



HAL
open science

Investigating the nucleation of Al₂O₃ on clean Si in ALD : plasma post and pre-processing

Pascal Dubreuil, Emmanuel Scheid

► To cite this version:

Pascal Dubreuil, Emmanuel Scheid. Investigating the nucleation of Al₂O₃ on clean Si in ALD : plasma post and pre-processing. School of Atomic Layer Deposition, Oct 2022, AUTRANS, France. 2022. hal-03845065

HAL Id: hal-03845065

<https://laas.hal.science/hal-03845065>

Submitted on 6 Dec 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

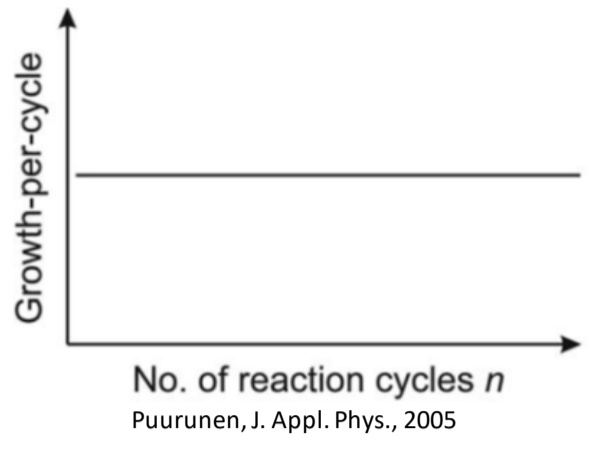
Investigating the nucleation of Al₂O₃ on clean Si in ALD : plasma pre and post-processing

P. DUBREUIL, E. SCHEID : LAAS, Université de Toulouse, CNRS, Toulouse, France.

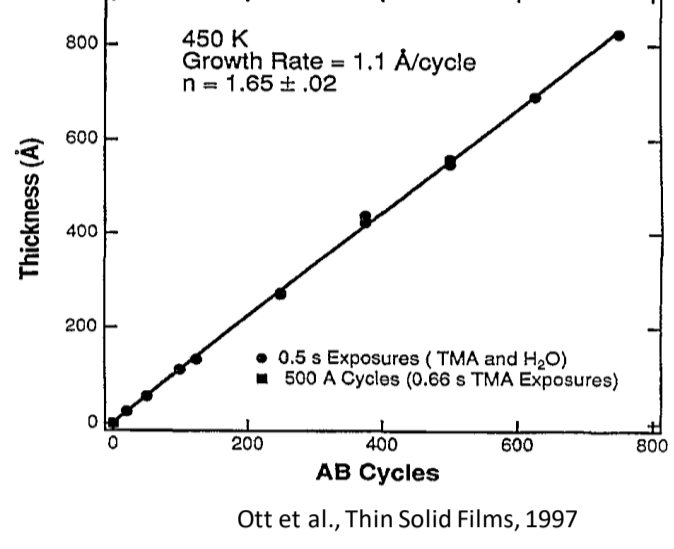
Motivation

Ideal ALD behavior

Steady GPC for all ALD cycles

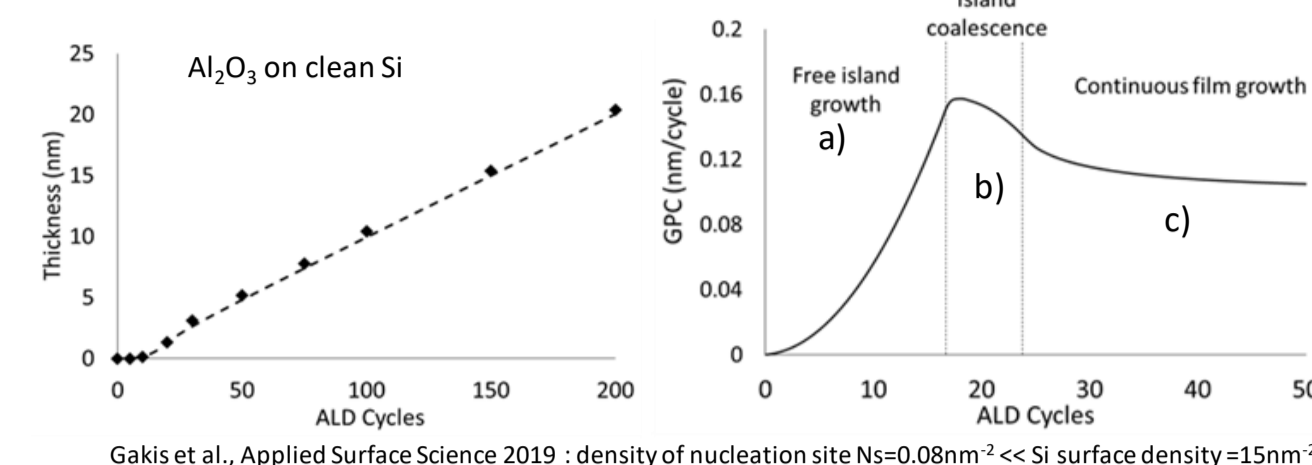


Continuous film grows layer by layer

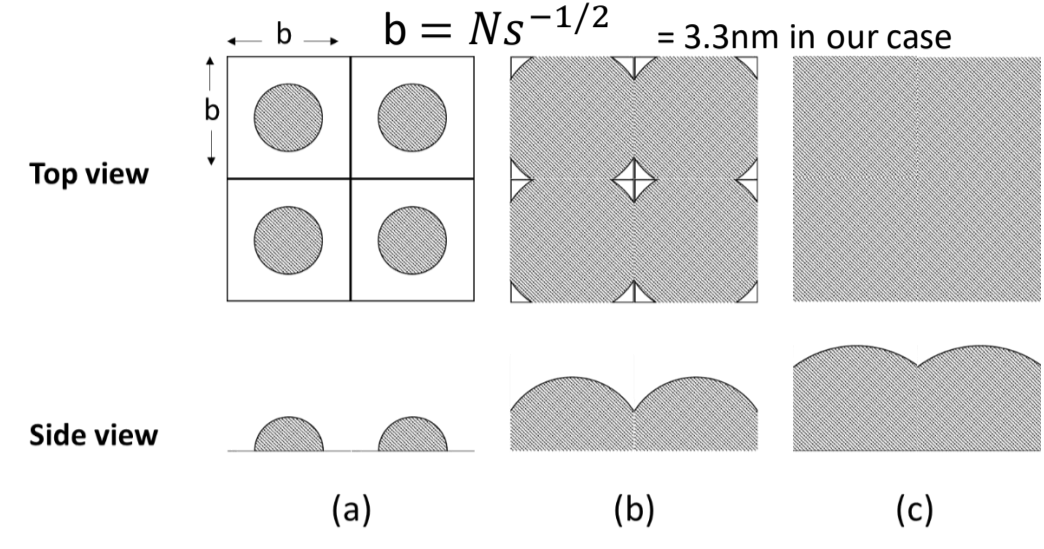


Actual case

Initial growth is non ideal

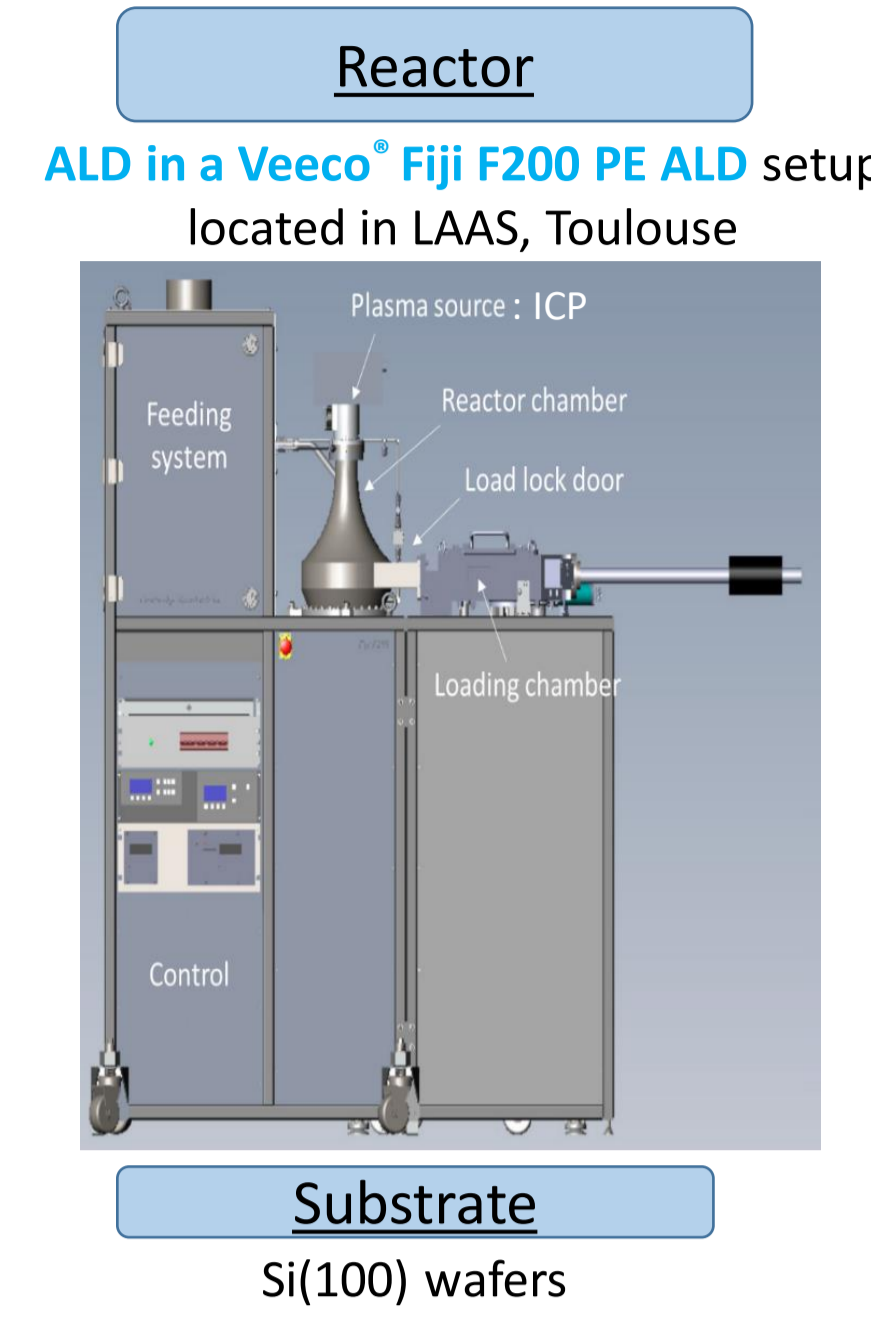


Non-continuous island growth

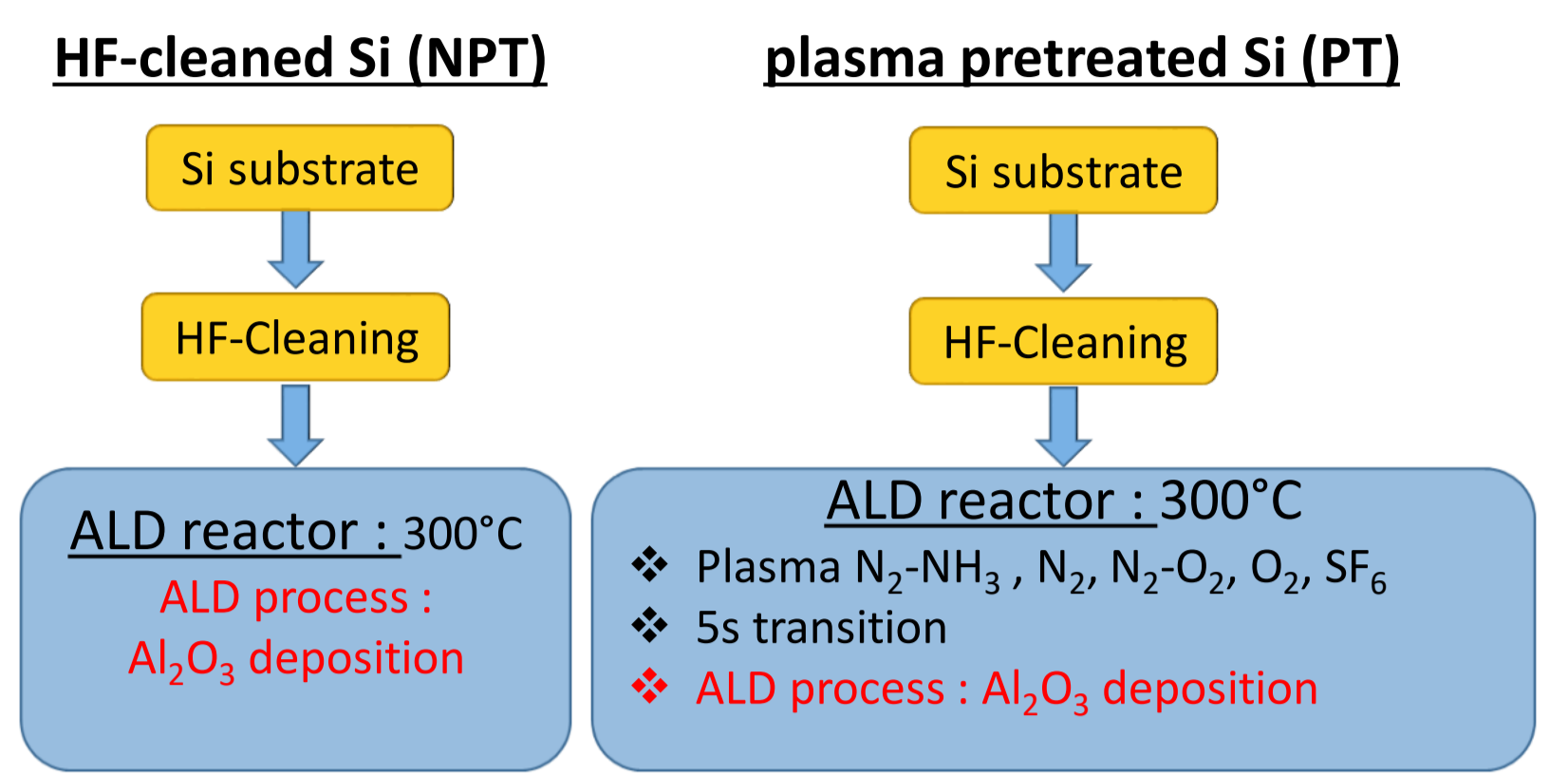


Setup for Pre-processing Experiments

Aim : to modify the nucleation on clean Si



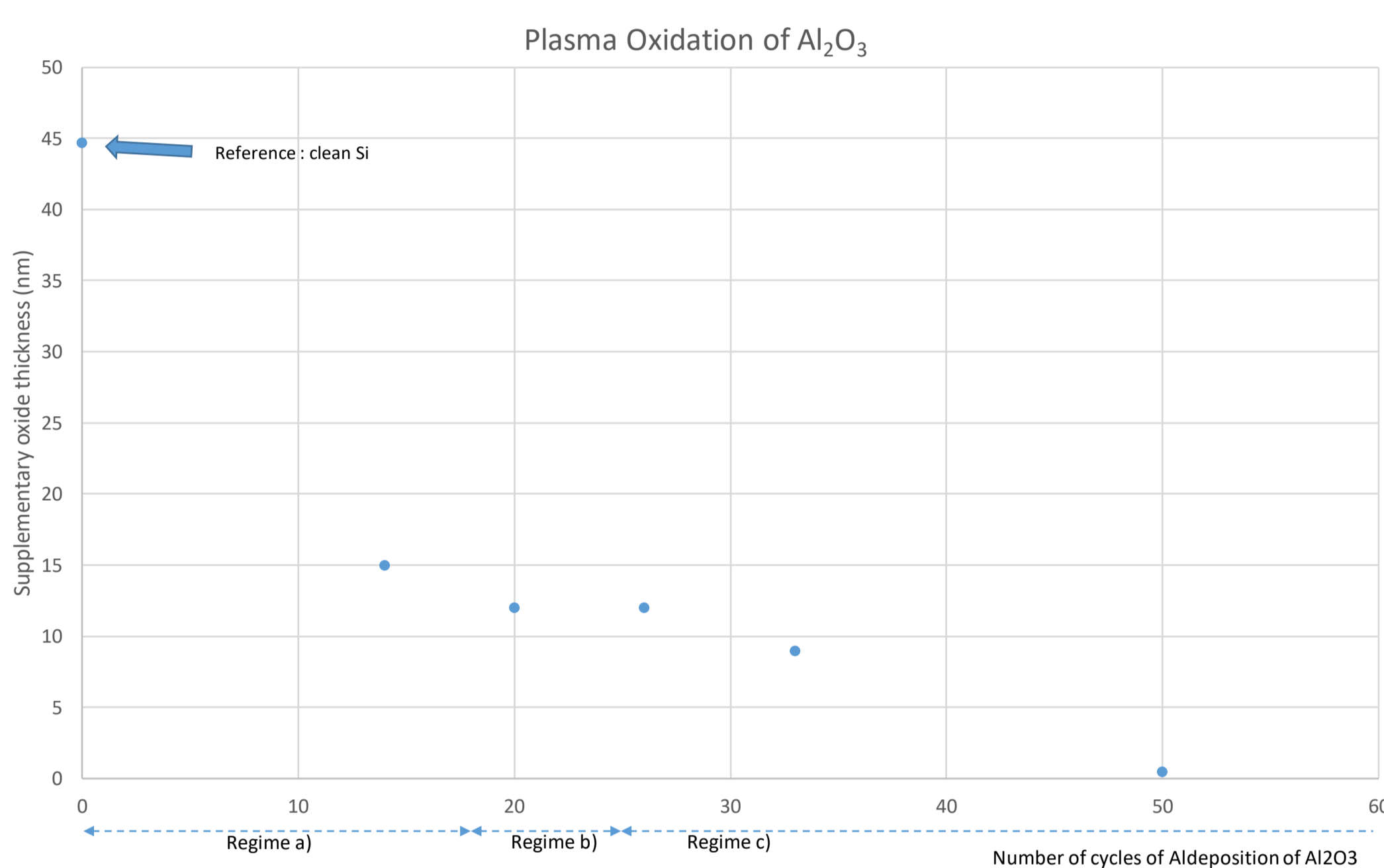
Comparison of samples



Setup for Post-processing Experiments

- Plasma oxidation of Al₂O₃ : Sentech Si500, ICP source setup located in LAAS, Toulouse
- (120min, 800W, T^{amb}) deposited in NPT conditions for different numbers of cycles in the a) b) and c) regimes.

Aim : densify the deposited layer and/or observe a direct evidence of non-continuous layers



Except after 50cycles, there is a noticeable oxidation : confirms the non-continuous character of the layers in the initial regimes

Effect on ALD growth

Gakis et al., J. Appl. Phys., 2019

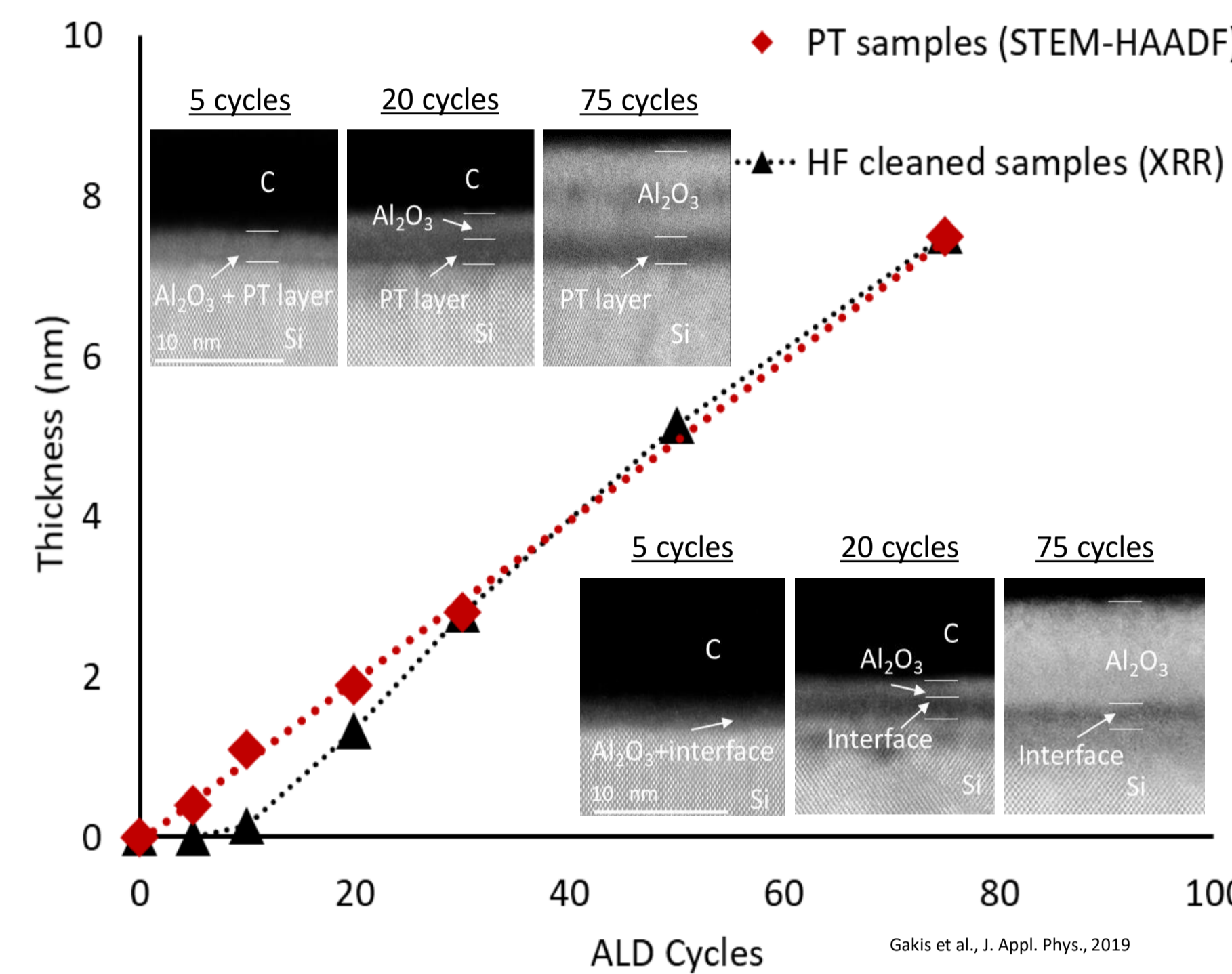
RAFALD 2019 Toulouse

HF-Cleaned Si :

- Growth inhibition: island growth
- Island growth: Low reactivity of Si-H
- Deposition starts on defects
- Continuous film after ~25 cycles

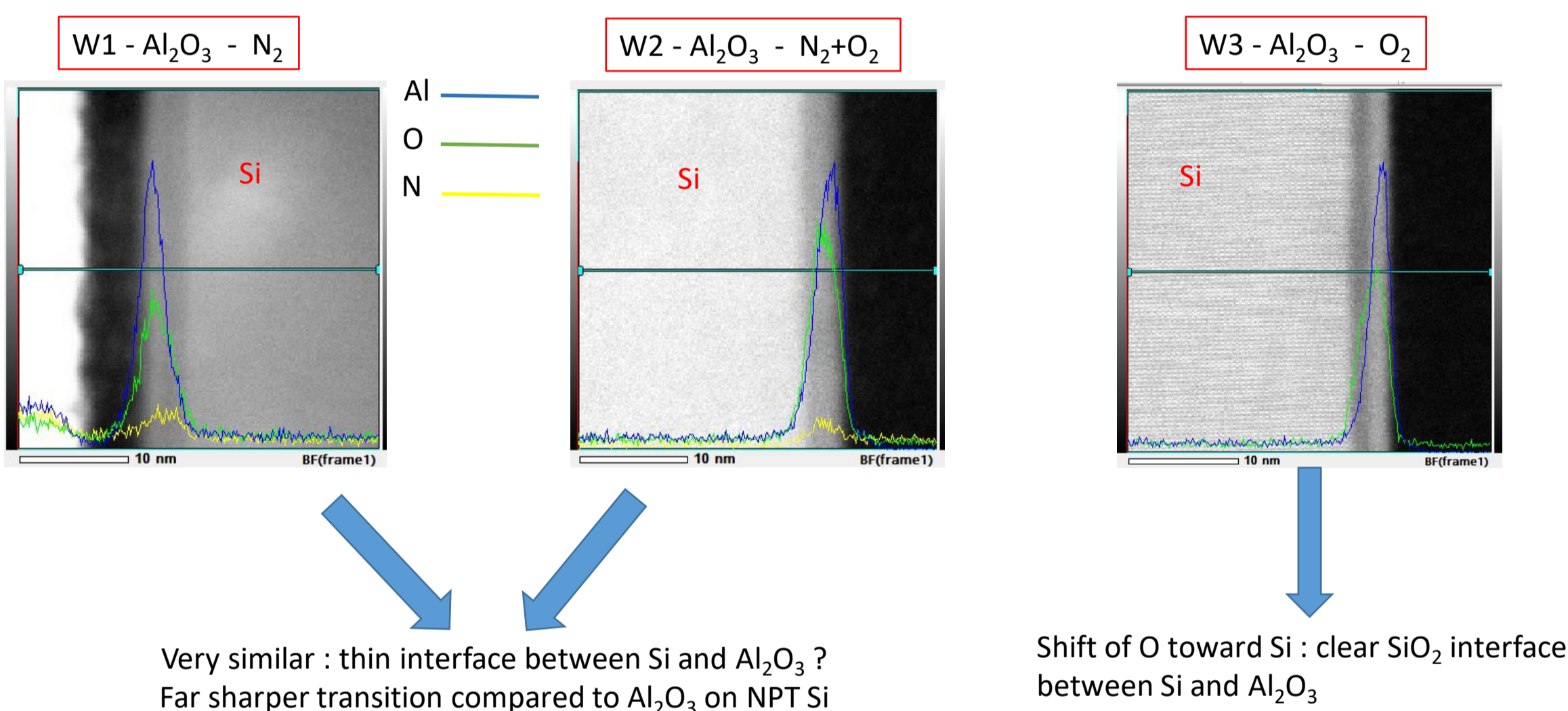
N₂-NH₃ pretreated Si :

- Enhanced initial ALD growth
- Linear regime already after 5 cycles (GPC = 1Å/cycle)
- Continuity with less cycles



Further attempts : 30 cycles of ALD of Al₂O₃ after N₂, N₂+O₂ or O₂ plasma in-situ pretreatments

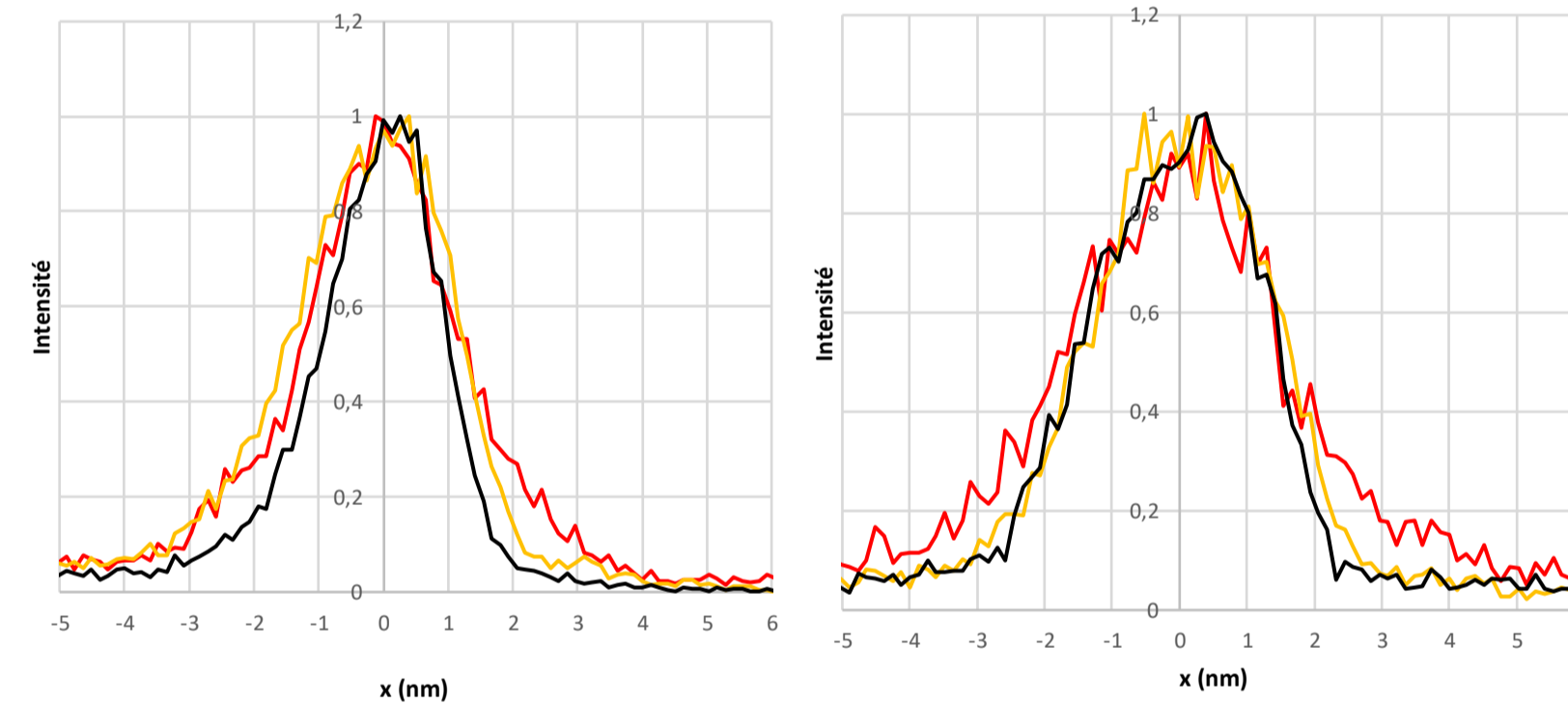
- Ellipsometry measurements of PT w/o Al₂O₃ indicate again an effective layer growth (≈1nm)
- Observations by TEM and EDX of concentration profile : width at half height and relative shifts



Very similar : thin interface between Si and Al₂O₃ ? Far sharper transition compared to Al₂O₃ on NPT Si

Shift of O toward Si : clear SiO₂ interface between Si and Al₂O₃

Quantitative measurements :



For N₂ and N₂+O₂ (W1 and W2) : similar results , very reduced interface between substrate and deposited material
For pure O₂ plasma (W3) more SiO₂ growth and less deposited Al₂O₃ : same problems mentioned for non-pretreated Si ? Not so positive .

Deduced thicknesses :

	Al or Al ₂ O ₃ (nm)	O (nm)	SiON or SiO ₂ (nm)
W1	2.8	3.2	0.4
W2	2.9	3.4	0.5
W3	2	3.1	1.1

Intermediate conclusions :

N₂ plasma (+O₂) seems to give better results than N₂+NH₃ (thinner interface) or pure O₂ (no reduction of kinetic , thinner interface)

But still an intermediate layer between substrate and deposited layer :

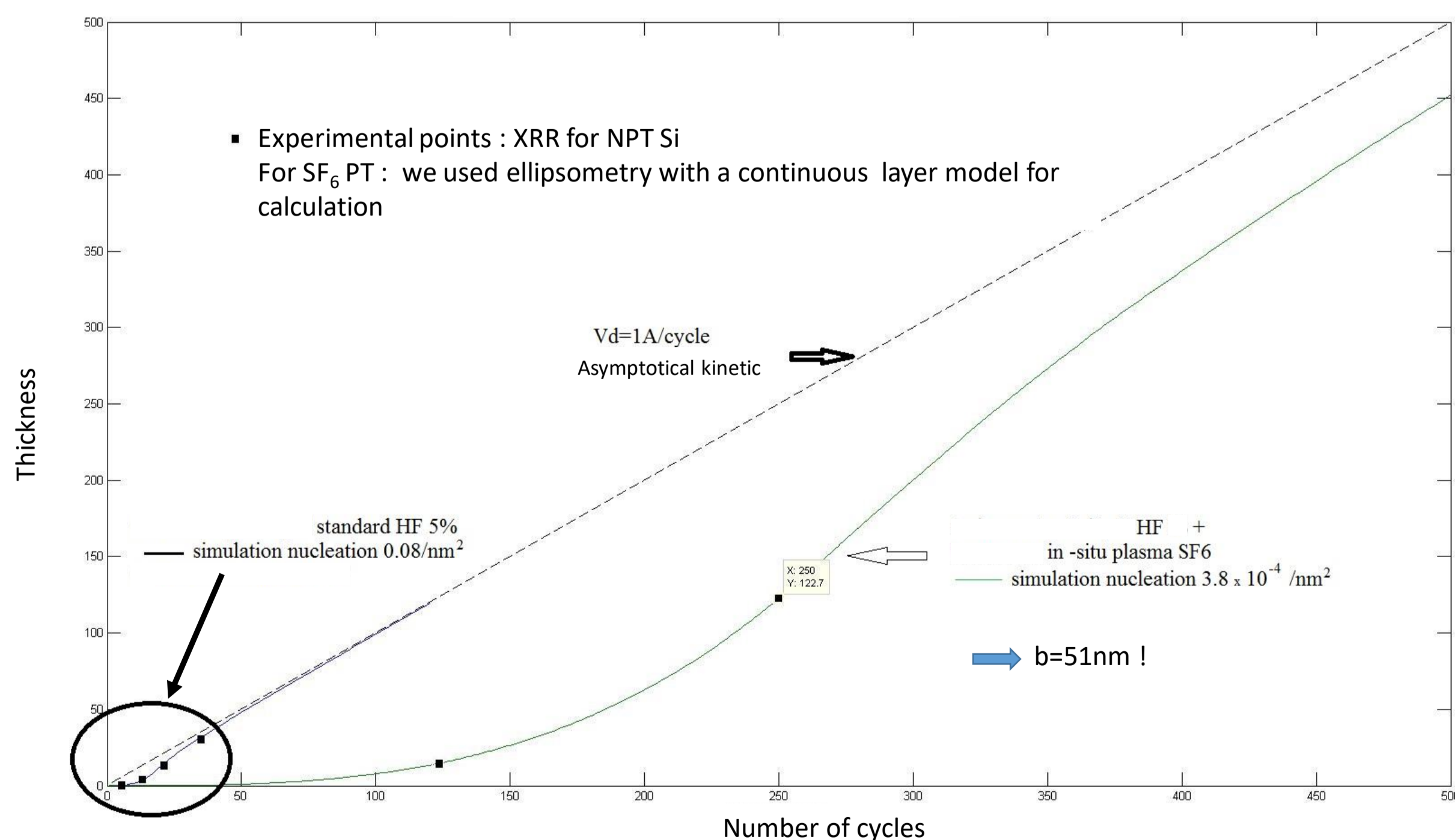
What if we try to remove Si-H bounds leaved by HF cleaning ?, to improve adsorption ?

→ Plasma pretreatment by SF₆ (still with prior ex-situ HF cleaning)

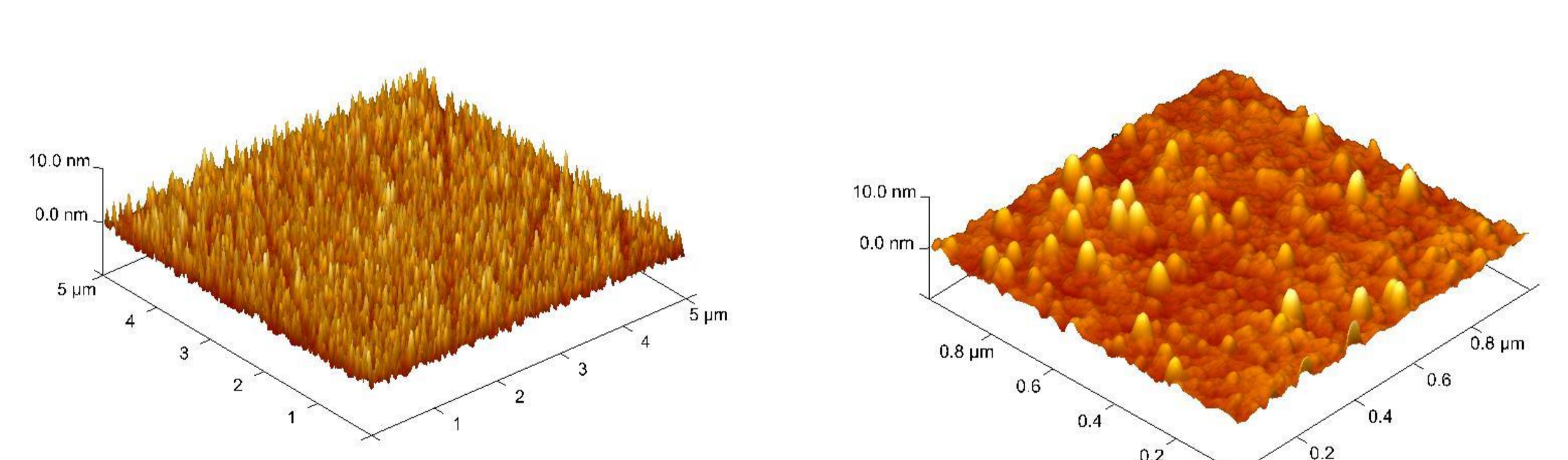
First results? :

- less deposition observed > 60 cycles : After «Plasma SF₆ optimization » : no deposition observed (30,60, 90 cycles), starts (120 cycles), observable (250 cycles)
- strong reduction of reactant adsorption with SF₆ : etching of the surface, removing remaining SiO₂, SiO, SiOH and impurities playing as nucleation sites

Comparison of deposition kinetic between NPT Si, SF₆ plasma PT Si and simulated kinetic with nucleation model



SF₆ PT samples : AFM observations after 120 and 250 cycles of ALD



- In terms of nucleation site (SiO, SiOH, SiO₂, impurities...), after SF₆ etching the surface is 200 times « cleaner ».
- Also a confirmation that Al₂O₃ cannot start on pure Si.

Conclusions - Prospectives

O₂ Posttreatments without pretreatment

- Noticeable oxidation for layers thinner than 3.5nm
- Confirmation of their non-continuous structure

N₂-NH₃, N₂, N₂-O₂, O₂ Pretreatments

- SiON intermediate layer growth
- Enhancement of TMA and H₂O adsorption, better Al₂O₃ growth
- N₂ or N₂-O₂ seems preferable (thinner interface, standard kinetic of Al₂O₃ deposition)

SF₆ Pretreatments

- Strong reduction of TMA and H₂O adsorption, weak Al₂O₃ growth
- «Ultra-clean» surface

Very encouraging for micro-electronic applications, move to the case of HfO₂