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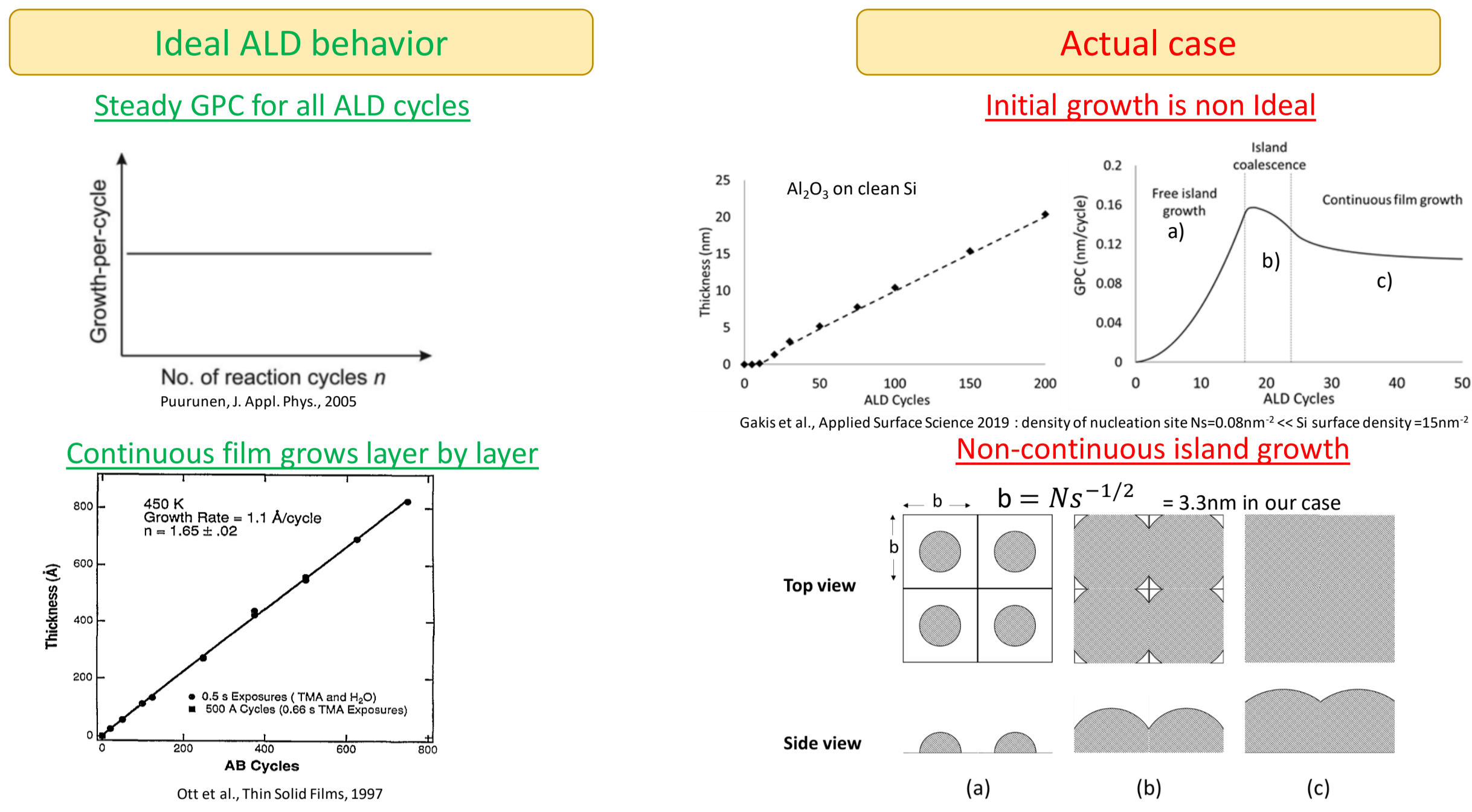
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Investigating the nucleation of Al₂O₃ on clean Si in ALD : plasma pre and post-processing

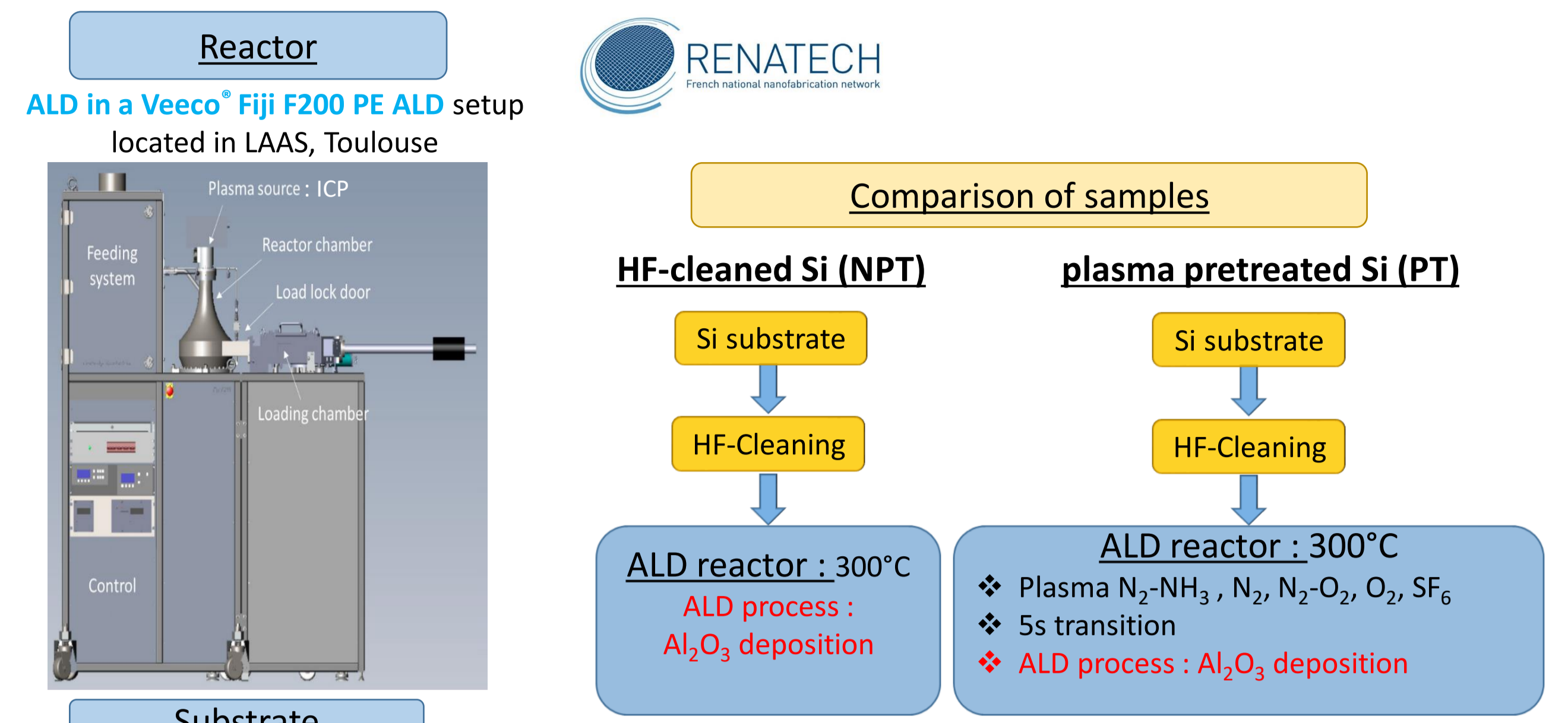
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Motivation



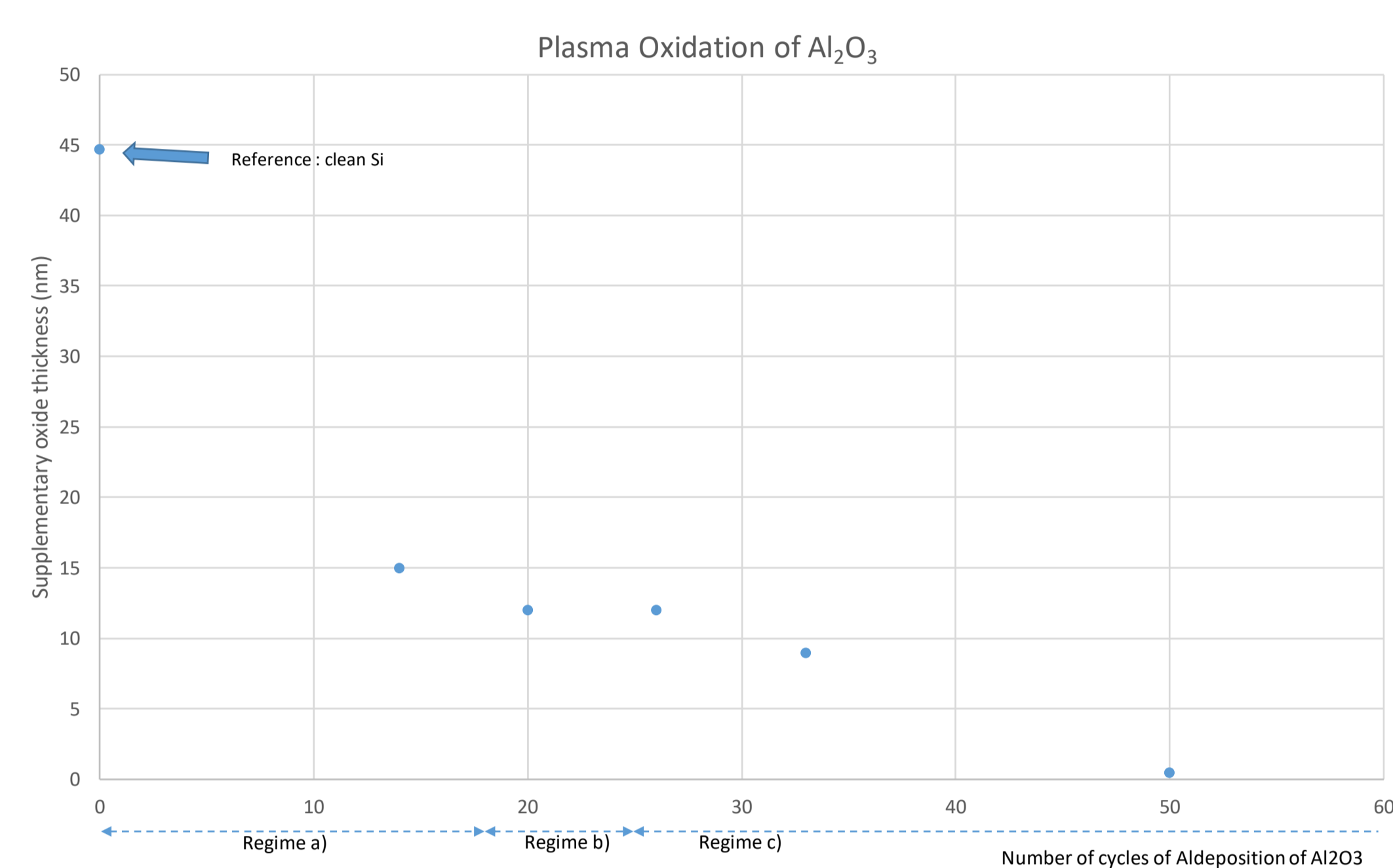
Setup for Pre-processing Experiments

Aim : to modify the nucleation on clean Si



Setup for Post-processing Experiments

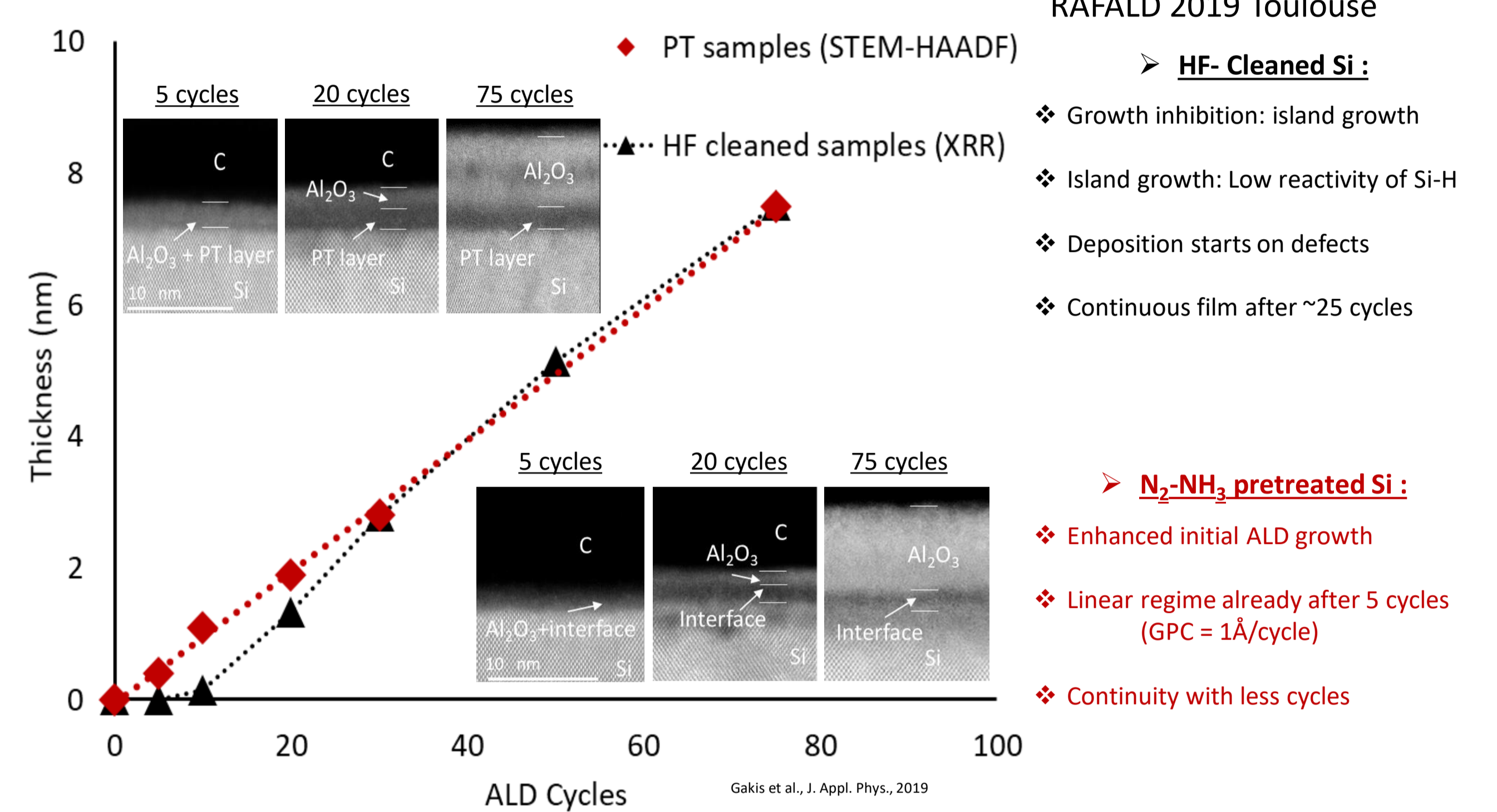
- Plasma oxidation of Al₂O₃ : **Sentech Si500**, ICP source setup located in LAAS, Toulouse
 - (120min, 800W, T^{amb}) deposited in NPT conditions for different numbers of cycles in the a) b) and c) regimes.
- Aim : densify the deposited layer and/or observe a direct evidence of non-continuous layers



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

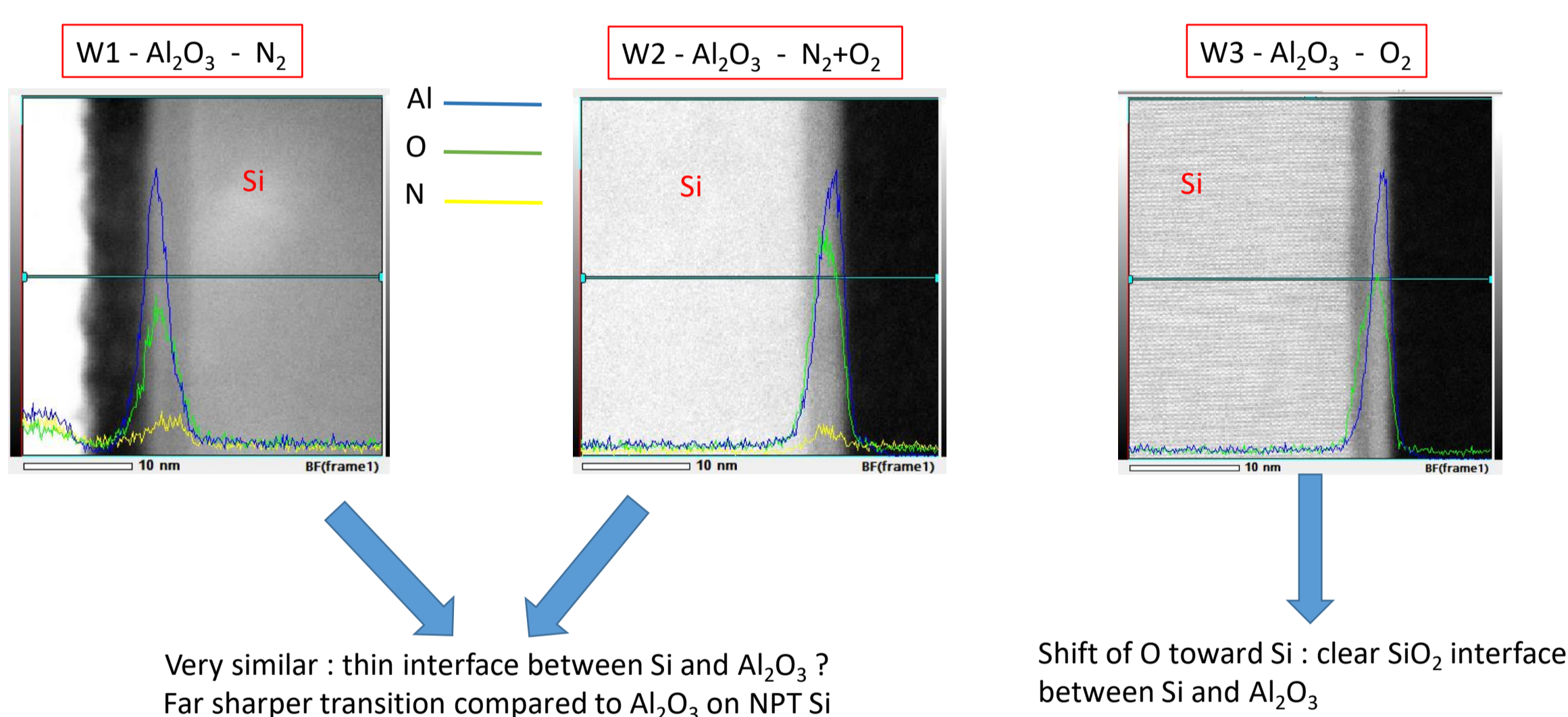
Effect on ALD growth

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

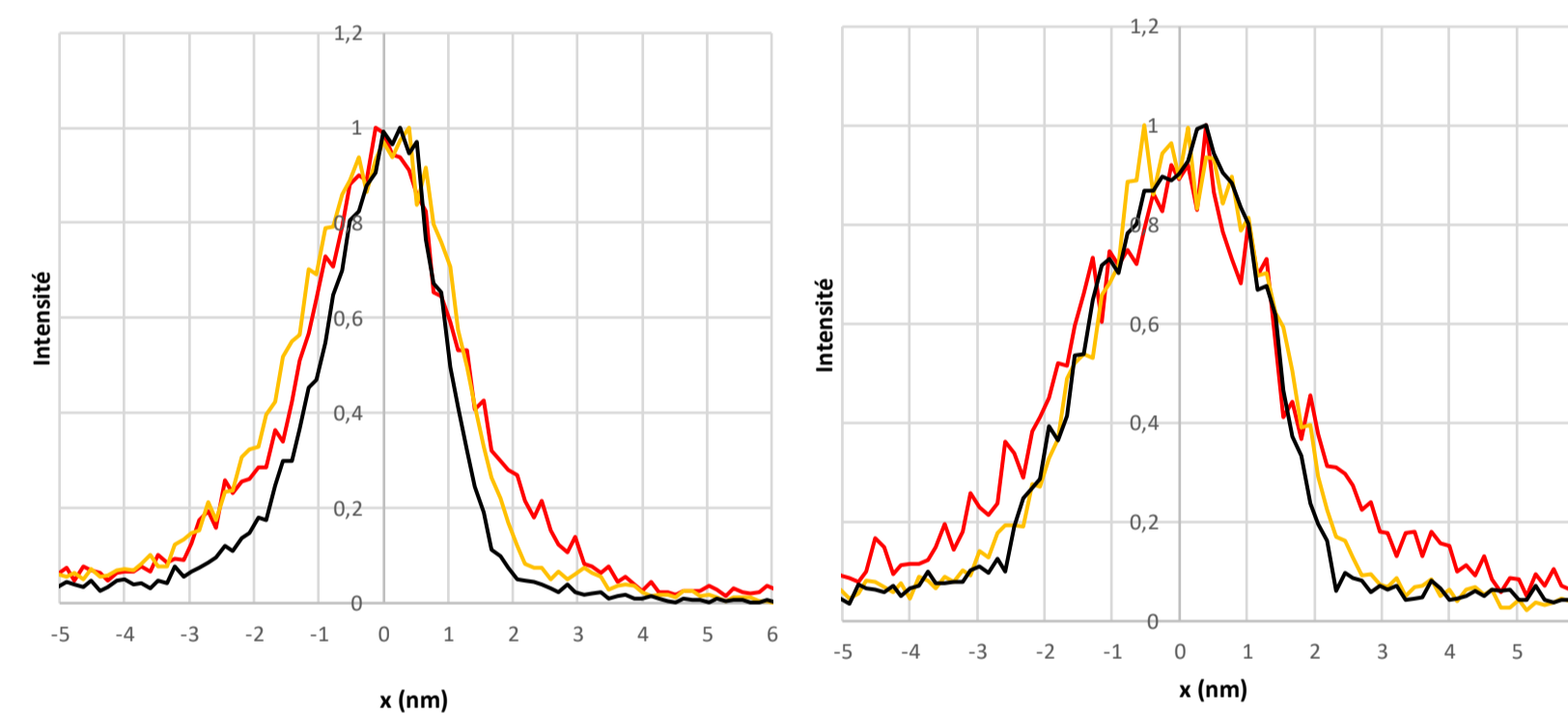


Further attempts : 30 cycles of ALD of Al₂O₃ after N₂, N₂+O₂ or O₂ plasma in-situ pretreatments

- 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



Quantitative measurements :



Deduced thicknesses :

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

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 .

Intermediate conclusions :

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

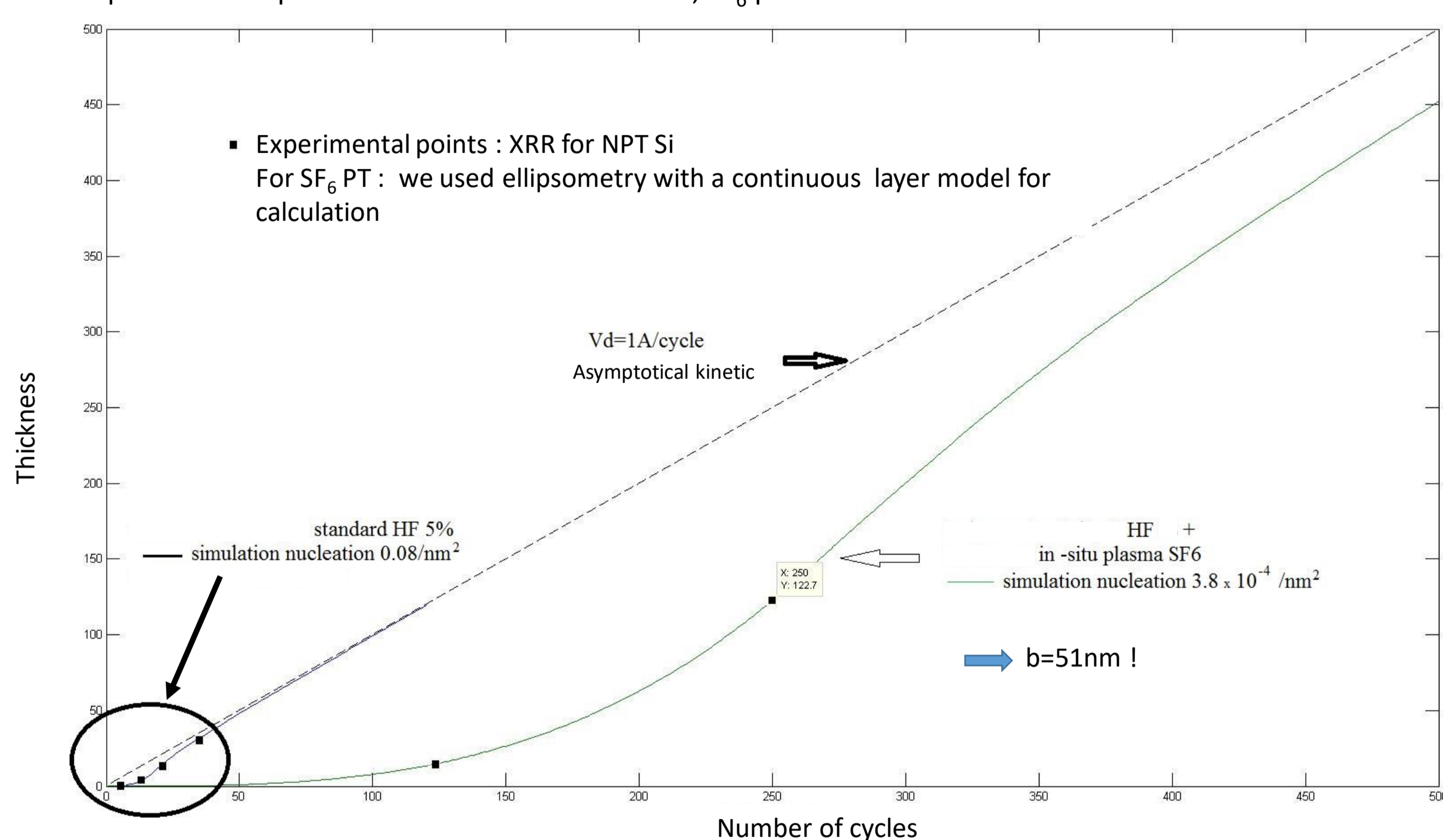
But still an intermediate layer between substrate and deposited layer : What if we try to remove Si-H bounds leaved by HF cleaning ?, to improve adsorption ?

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

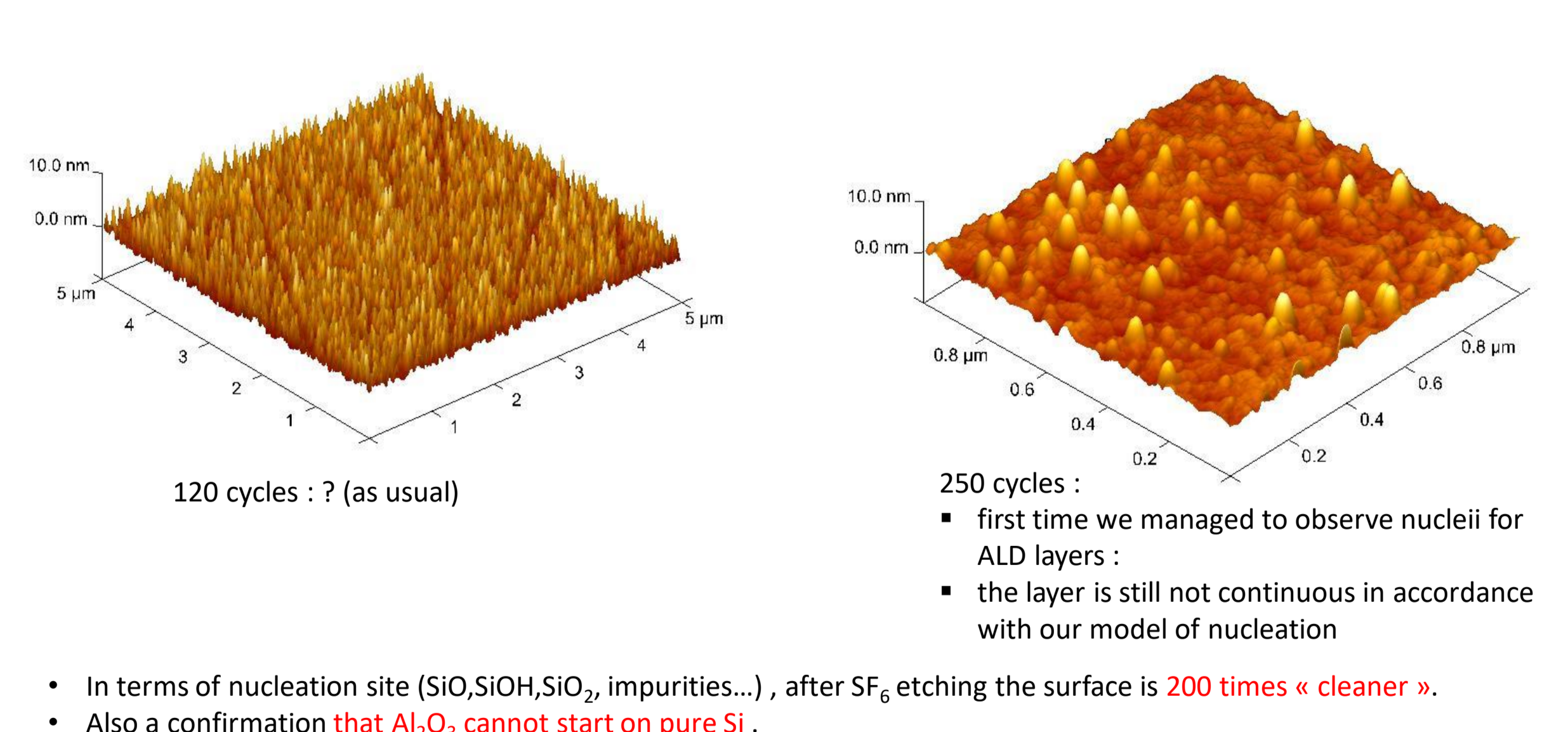
First results? :

- 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



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

- SiO_n 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