Atomic Layer Deposition of functional oxide perovskites ABO_3 on large surface: cases of $SrTiO_3$, $BiFeO_3$

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Flagship AXION: nAnoXItrONics

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ALD — *Atomic Layer Deposition*

Films

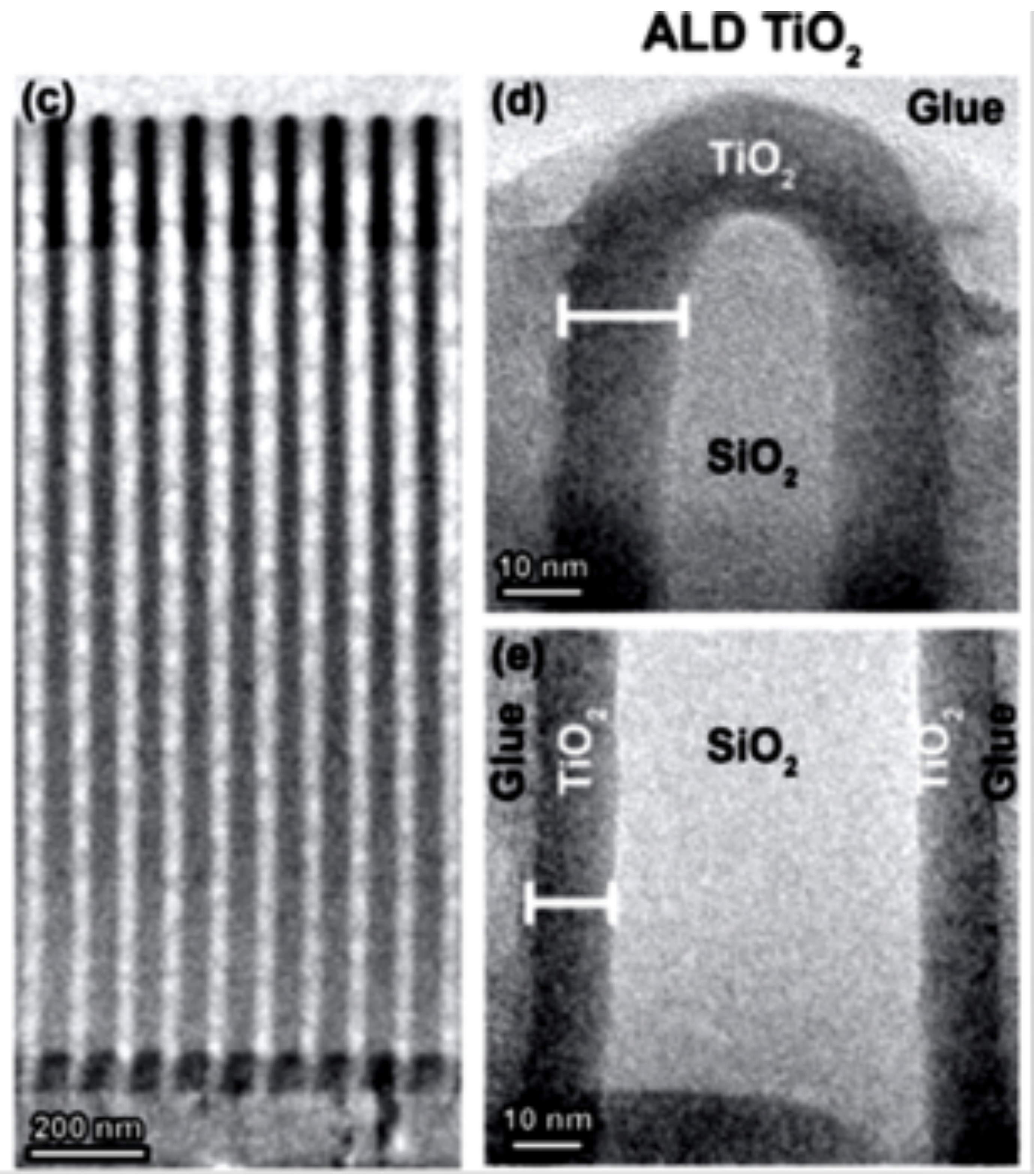
- Easy control of film thickness and stoichiometry
- Excellent repeatability
- 100% film density
- Complex heterostructure

Conformal Coating

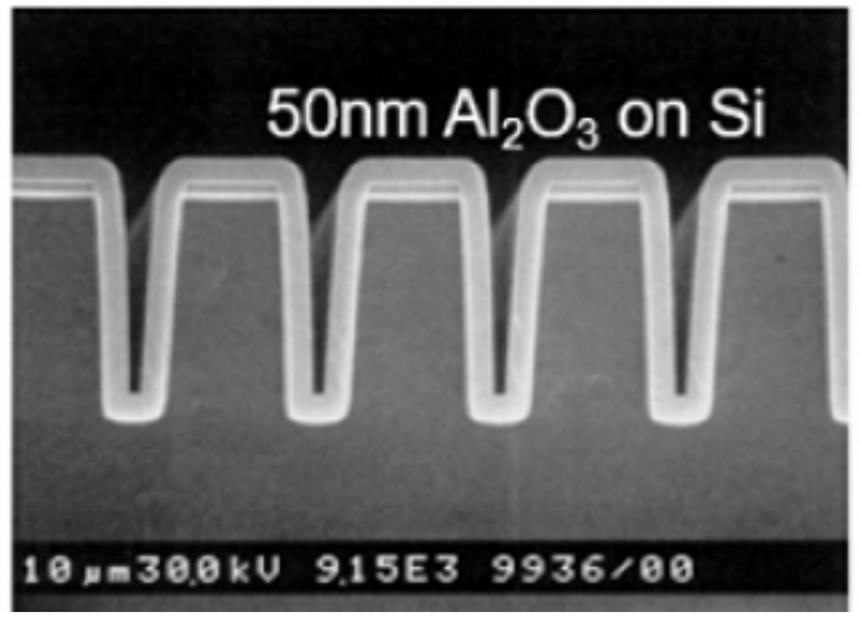
- Excellent 3D conformity
- Large area thickness uniformity
- Atomically flat and smooth coating

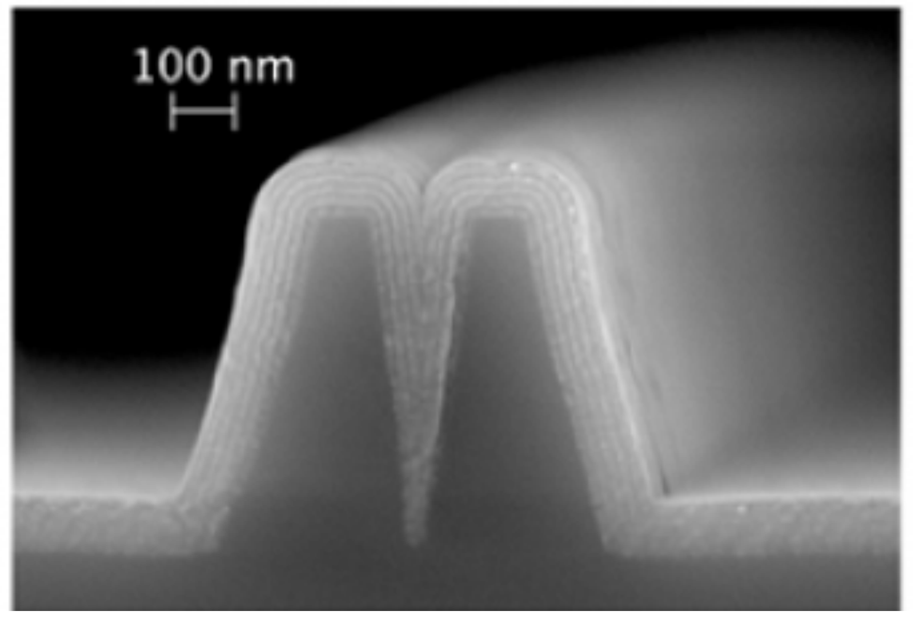
Challenging Substrates

- High aspect ratio materials
- Low temperature and low stress
- Batch process



P. Schindler, Langmuir 2015, 31, 5057





Already in industry for:

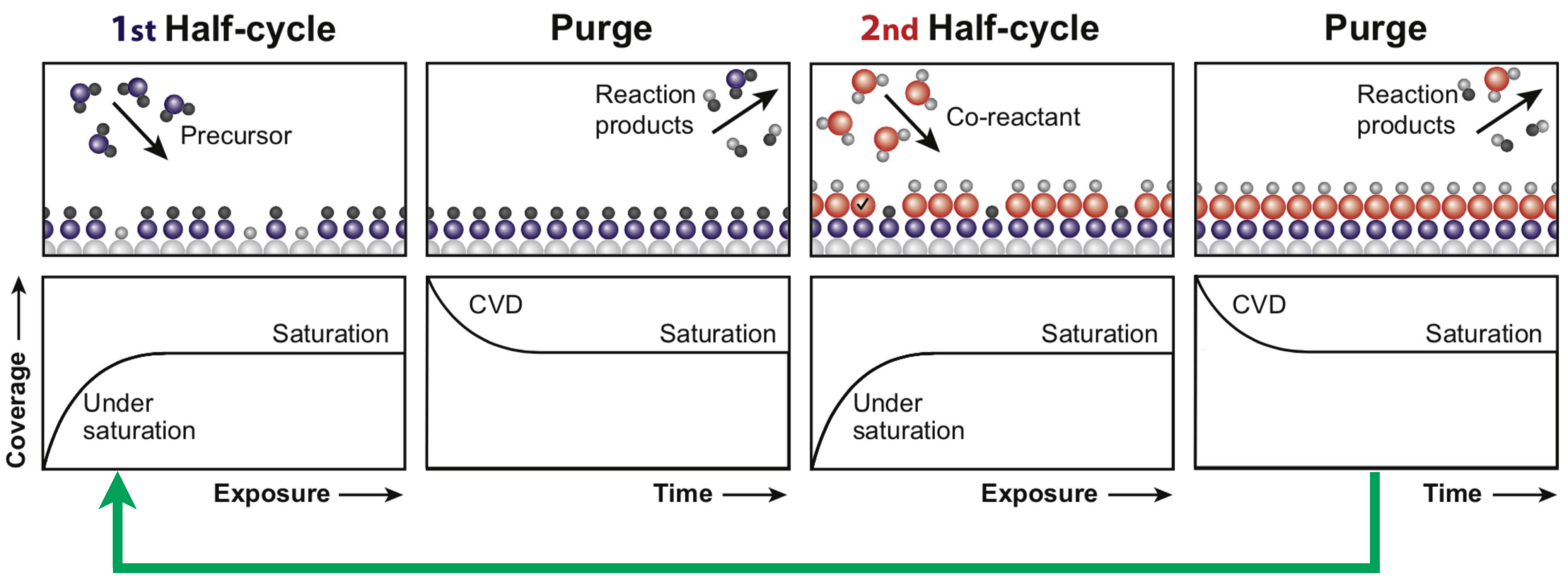
- Passivation, diffusion barrier layers (TiN, etc.)
- Dielectric, High-k layers (HfO_2, $SrTiO_3$, etc.)
- Electrodes (Al:ZnO, etc.)

Perspectives for:

- Photovoltaic, SOFC
- New architectures with high aspect ration (nanowires)
- 2D materials (graphene, chalcogenides, nitrides)

ALD — *Atomic Layer Deposition*. Principle

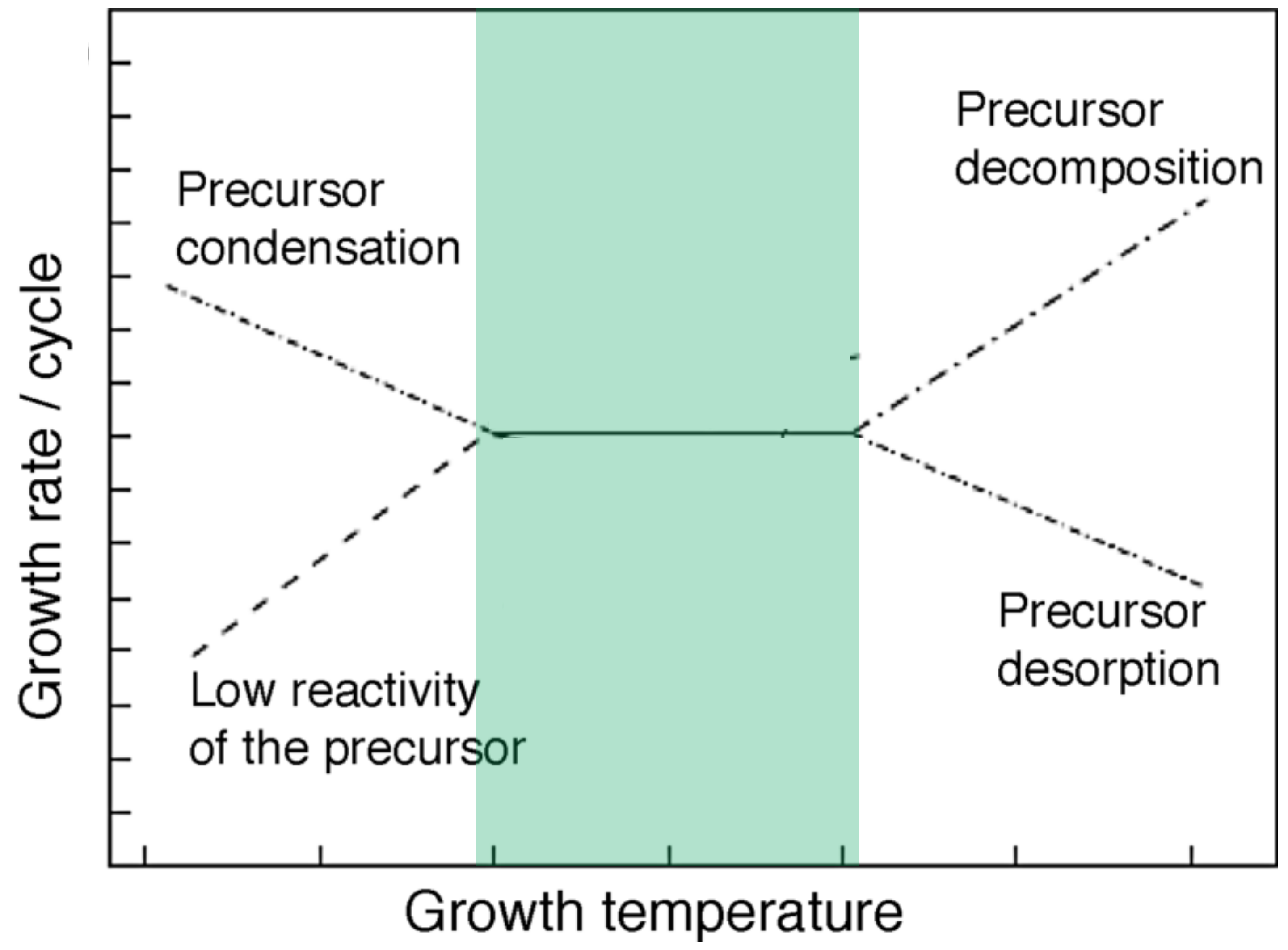
ALD is based on repeated *self-terminating irreversible* gas-solid reactions (chemisorption)

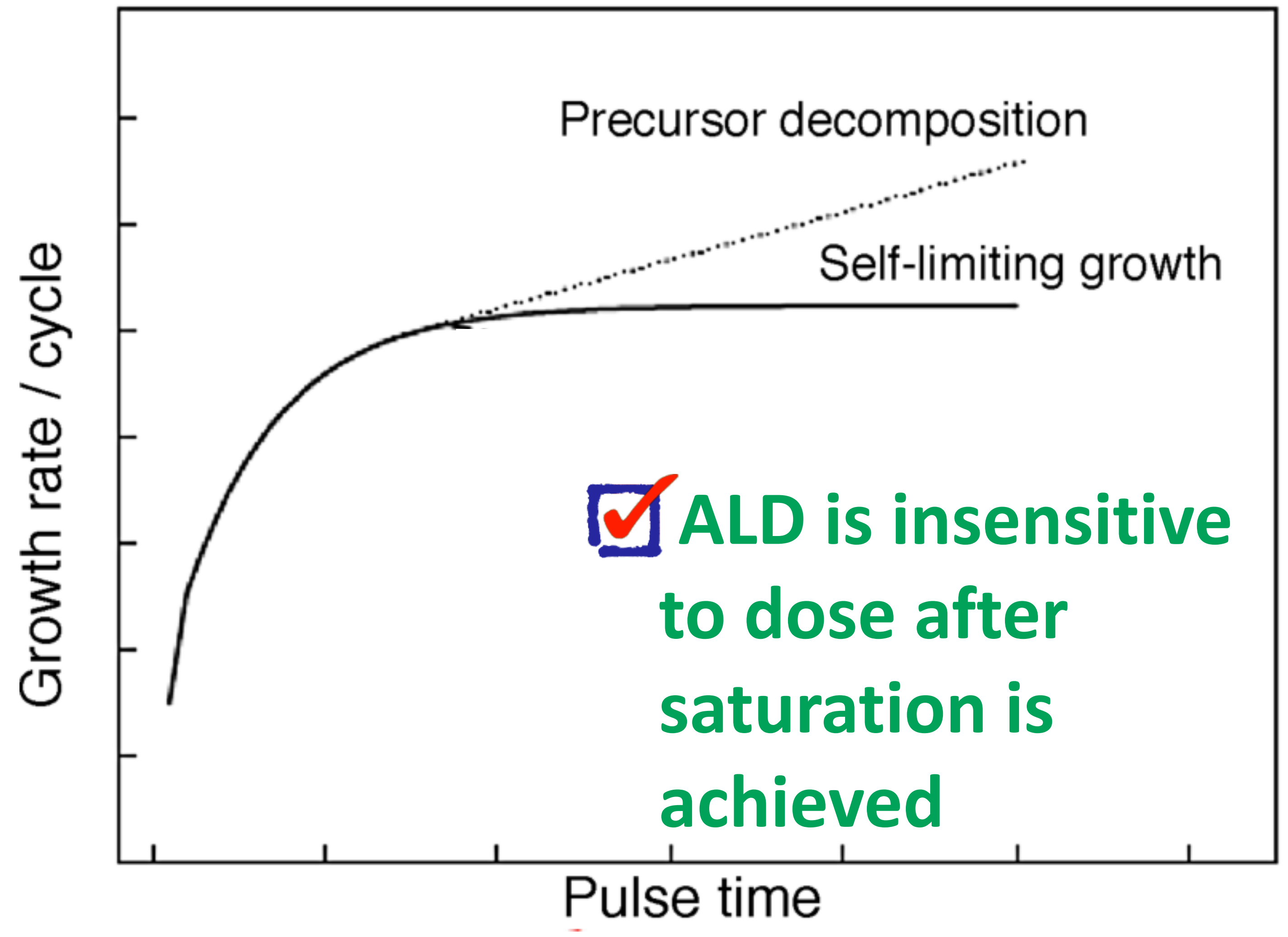


n cycles

GPC — *Growth per Cycle* (Å/cycle)

☑ ALD window (GPC is constant) :





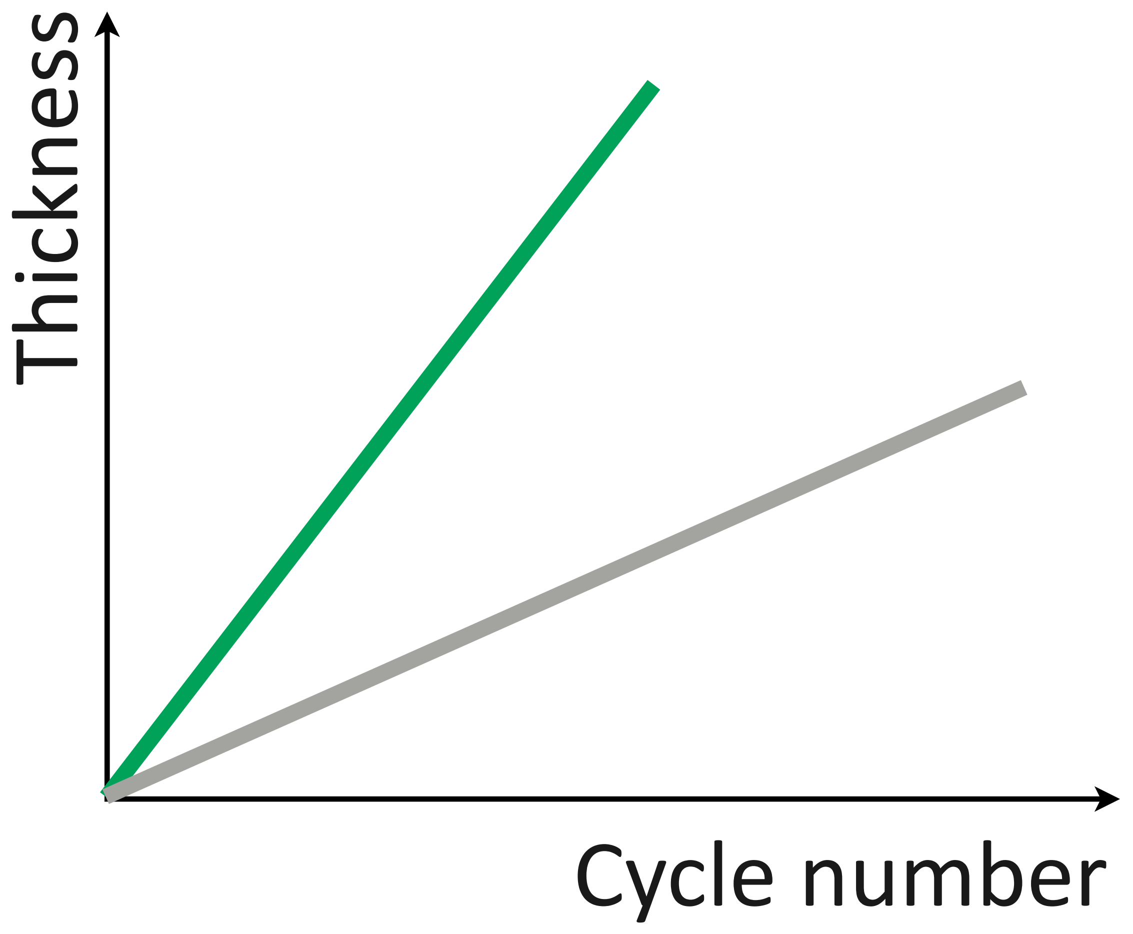
☑ ALD is insensitive to dose after saturation is achieved

Synthesis of ternary materials by ALD
Supercycle approach

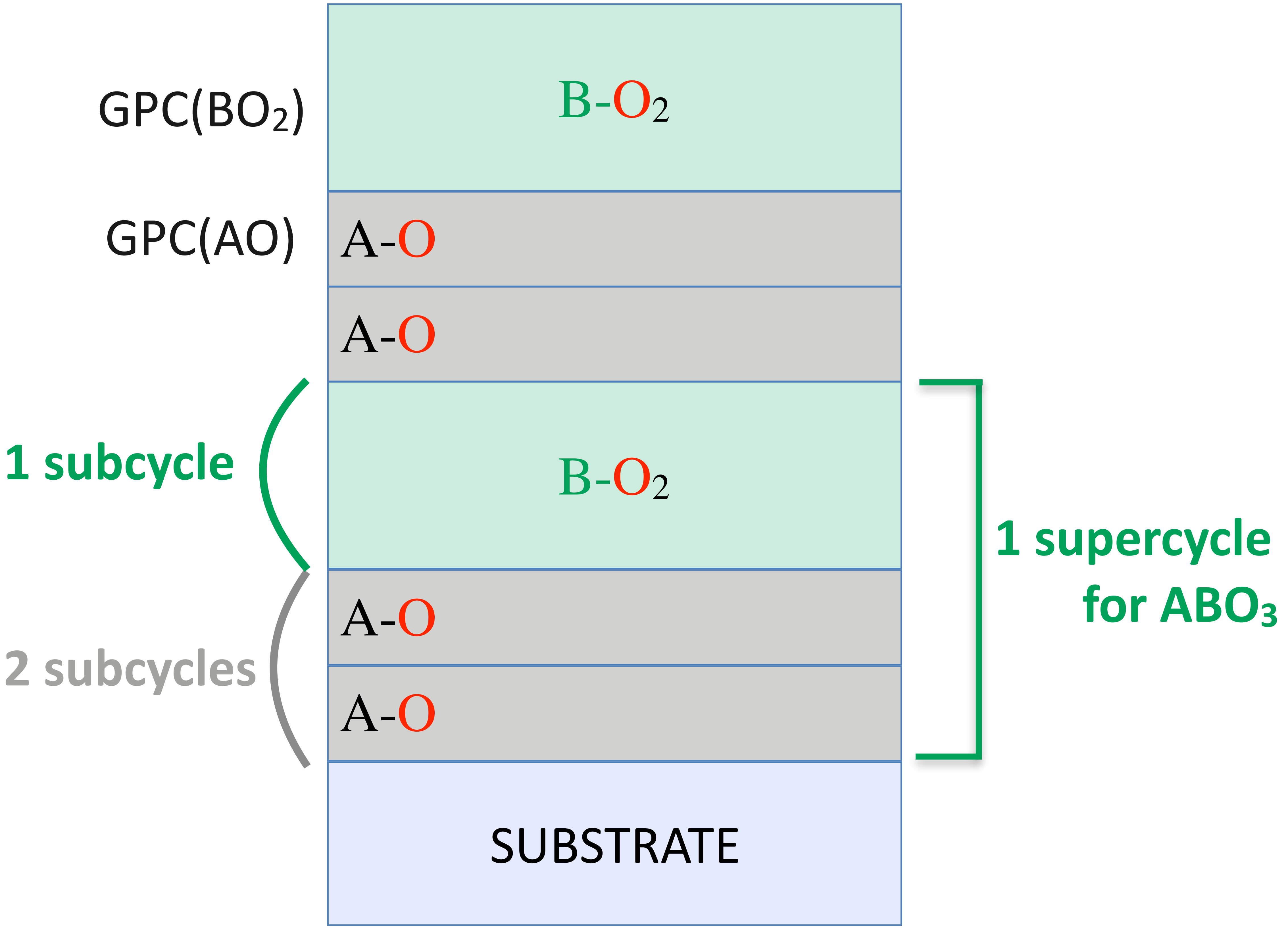
Supercycle approach involves the use of two metalorganic precursors that are dosed in separate cycles

This example:

$GPC(BO_2) = 2 \cdot GPC(AO)$



ABO_3



Cycle ratio = 2

Conditions:

- Compatible physico-chemical properties of the two precursors (evaporation temperature, adsorption kinetics)
- Compatible ALD windows (temperature range of linear growth rate)

ANNEALSYS MC-050 DLI-CVD/ALD machine

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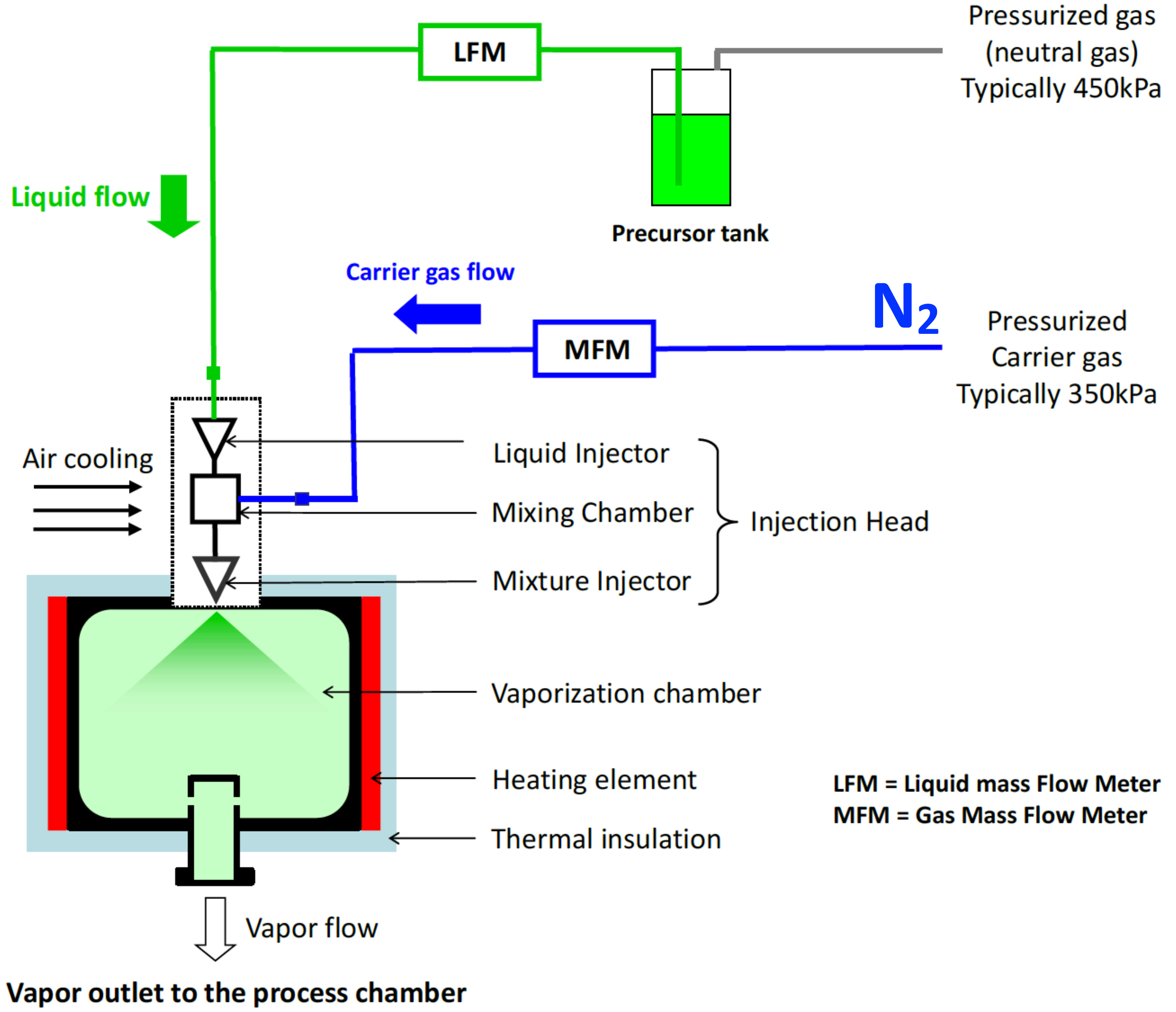
DLI — *Direct Liquid Injection*

Interest of the DLI:

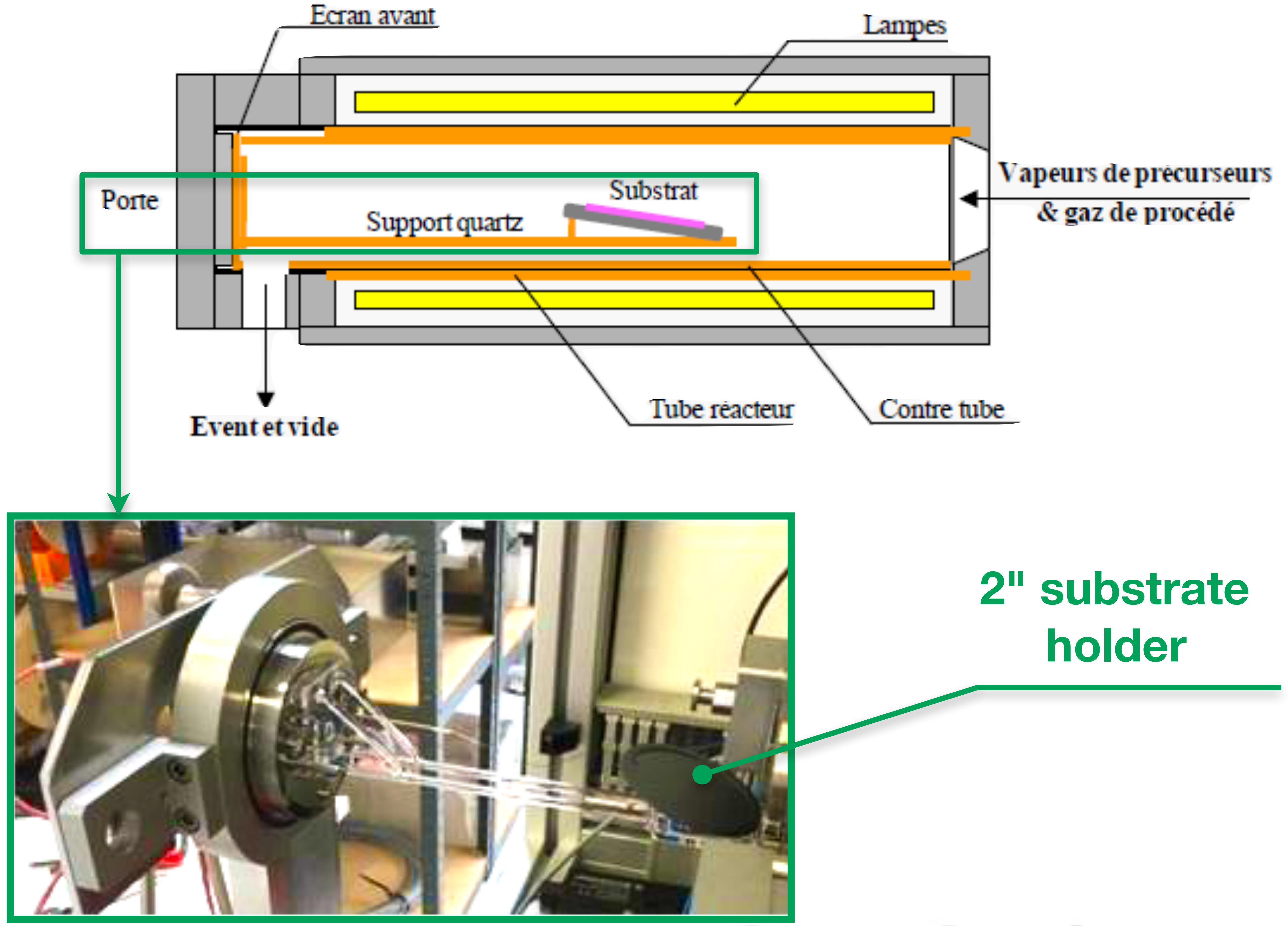
- use of **diluted** chemical precursors
- use of precursors with **low vapor pressure**
- sources kept ambient temperature (stability)
- short pulse times (few ms fast DLI injectors)

Process chamber:

- CVD, ALD, MOCVD, RTP and RTCVD
- **RTA to 1100°C**
- infrared lamp furnace
- atmosphere to 10^{-3} Torrs
- **H_2O / O_3 / H_2** / remote plasma (optional)



LFM = Liquid mass Flow Meter
MFM = Gas Mass Flow Meter



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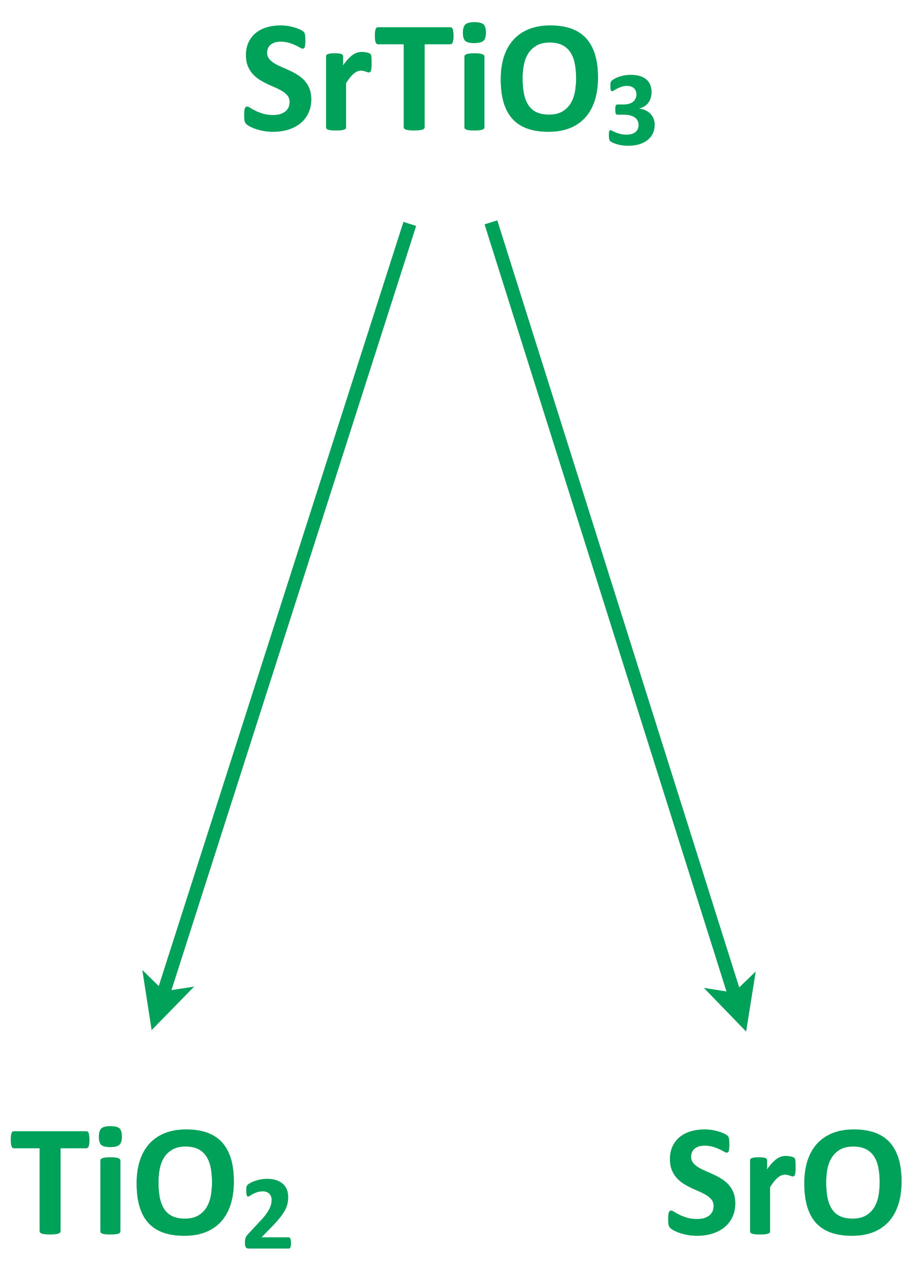
Main results



$SrTiO_3$

TiO_2 SrO

$BiFeO_3$

Fe_2O_3 Bi_2O_3

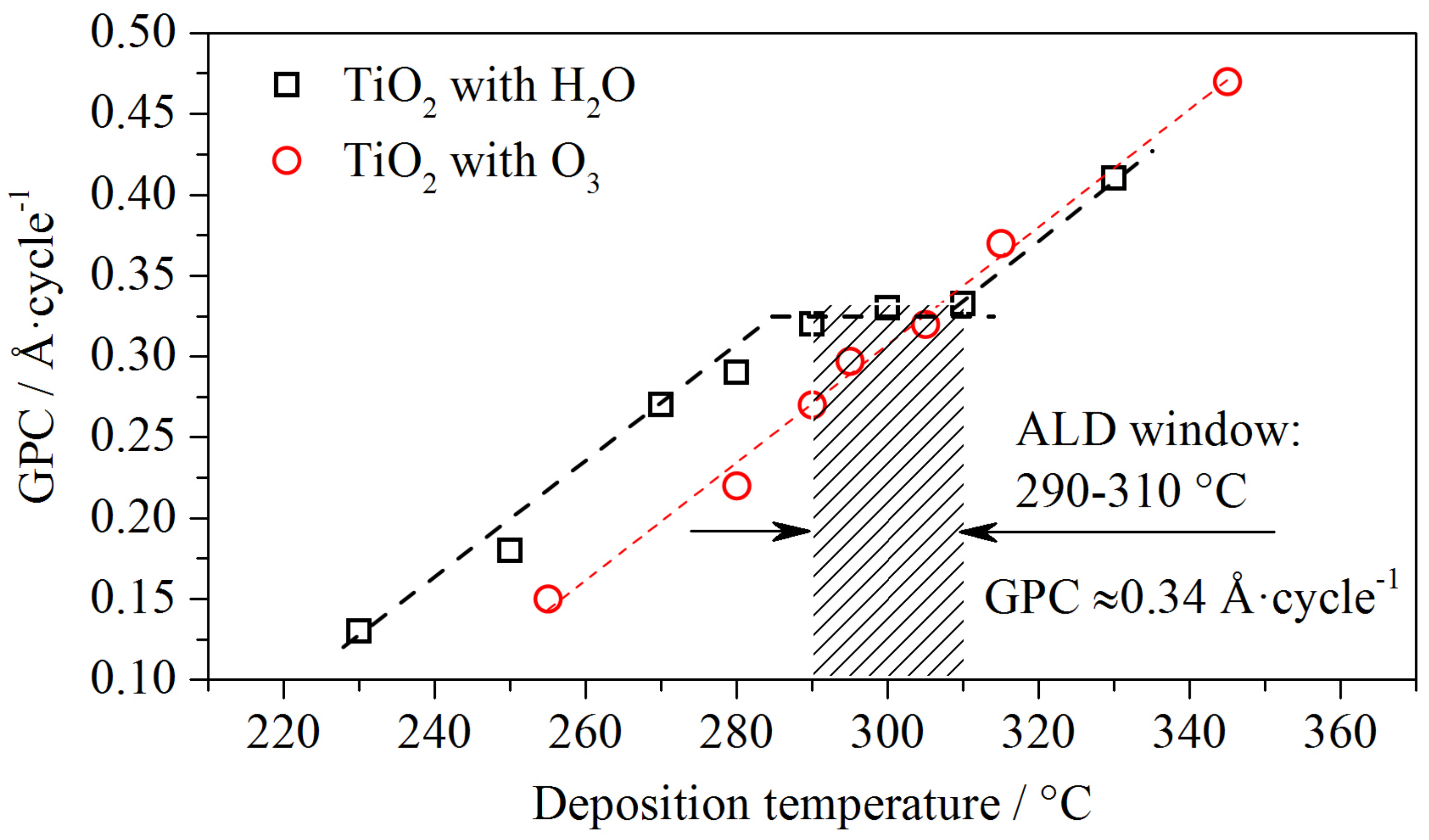
TiO_2 growth process optimization

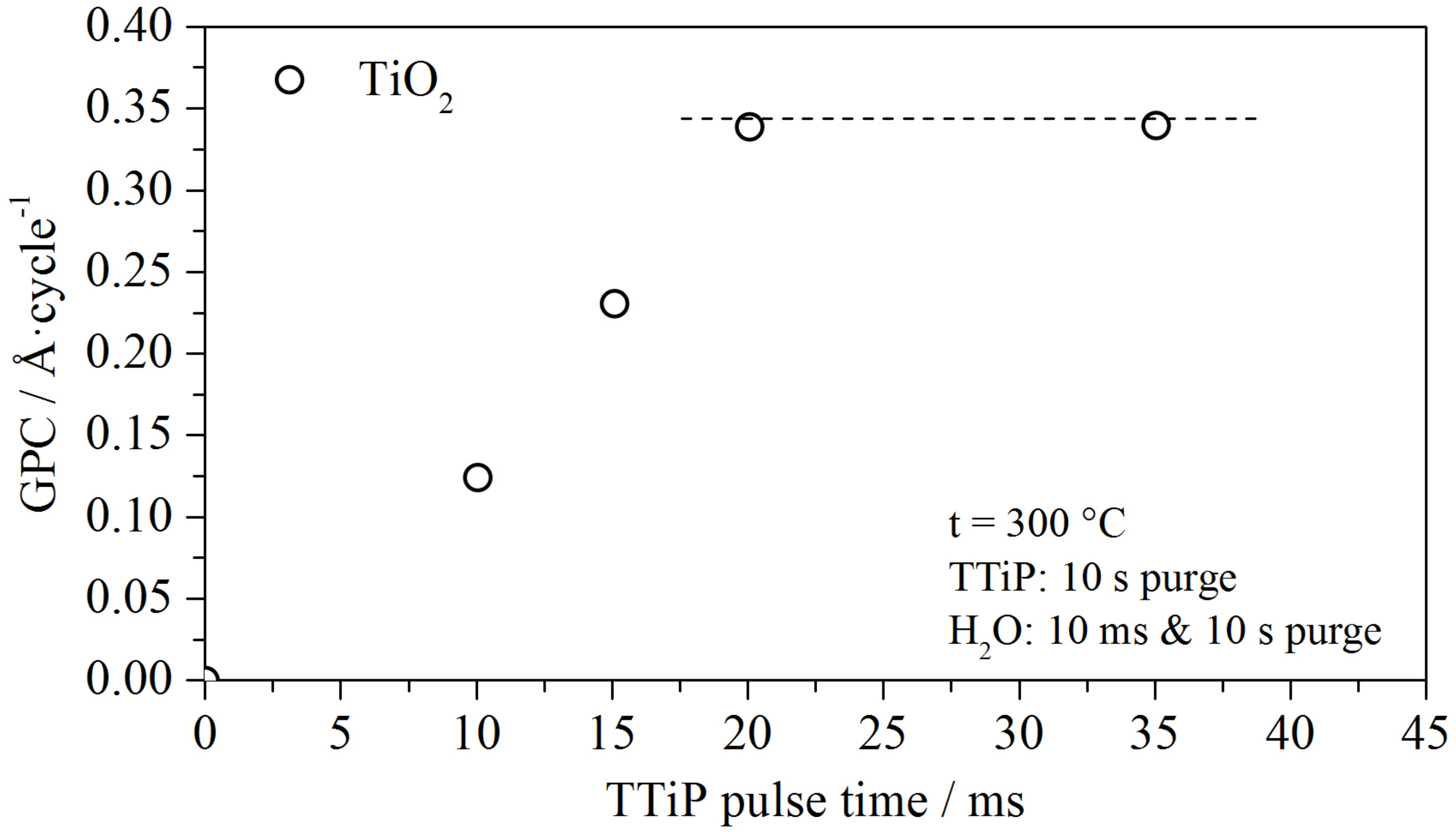
Precursor solution:

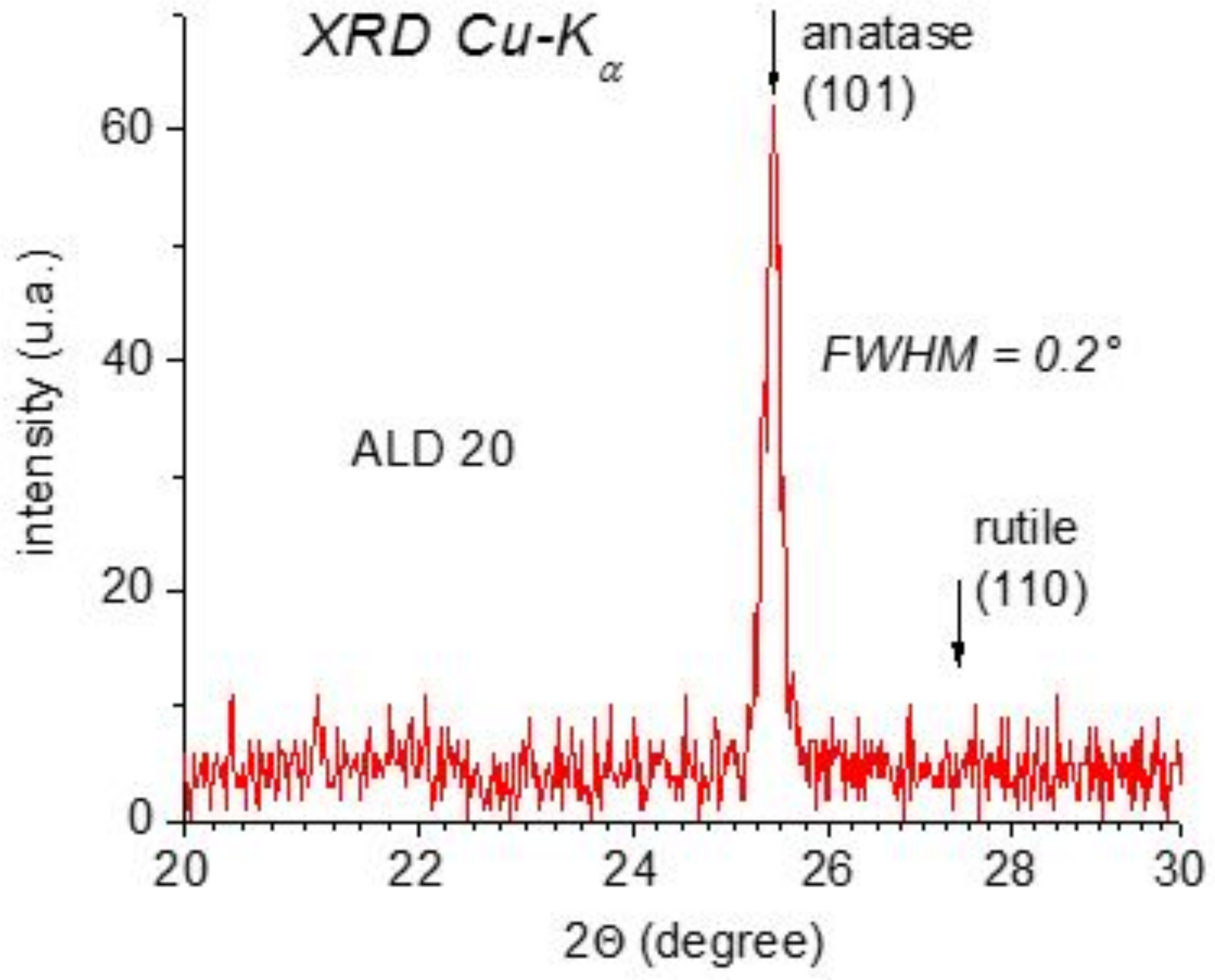
- $[TTiP]=5 \cdot 10^{-3}$ M in toluene ($C_6H_5CH_3$)

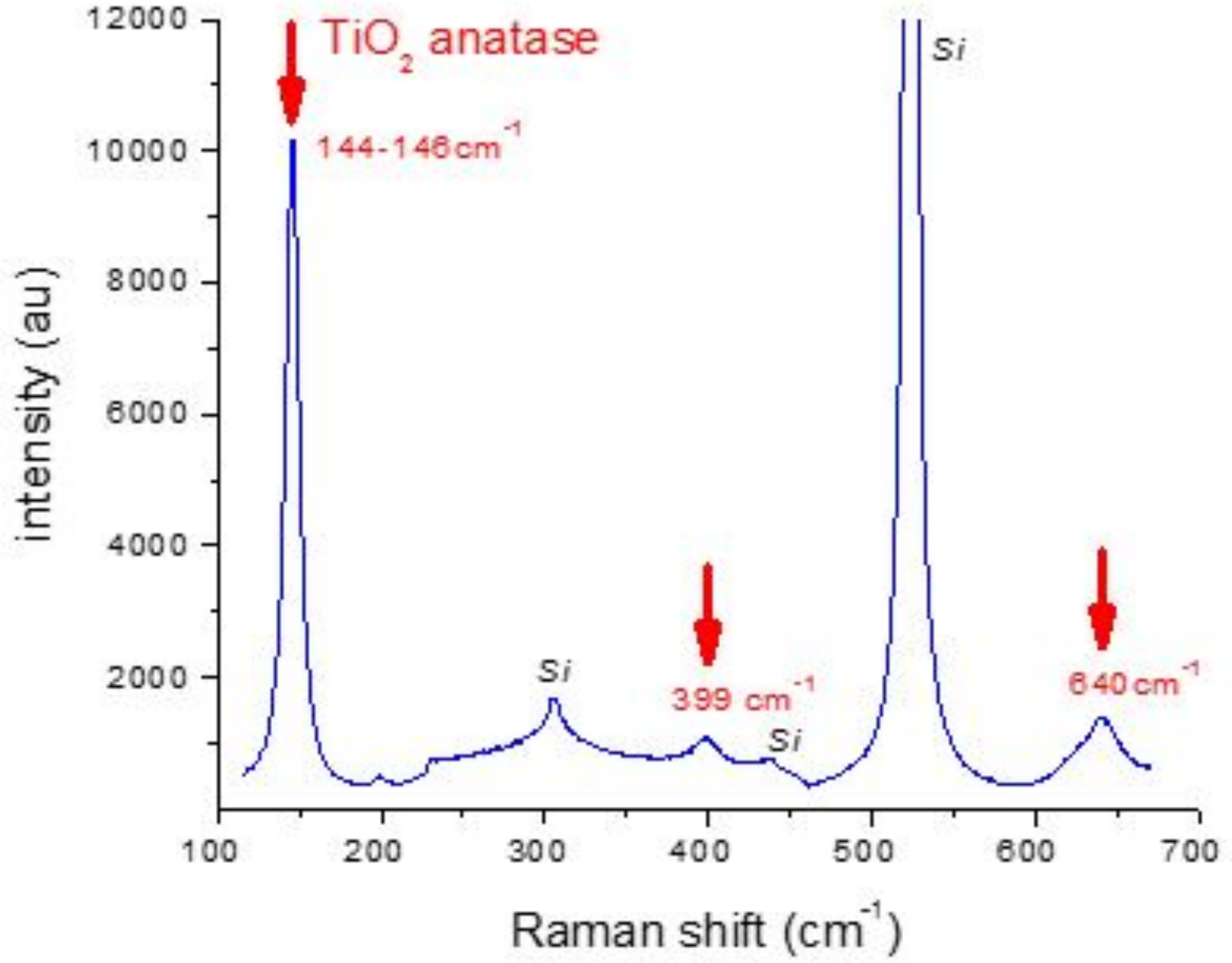
TTiP — $Ti[OCH(CH_3)_2]_4$ titanium isopropoxide

Oxidizing agents: O_3 or H_2O









Ellipsometry measurements (thickness/RMS):

TiO_2 with H_2O :

- cristalline as grown: anatase phase
- well covered film
- high thickness homogeneity (<5% variation)
- low roughness ($R_q \approx 4$ nm by AFM)
- no carbon contamination (by XPS)

SrO growth process optimization

Precursor solution:

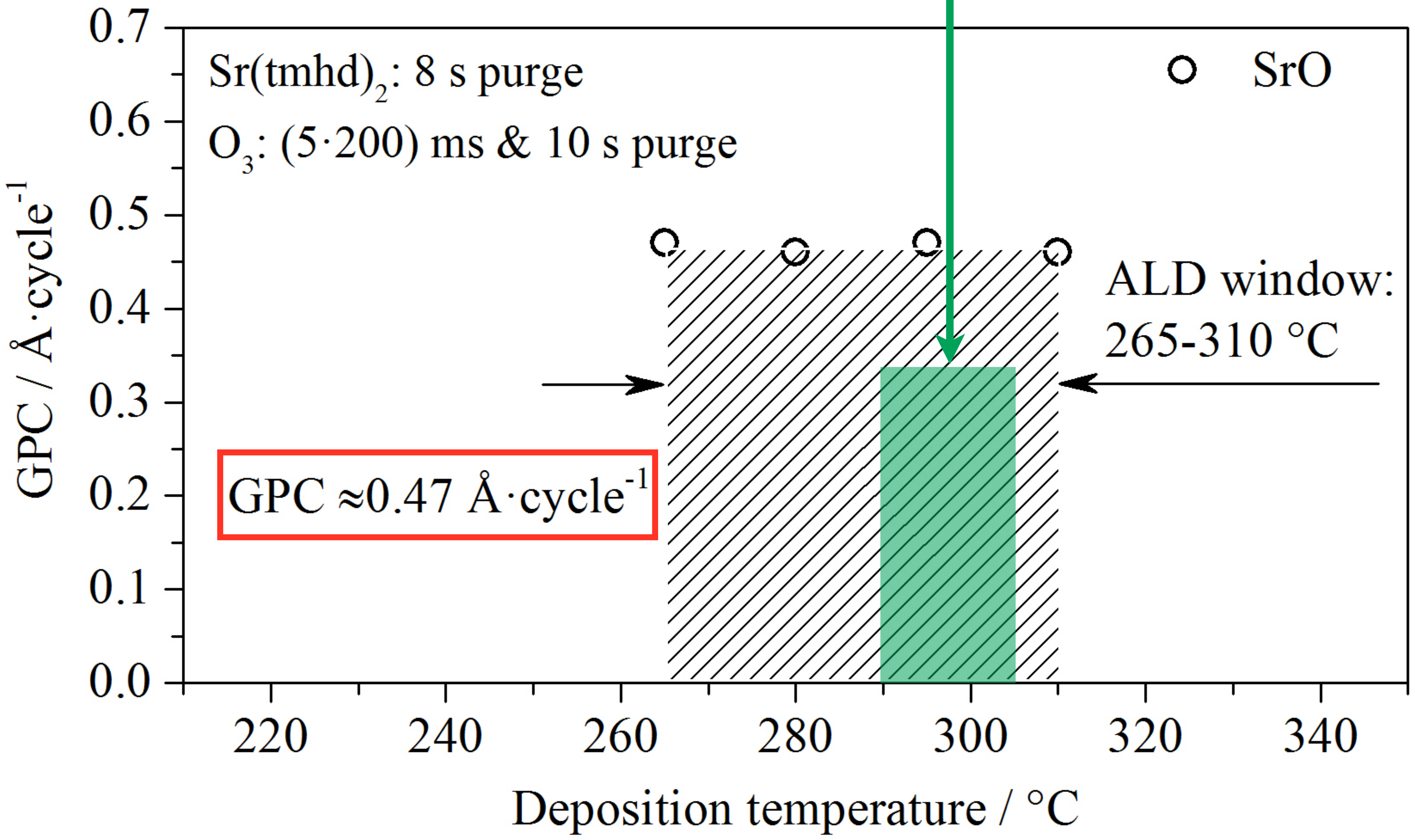
- [Sr(tmhd)$_2$]=5·10^{-3} M in toluene ($C_6H_5CH_3$)

Sr(tmhd)$_2$ — Bis(2,2,6,6-Tetramethyl–3,5-heptanedionato)strontium(II)

Oxidizing agent: only O_3

TiO_2 ALD window

GPC(TiO2) = 0.34 Å·cycle^{-1}



SrO:

- large ALD window (min. 265-310°C) compatible with TiO_2
- GPC(SrO) = 1.4·GPC(TiO_2)
- XPS: high carbon content (partial $SrCO_3$ formation ?)
- CO_3^{2-} to be removed with H_2O injection

$SrTiO_3$ growth. ALD supercycle approach

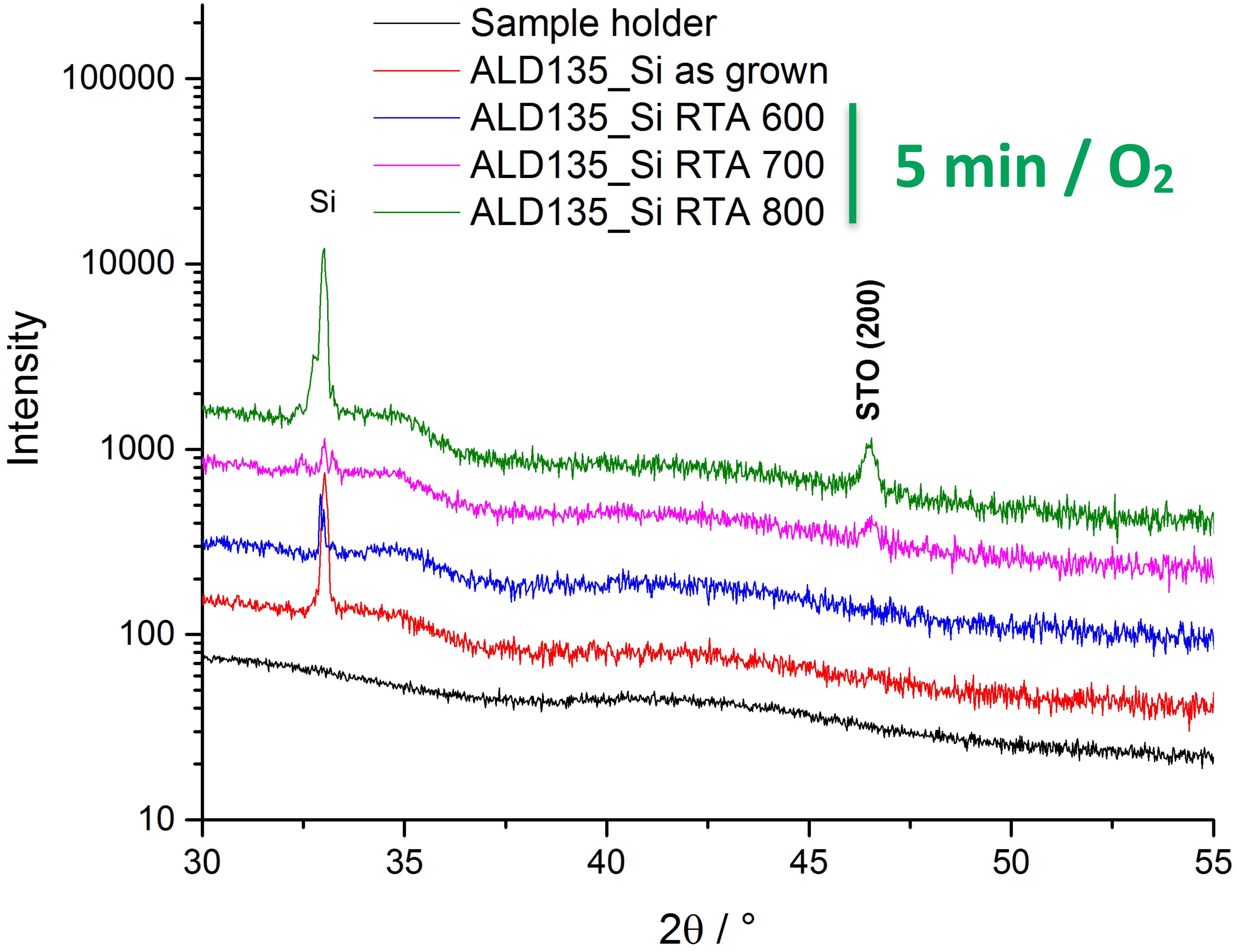
Input: **$GPC(SrO) = 1.4 \cdot GPC(TiO_2)$**

$SrTiO_3$ growth at 295 °C :

Cycle ratio Ti : Sr	Thickness, nm	Cation elementary composition (Ti : Sr), %at.
2 : 1	80	58 : 42
1 : 1	77	**45 : 55**
3 : 2	56	65 : 35

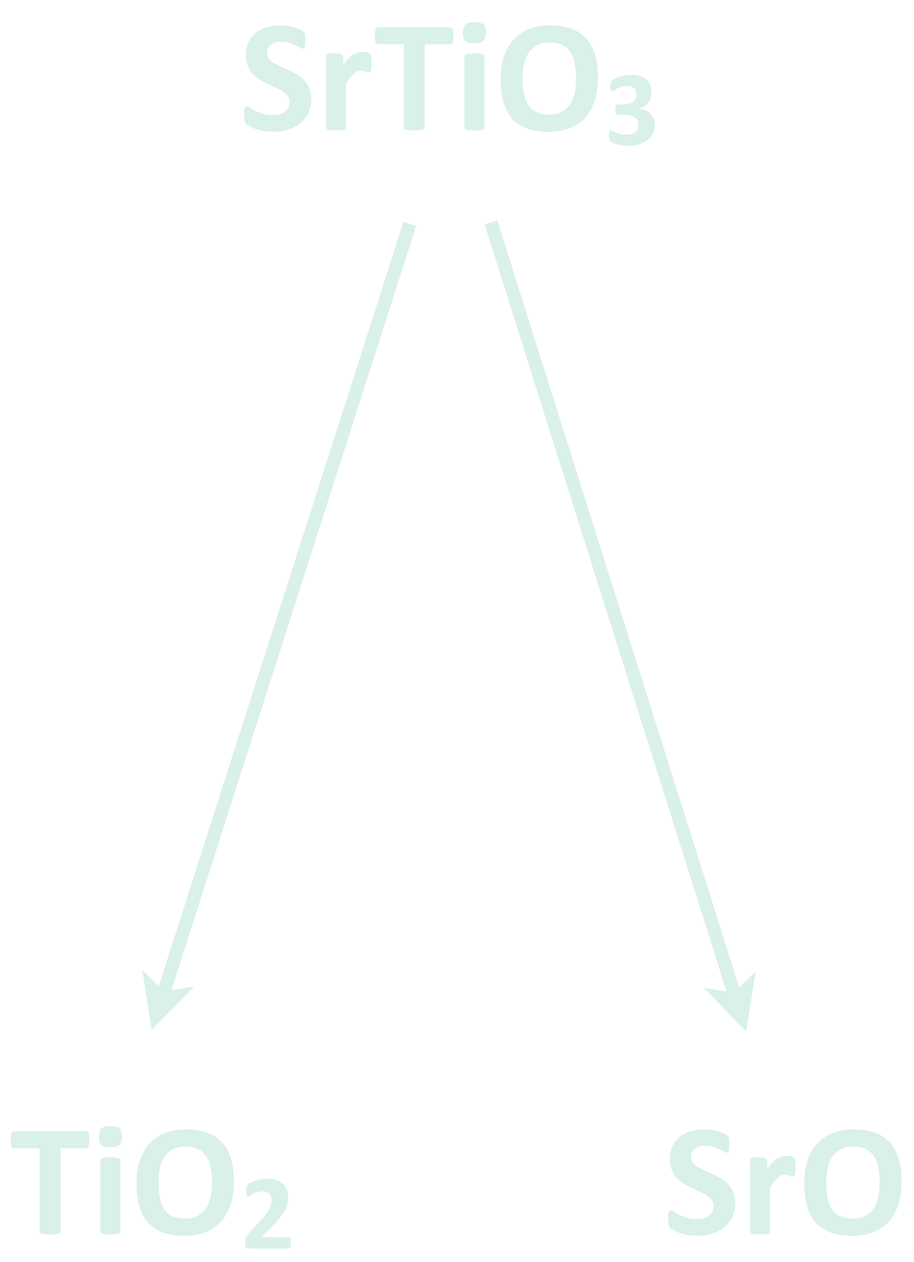
Center for Study and Training in Electron Spectroscopies (CEFS2)

by XPS



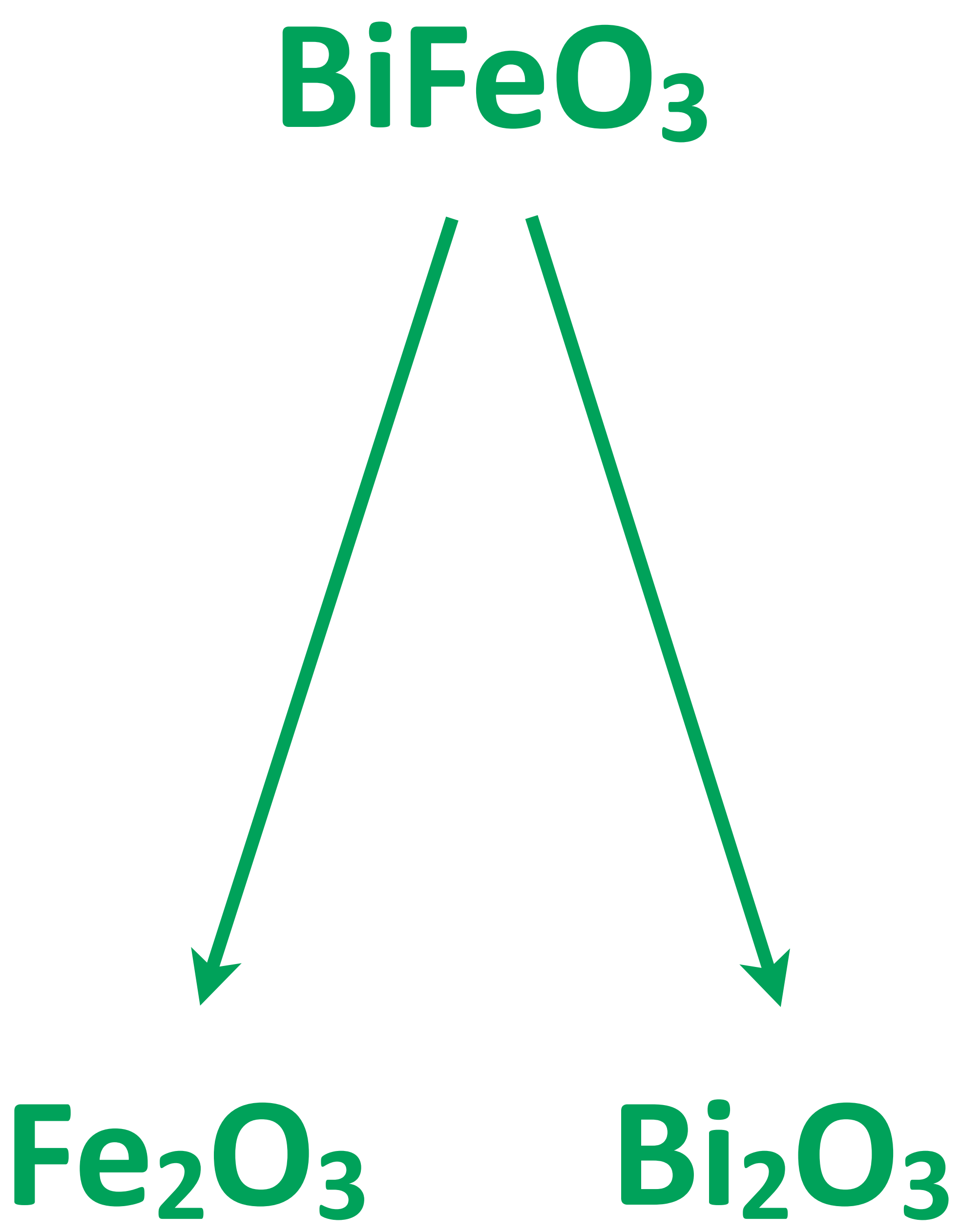
- amorphous as grown STO/Si(100) or STO/LAO
- further annealing is required to crystallize
- Sr excess leads to more easy crystallization of STO
- no carbon contamination (by XPS)

Main results



$SrTiO_3$

TiO_2 SrO



$BiFeO_3$

Fe_2O_3 Bi_2O_3

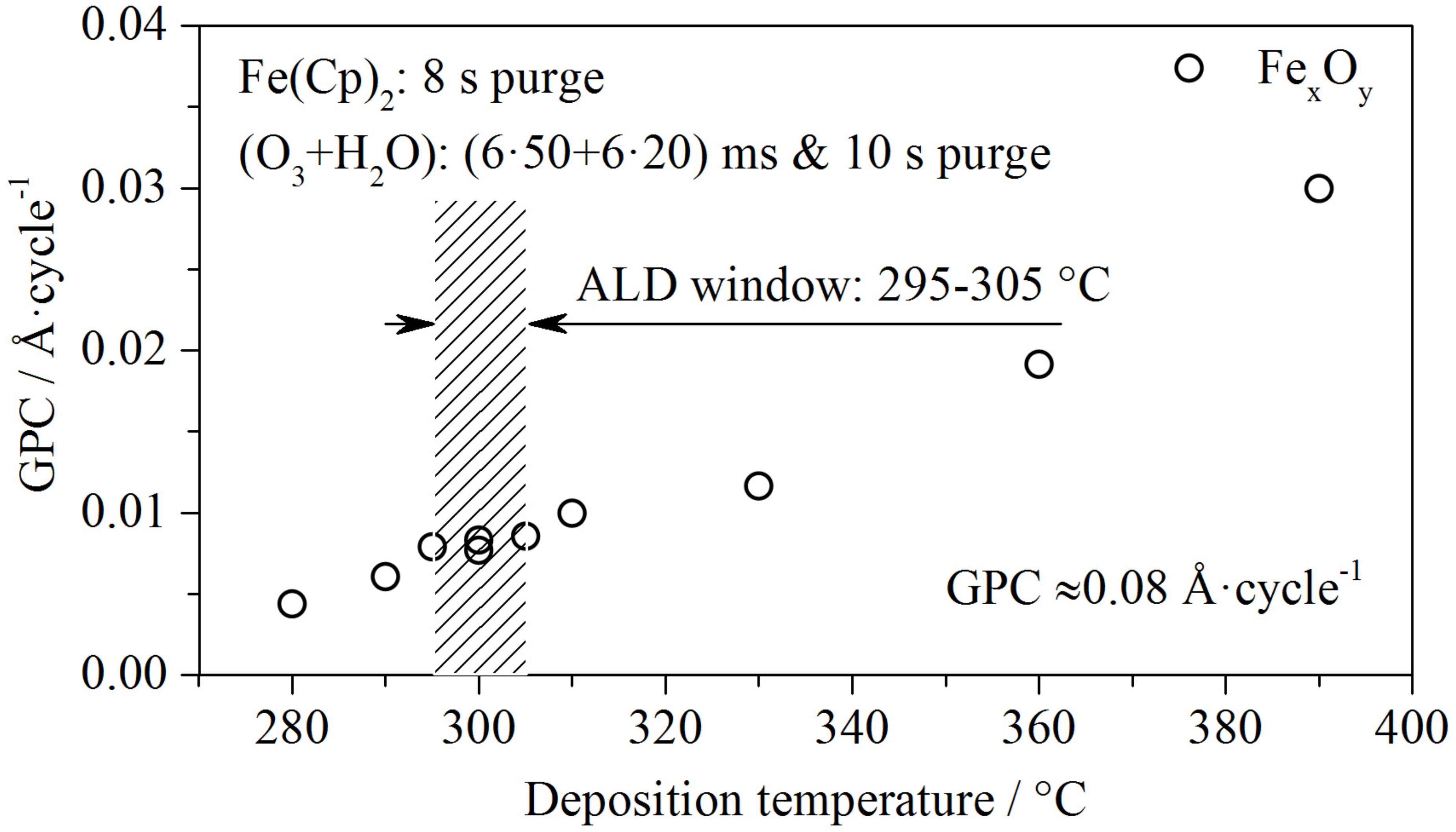
Fe_2O_3 growth process optimization

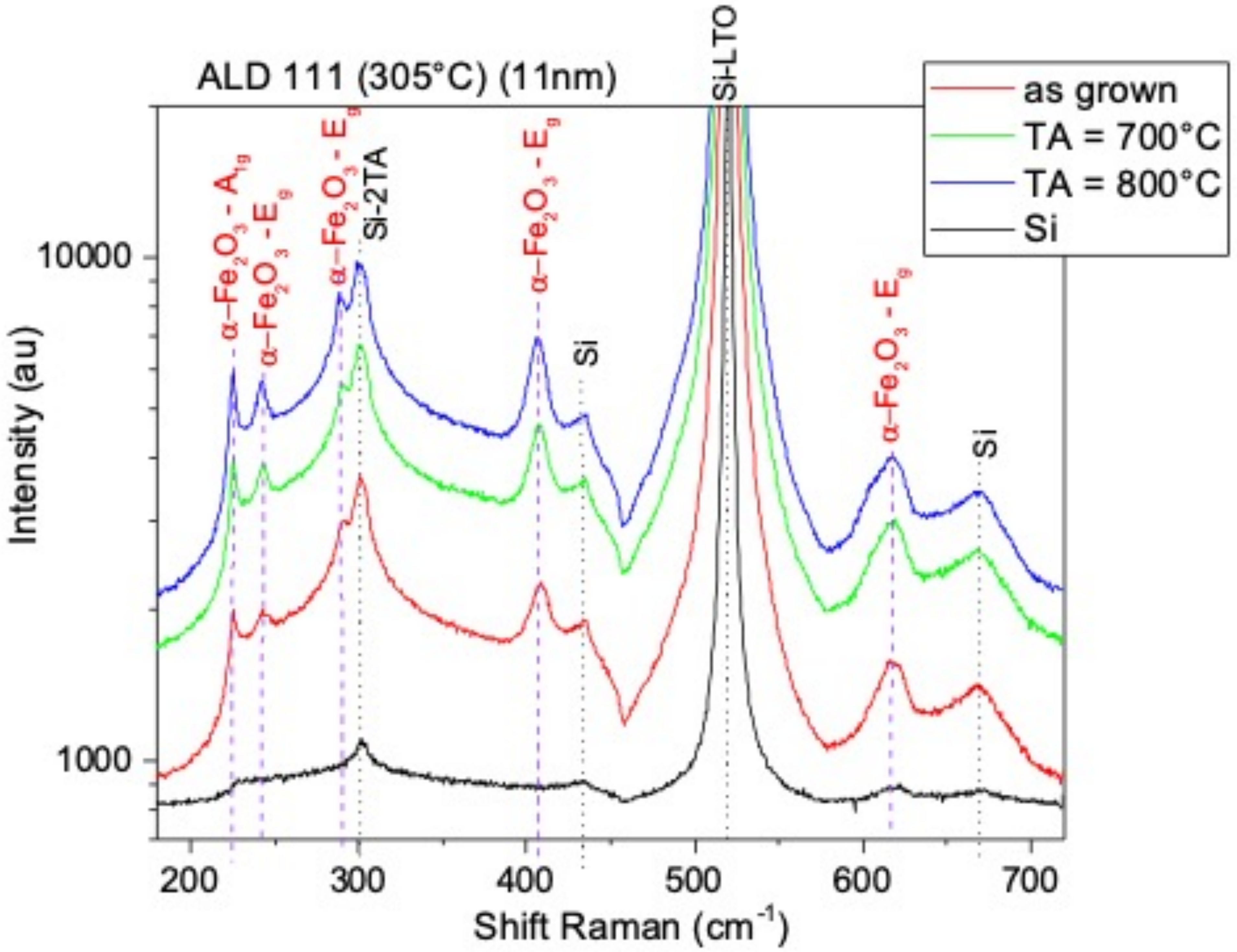
Precursor solution:

- $[Fe(Cp)_2]=6\cdot10^{-3}$ M in toluene ($C_6H_5CH_3$)

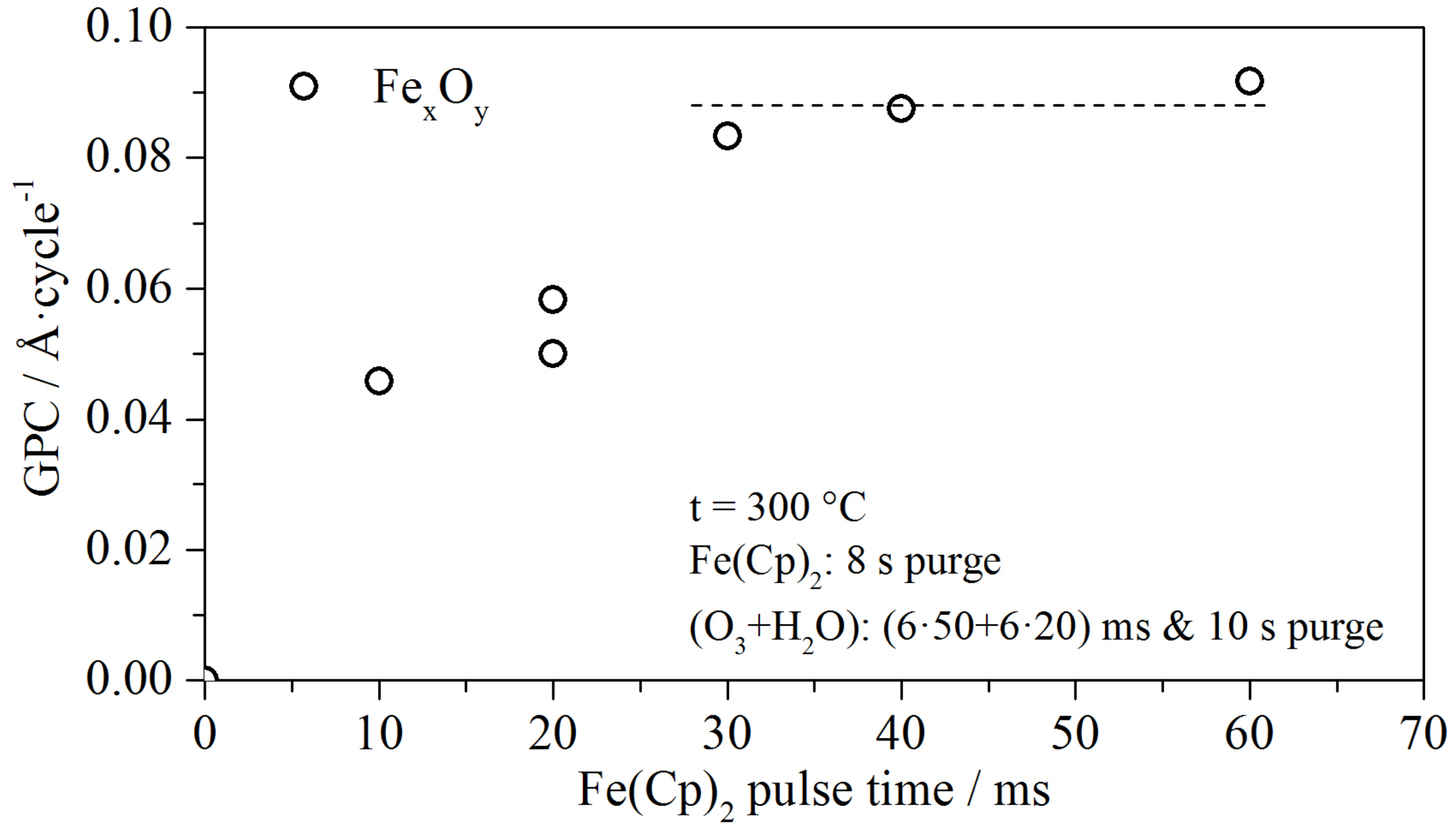
$Fe(Cp)_2$ — $Fe(C_5H_5)_2$ ferrocene

Oxidizing agents: O_3 & H_2O





XPS: O/Fe = 1.325
(1.5 expected for Fe_2O_3)



- growth rate (GPC) is extremely slow
- Raman: α-Fe_2O_3 phase without annealing
- XPS: no carbon contamination

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %
Fe2p3	709.22	4.05	252247.63	42.34
C1s	284.06	0	435.57	0.64
O1s	529.9	1.19	103115.2	56.12
Si2s	148.37	0.11	608.94	0.9

Bi_xO_y growth process optimization

Precursor solution:

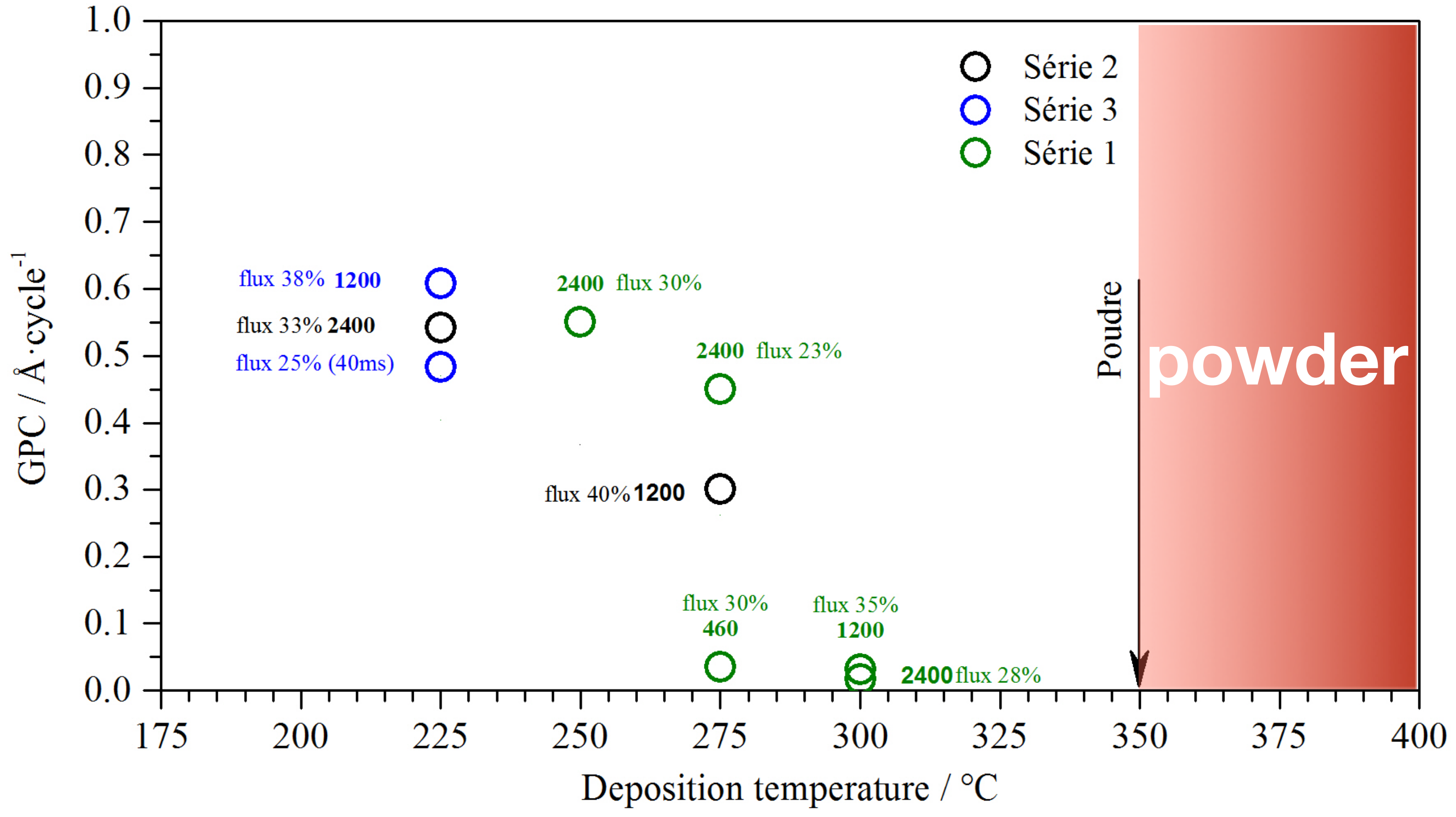
- $[Bi(Ph)_3]=6\cdot10^{-3}$ M in toluene ($C_6H_5CH_3$)

$Bi(Ph)_3$ — $Bi(C_6H_5)_3$ Triphenylbismuth

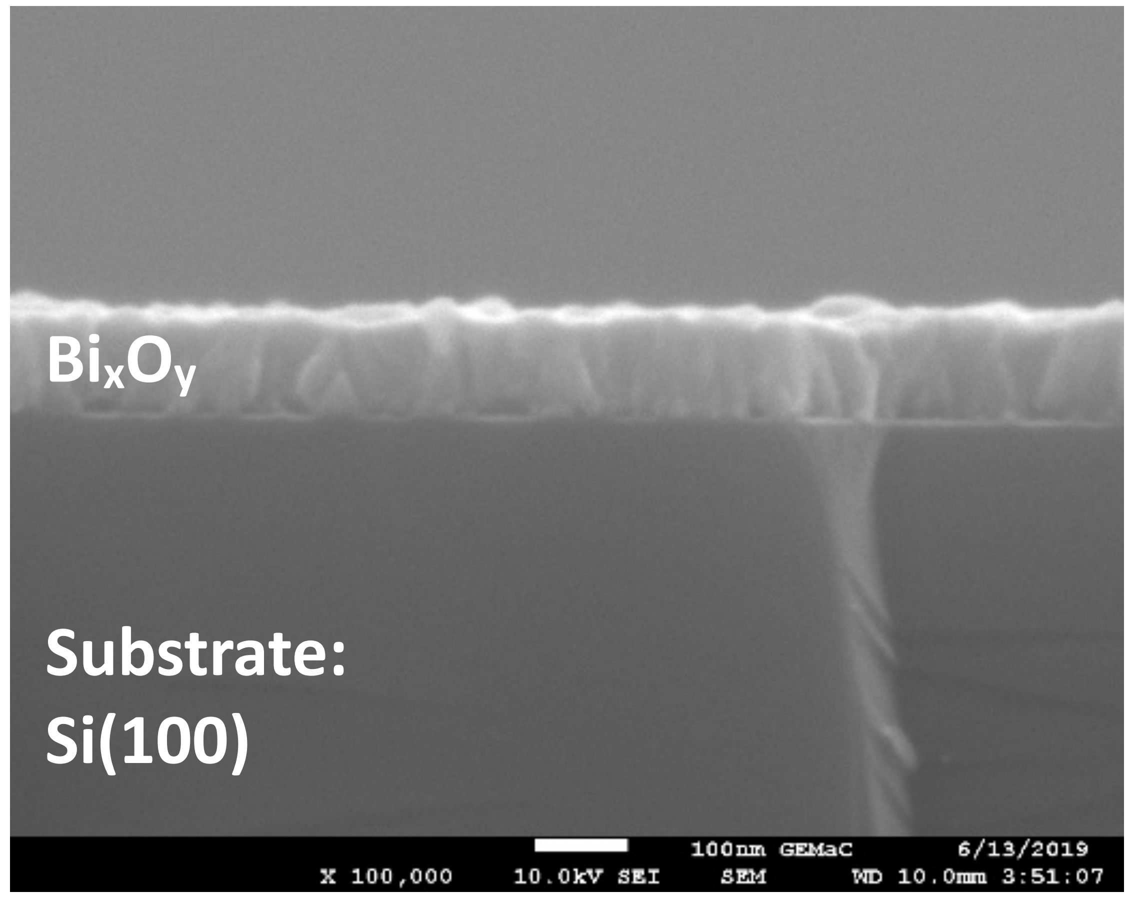
Oxidizing agents: O_3 & H_2O

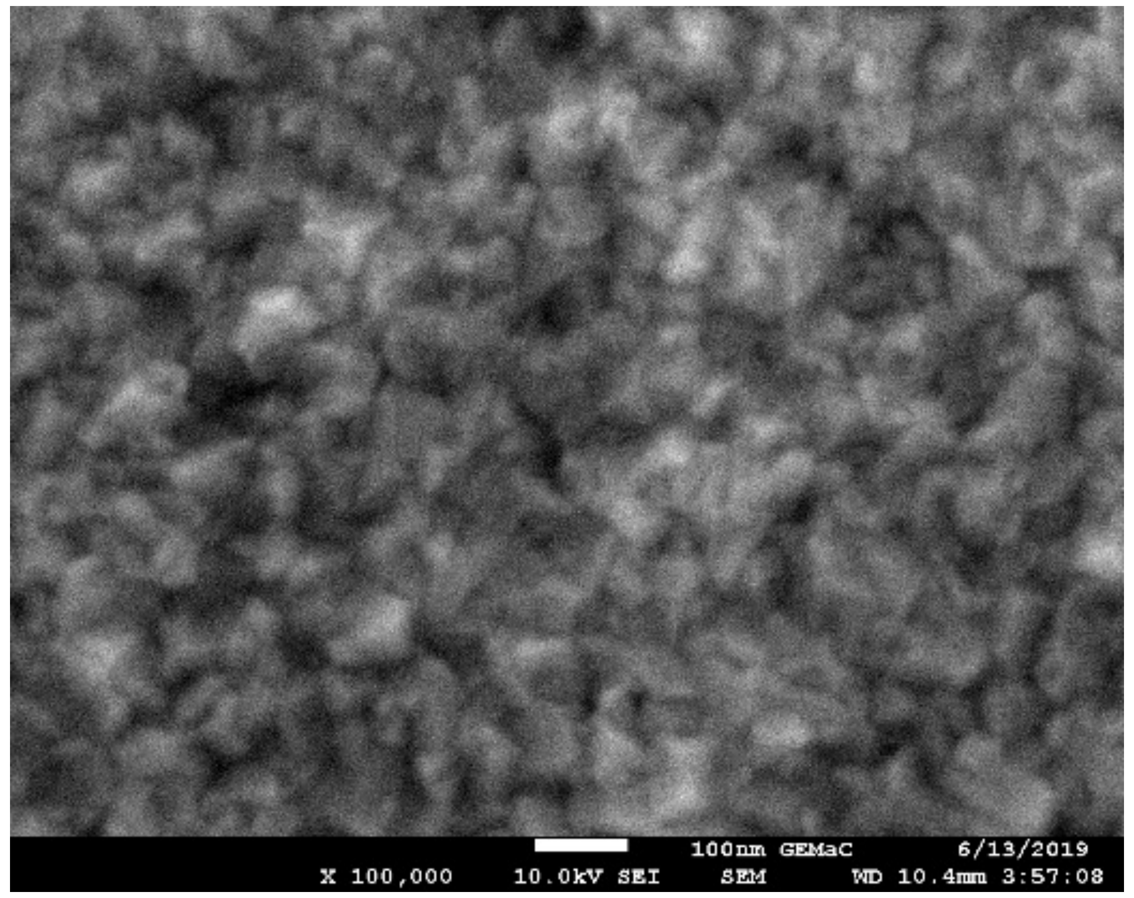
XPS: O/Bi = 1.716
(1.5 expected for Bi_2O_3)

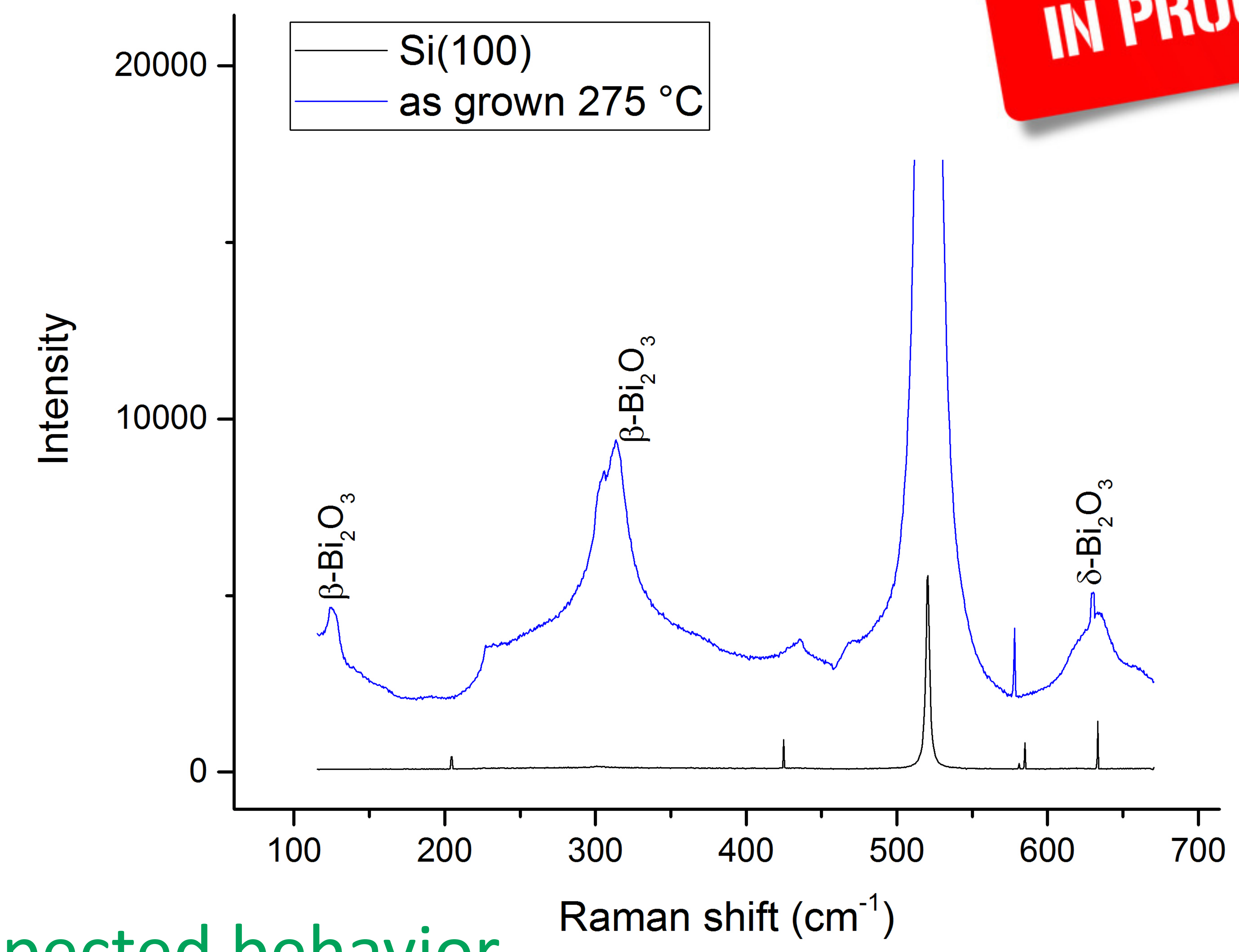
Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %
O1s phys. spec	/	/	/	/
O1s oxide	528.57	1.44	182062	39.94
C1s	/	/	/	/
Bi 4f5	163.1	1.15	681103	23.27
Bi5d	24.89	1.25	207099	36.79



SEM:
t=225°C
2400 cycles ; ≈80 nm







- unexpected behavior
- no clear ALD window
- non homogenius samples
- Raman: β and γ-Bi_2O_3 without annealing
- non stoichiometric phase(s)
- XPS: no carbon contamination

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Conclusions & Perspectives (by the end of 2020)

$SrTiO_3$ growth

- ☑ optimized TiO_2 DLI-ALD process
- ☑ anatase phase and good homogeneity
- ☑ ALD window for SrO
- ☑ SrO carbon contamination
- ☑ $SrTiO_3$ obtained after annealing

- Further optimization of stoichiometry
- Thermal treatment:
  - *in situ* RTA
- Si(100) substrate treatment
  - native SiO_2 layer reduction by H_2
  - chemical etching
  - intermediate phase deposition (SrO ?)

$BiFeO_3$ growth

- ☑ optimized Fe_2O_3 DLI-ALD process
- ☑ α-Fe_2O_3 as-grown obtained
- ☑ Bi_2O_3 in progress

- Phase growth
  - optimisation of stoichiometry (ALD cycle ratio)
  - influence of substrate on phase composition
- Thermal treatment:
  - as grown crystallization ?
  - post-growth annealing ?

Large scale

- 2 inch surface (Si and Ge)
  - homogeneity (phase and thickness)
  - control of interface quality

Acknowledgements

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