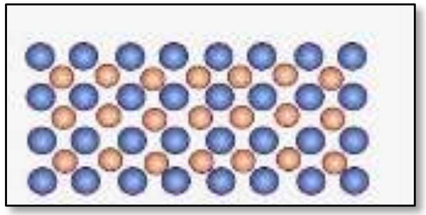
precursor solution

Deposited at once



thermal treatment

crystalline



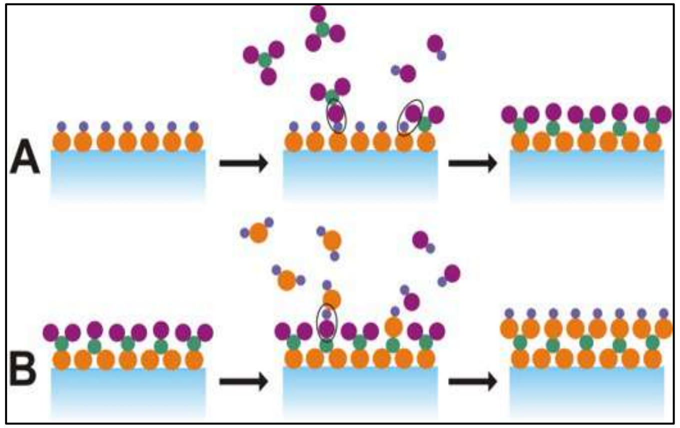
-Thickness (~ 800 nm)
-Versatility of compositions (PAD)
-Epitaxy
-Low initial investment, no vacuum

- Thickness > 1 μm
- Hybrids (2D+NP)
- Lower Processing T (UV light instead)
- Complex stoichiometries
- New precursor chemistries
- Homogeneity large areas

ALD

Gas precursors

Layer by layer



No solvent
Optimized material dose

- Ultrathin films (atomic control)
- Conformality/dense
- Versatility compositions: binary, doping...
- Area selective deposition
- Selective etching
- Epitaxy
- Mid-cost initial investment, low T process

- Complex compositions
- Nanoparticle coating
- In situ analysis
- Precursor chemistries