



Modélisation multi-échelle du dépôt des matériaux à fortes permittivités

Cédric MASTAIL

Mehdi DJAFARI-ROUHANI, Alain ESTEVE, Nicolas RICHARD

GDR CoDFT 15-12-2009

Contractual frame



- **ANR project “LN3M”** -
Logiciels **N**ouvelle génération pour la
Modélisation **M**ulti-échelle des **M**atériaux

- ERC **PREA** -

ÉQUIPE DE RECHERCHE COMMUNE – LAAS-CNRS / CEA
ÉTUDE **PR**ÉDICTIVE À L'ÉCHELLE **A**TOMIQUE

LAAS-CNRS

- LAAS-CNRS
C. Mastail, M. Djafari Rouhani, A. Estève

cea

- CEA-DIF
C. Mastail, N. Richard

Outline

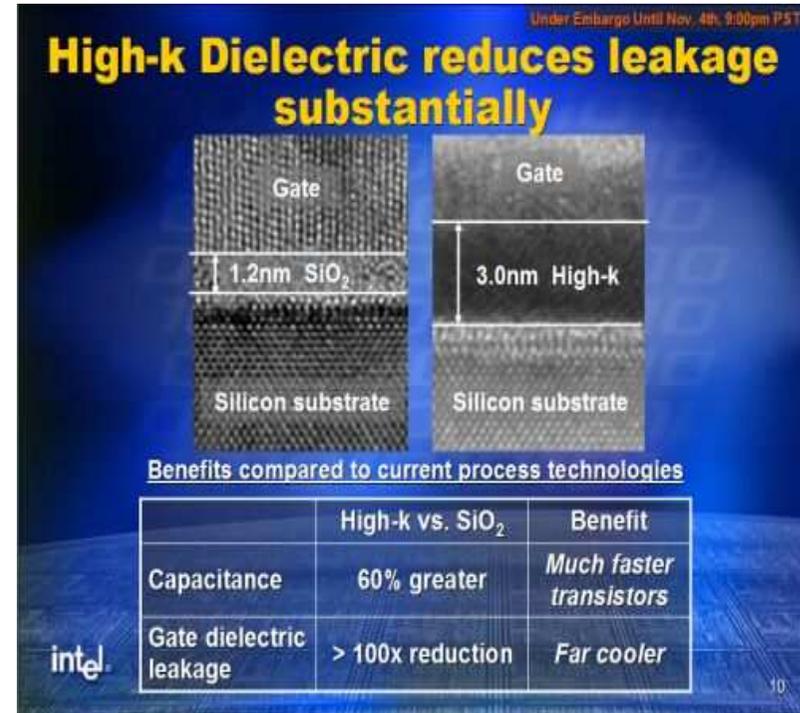
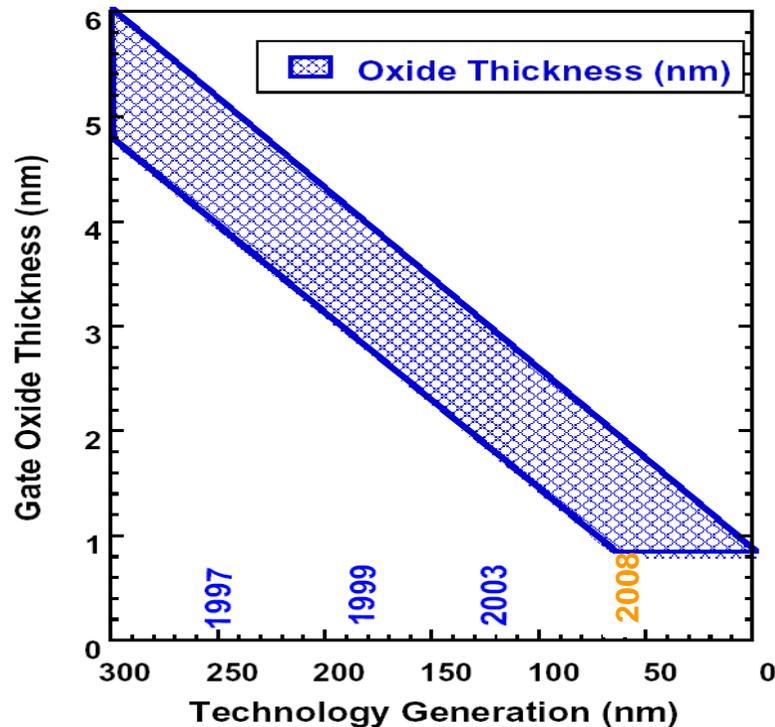
- **Part 1:** Introduction, general context
- **Part 2:** Hikad 2, basic ingredients
- **Part 3:** Exploitation, results

Outline

- **Part 1: Introduction, general context**
 - High-k: Why? How?
 - Our goals
 - General methodology: Multi-scale strategy
- Part 2: Hikad 2, basic ingredients
- Part 3: Exploitation, results

Evolution of CMOS Size

Limit of miniaturisation & alternatives



Problem: high leakage current through the gate

$$C = \frac{\epsilon_r \epsilon_0 S}{e}$$

Solution: use a gate oxide with greater permittivity than SiO₂

General issues

- What are the mechanisms?
- How to avoid layer contamination?
- How to optimize and control the growth?
(roughness, stoichiometry, amorphous phase)
- Which type of initial surface?
- How to avoid SiO₂ re-growth?

Our goals

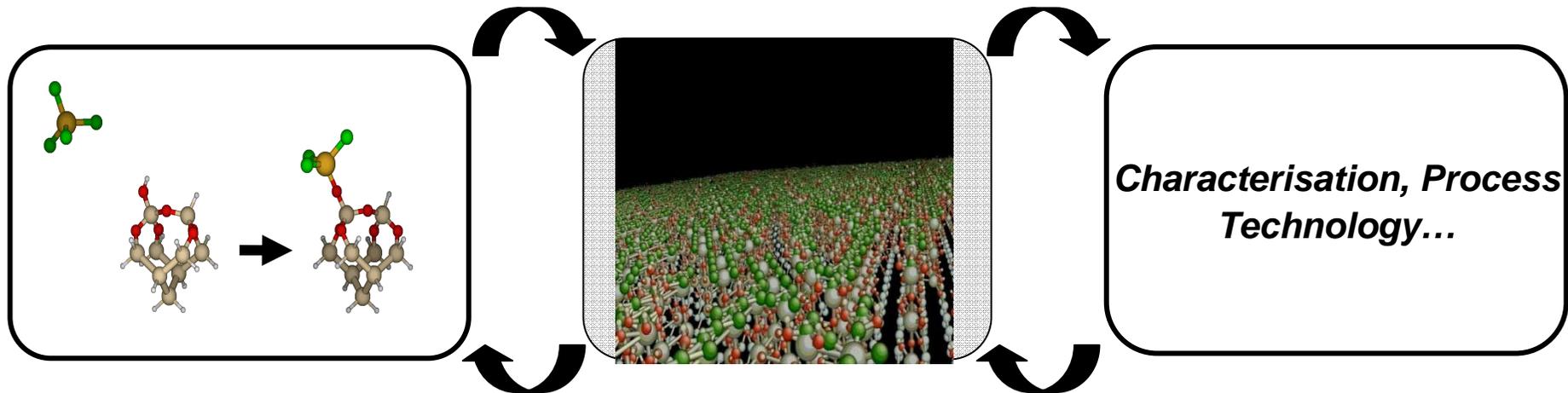
- Understanding key chemical mechanisms which control the growth
- Develop a new atomic scale predictive software for high-k oxides deposition
based on a kinetic Monte Carlo technique

Multi-scale simulation strategy

Ab-initio / DFT

Kinetic Monte-Carlo

Experiment



*Time scale: picoseconds
About ~100 atoms*

*Time scale: seconds
Up to a million of atoms*

Outline

- **Part 1:** Introduction, general context
- **Part 2:** Hikad 2, basic ingredients
 - Temporal dynamics
 - Lattice based model
 - Site occupation chemistry
 - List of elementary mechanisms
- **Part 3:** Exploitation, results

Simulation choice

Dielectric choice: Hafnium oxide

- High permittivity ~ 30 ($\epsilon_{\text{SiO}_2} = 3,9$)
- A wide band gap ~ 6 eV ($\text{SiO}_2 = 8,9$ eV)
- A large band offset with Si ~ 3.5 eV ($\text{Si/SiO}_2 = 3,3$ eV)

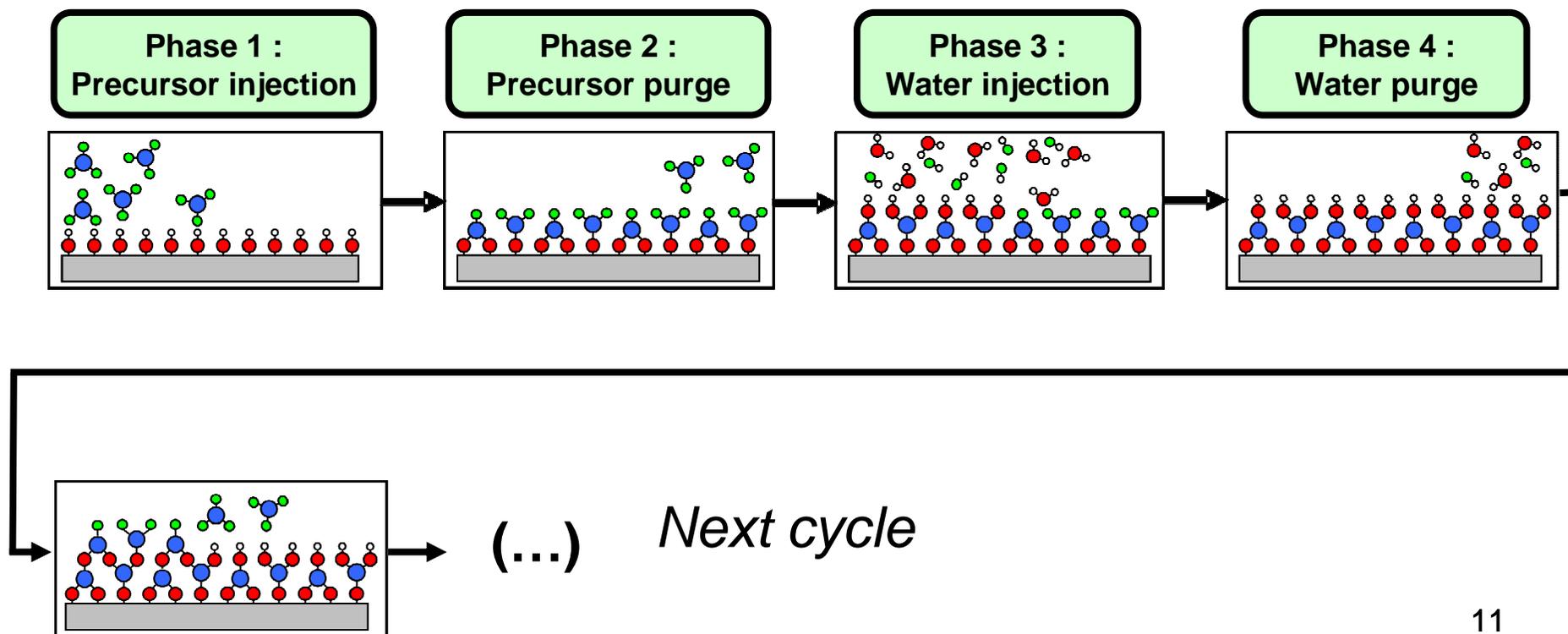
Deposition process: Atomic layer deposition

- Compatible with CMOS technologies
- Reliable
- Reproducible
- Efficient deposition properties control: roughness and thickness

Precursor molecules: HfCl_4 and H_2O

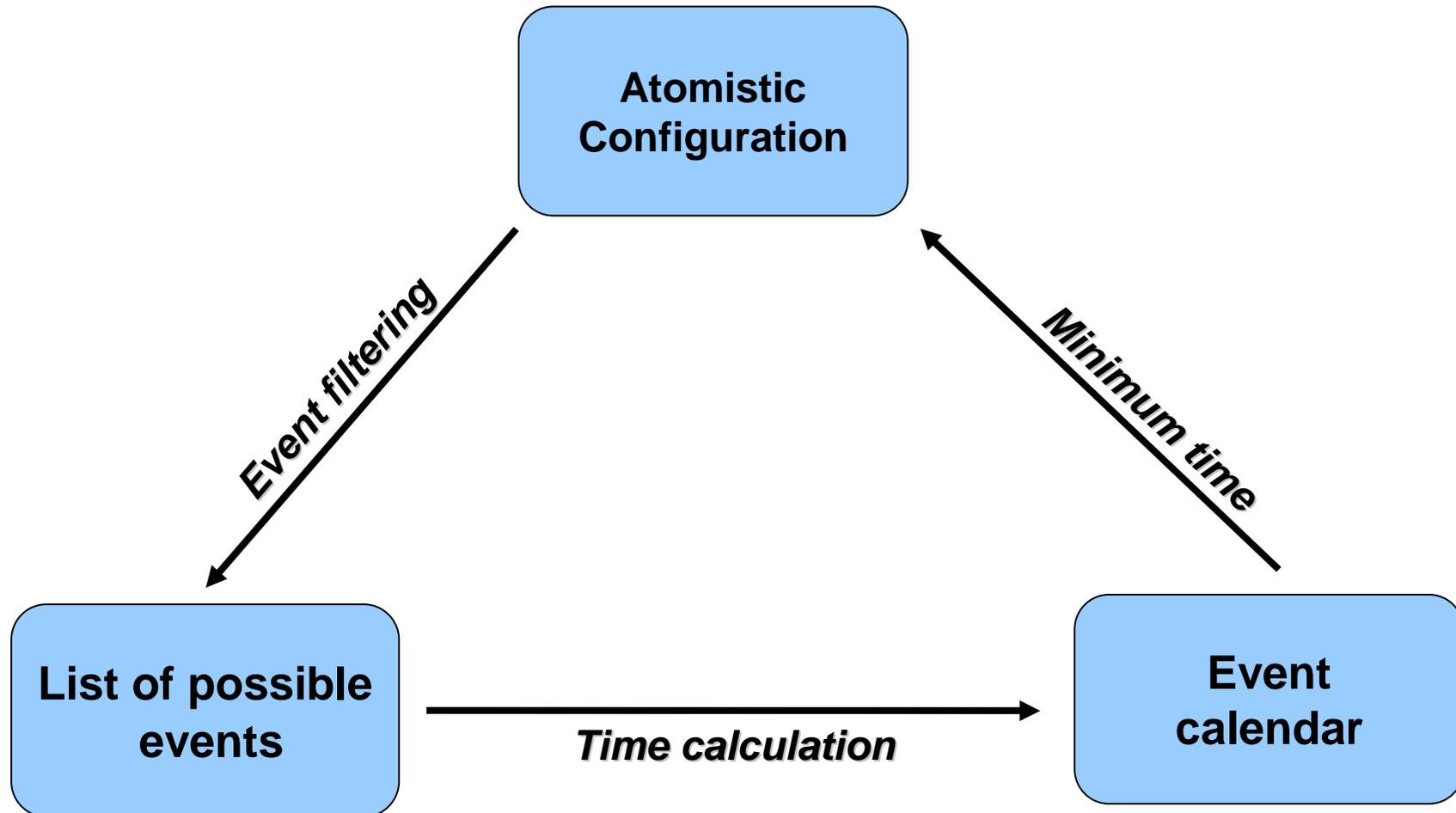
Deposition process

➤ *Atomic layer deposition*



Kinetic Monte-Carlo cycle

➤ *Atomistic configuration change*



Occurrence time calculation

➤ **Occurrence time of event « mechanism m on (i,j,k) site » :**

authorized mechanism

$$T_{i,j,k,m} = \frac{-\log(Z)}{\lambda_m}$$

Z random number between 0 and 1

Prohibited mechanism

$$T_{i,j,k,m} = \infty$$

➤ **Occurrence probability of a mechanism m**

For arrival mechanisms:
Maxwell-Boltzmann statistics

$$\lambda_{1,2} = \frac{\text{Cst.P.S}}{\sqrt{M_{1,2} \cdot T}}$$

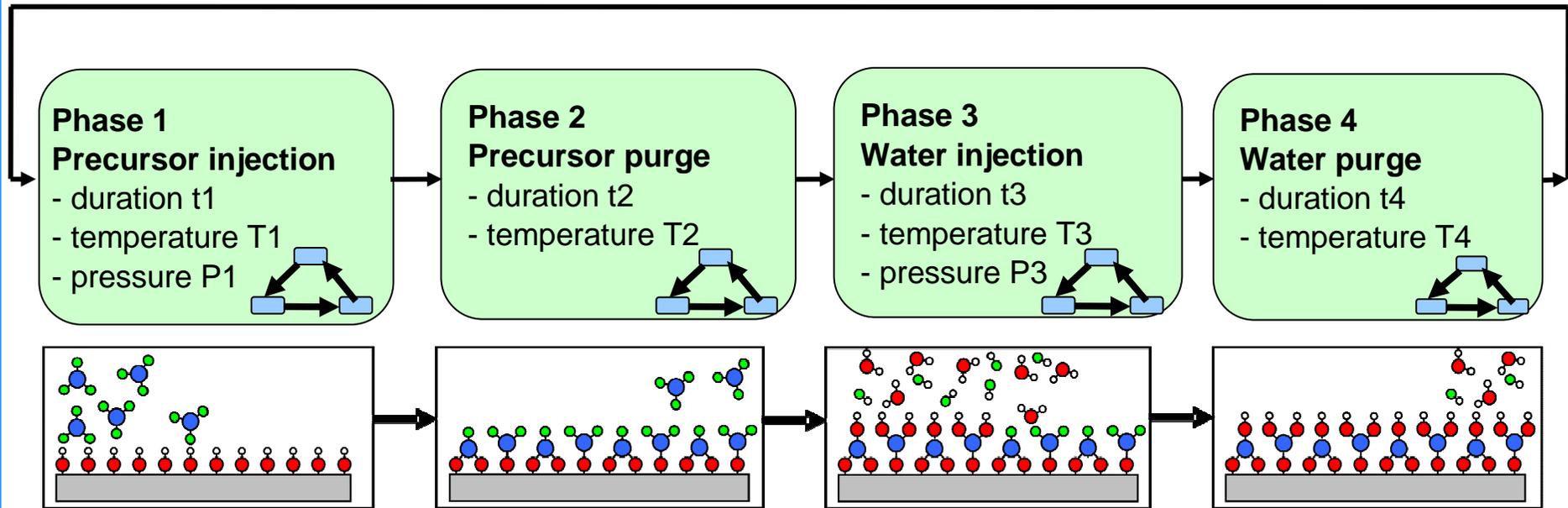
1-precursor 2- water

For all other mechanisms:
Arrhenius law

$$\lambda_m = v \cdot \exp\left(-\frac{\Delta E_m}{k_B T}\right)$$

Simulation of the ALD process via kMC

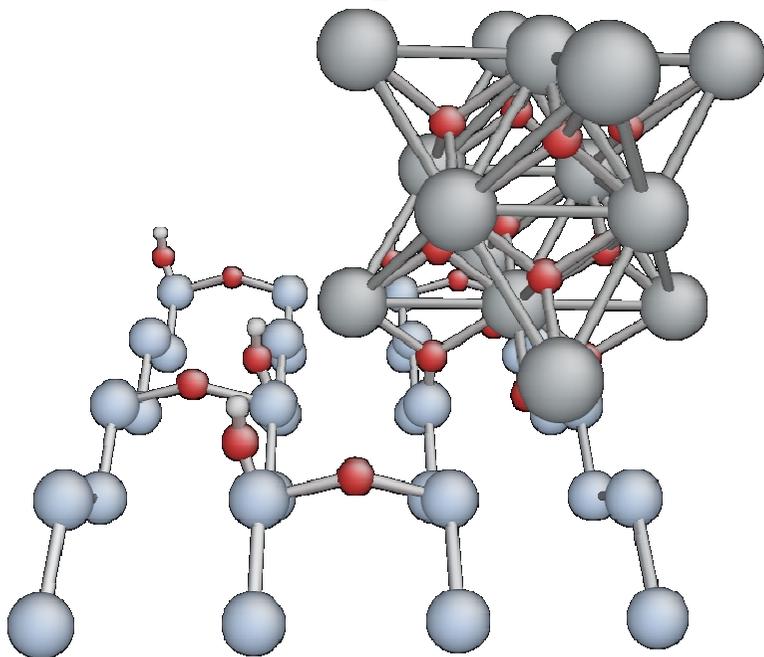
➤ Realistic implementation of ALD cycle



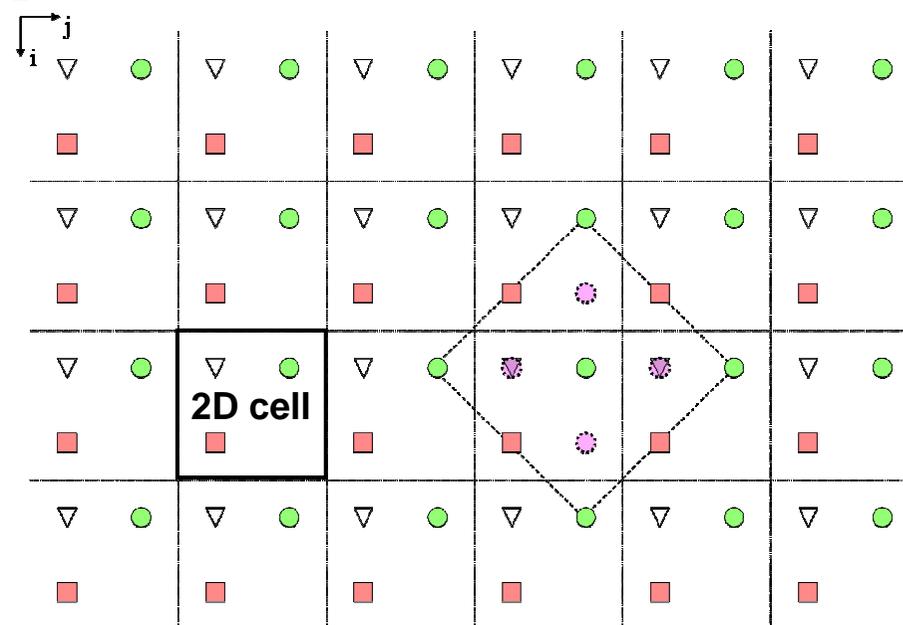
Description of atomic configuration

➤ *Lattice model able to describe the HfO_2 oxide onto Si*

Conventional HfO_2 fcc cell on Si (100) / SiO_2



Lattice model



● ∇ Si (layer $k=1$)

● Ionic oxygen ($k + 1/2$)

● Hf ($k=2$ and even layers)

● Hf ($k=3$ and odd layers)

Precursor/substrate interaction

➤ *HfCl₄ precursor dissociation on 2 neighbouring OH*

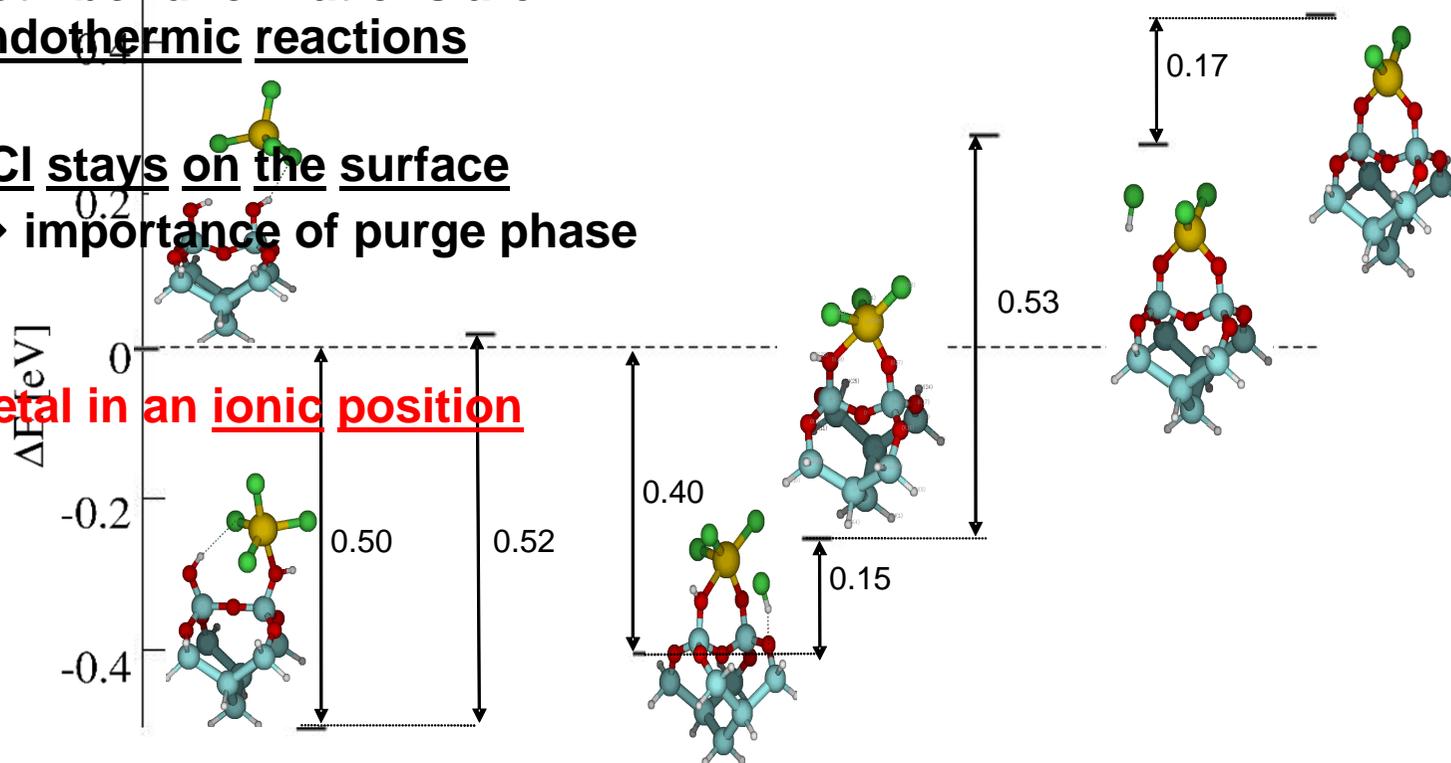


- Both bond formations are endothermic reactions

- HCl stays on the surface

→ importance of purge phase

- Metal in an ionic position



Precursor/HfO₂ layer interaction

➤ *HfCl₄ precursor dissociation on Hf-OH*

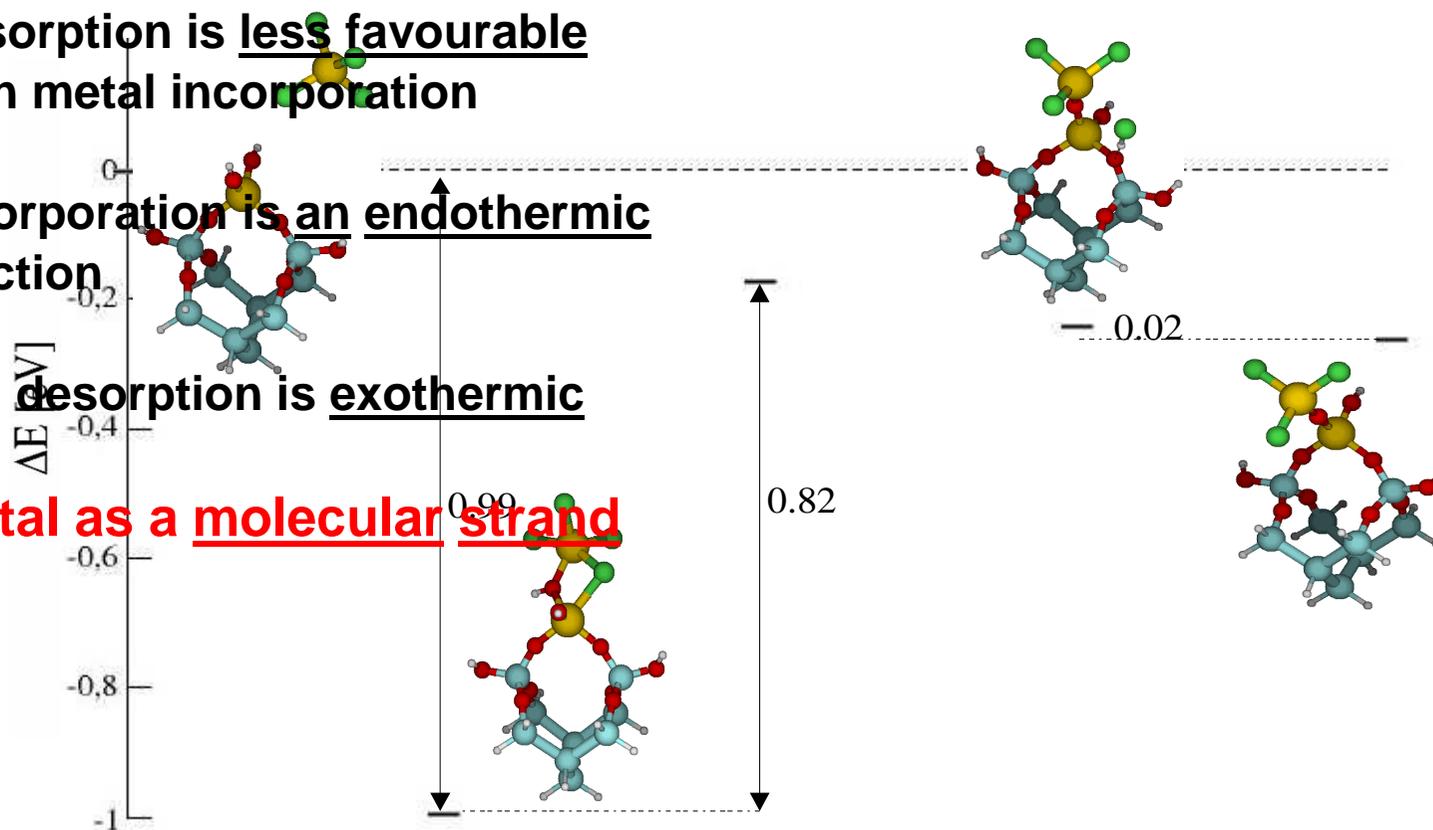


- Desorption is less favourable than metal incorporation

- Incorporation is an endothermic reaction

- HCl desorption is exothermic

- **Metal as a molecular strand**

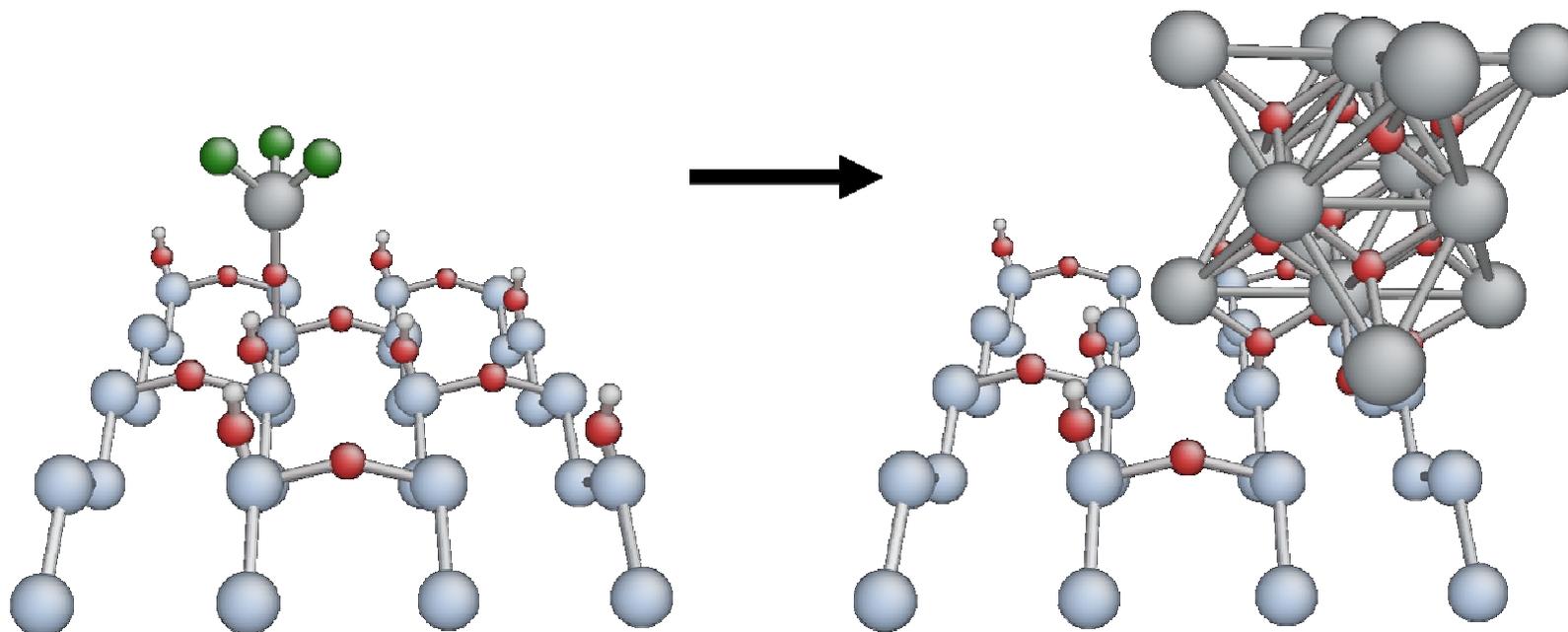


Densification mechanisms

Transition between molecular strand species to the final ionic bulk structure

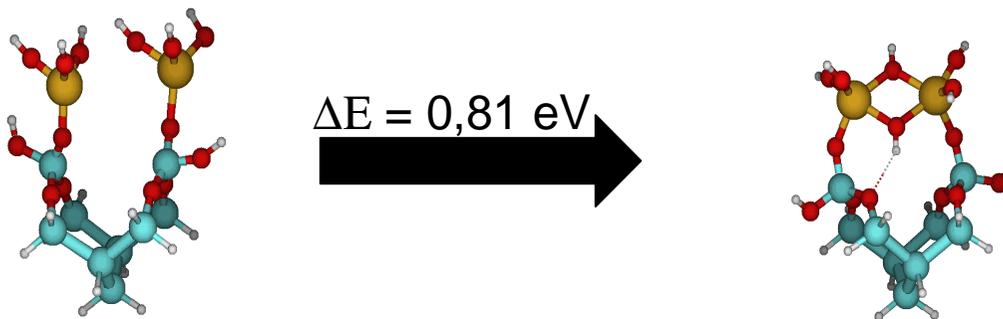
A mechanism involving several atoms

Increase of coordination number (metal, oxygen)



Precursor dimer formation

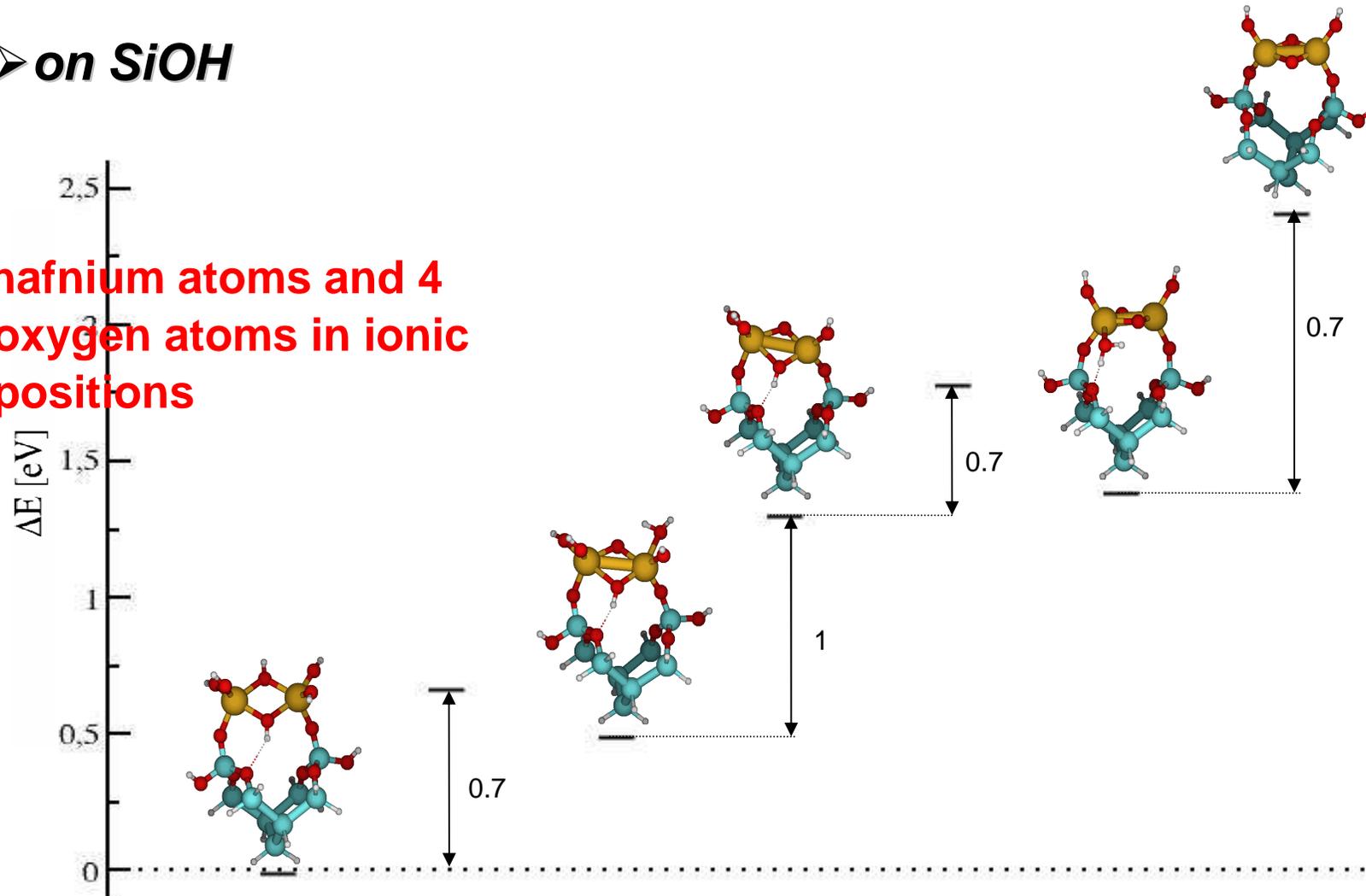
➤ *on SiOH*



Precursor dimer formation

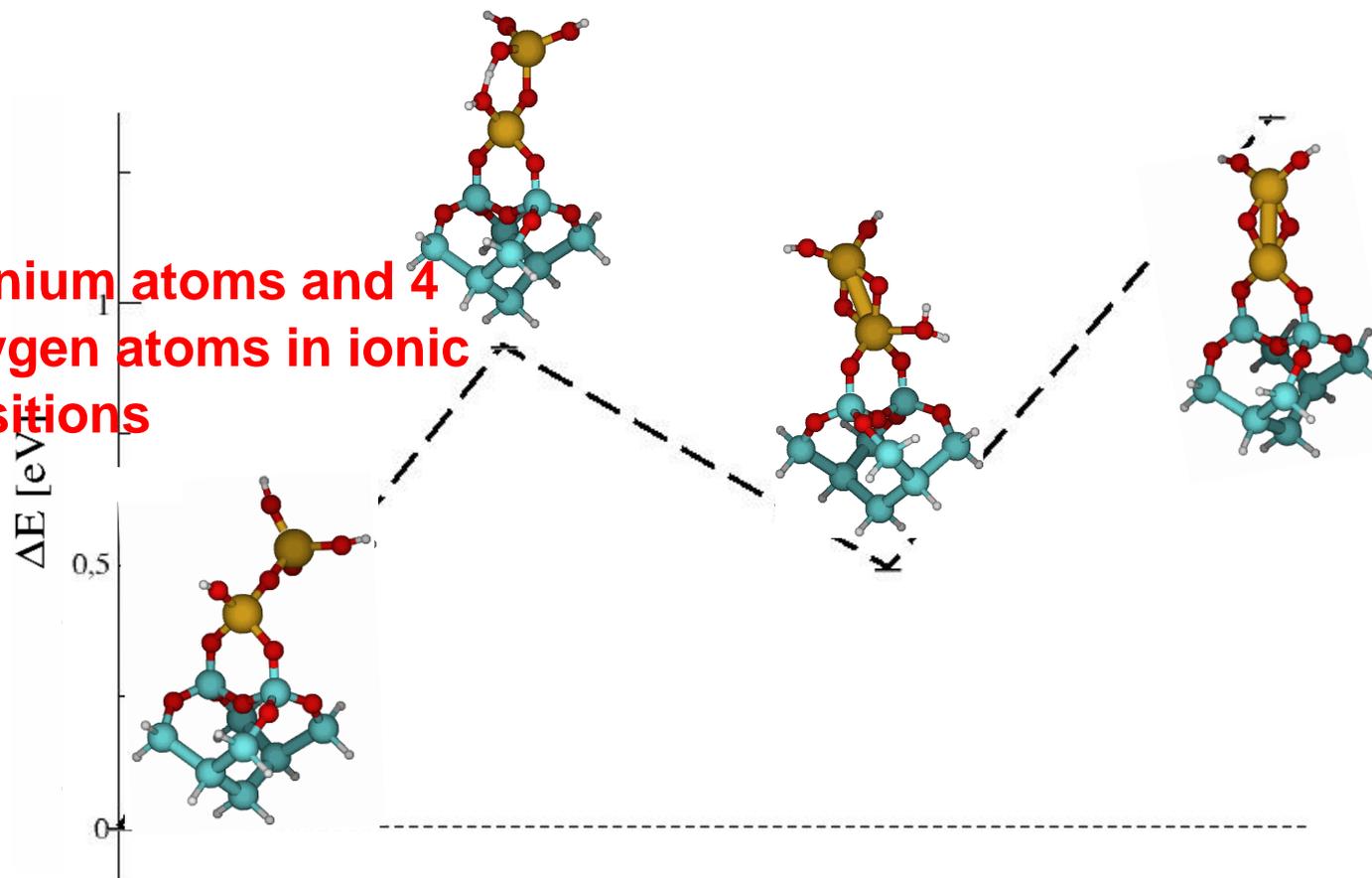
➤ on SiOH

- 2 hafnium atoms and 4 oxygen atoms in ionic positions



Tree densification

- 2 hafnium atoms and 4 oxygen atoms in ionic positions



Complete list of mechanisms (1)

Gas/surface reactions – activation barriers

Mechanisms link to precursor incorporation

on SiO₂ | on HfO₂

01 MeCl₄ adsorption

02 Chemisorption of HfCl₄ on a isolated OH

0.88eV | 0.82eV

03 Recombination of HCl in HfCl₃ isolated

0.62eV | 0.07eV

04 Chemisorption of HfCl₄ on a OH having a OH neighbouring

0.52eV | 0.99eV

05 Recombination of HCl in HfCl₃ having a OH neighbouring

0.38eV | 0.07eV

06 Desorption of HCl

0.38eV | 0.07eV

07 Desorption of HCl₄

0.48eV | 0.99eV

Mechanisms link to hydrolysis

in the gas phase

08 Adsorption of H₂O

09 Hydrolysis of a Cl ligand

0.916eV

10 Desorption de H₂O

0.619eV

11 Decomposition of HfCl₃

0.530eV

Complete list of mechanisms (2)

➤ *Densifications – activation barriers*

Mechanism of layer densification

12 Recombination of HCl in HfCl ₂	0.02eV
13 Decomposition Hf(OH) ₃	0.13eV
14 Recombination of HCl in Hf(OH) ₂	0.35eV
15 Dimer formation	0.94eV
16 Tree Densification	0.92eV

Outline

- Part 1: Introduction, general context
- Part 2: Hikad 2, basic ingredients
- **Part 3: Exploitation, results**
 - Growth kinetics
 - Structural characterisation
 - Influence of processing parameters

Experimental growth conditions

10 first cycles under experimental conditions

- Temperature 300°C and pressure 1.33 millibar
- Precursor injection phase duration 0.05s
- Water injection phase duration 0.1s
- Purge phase duration 3.5s
- Substrate 20 x 20 atoms with siloxane bridge and 52% OH according to Zhuravlev

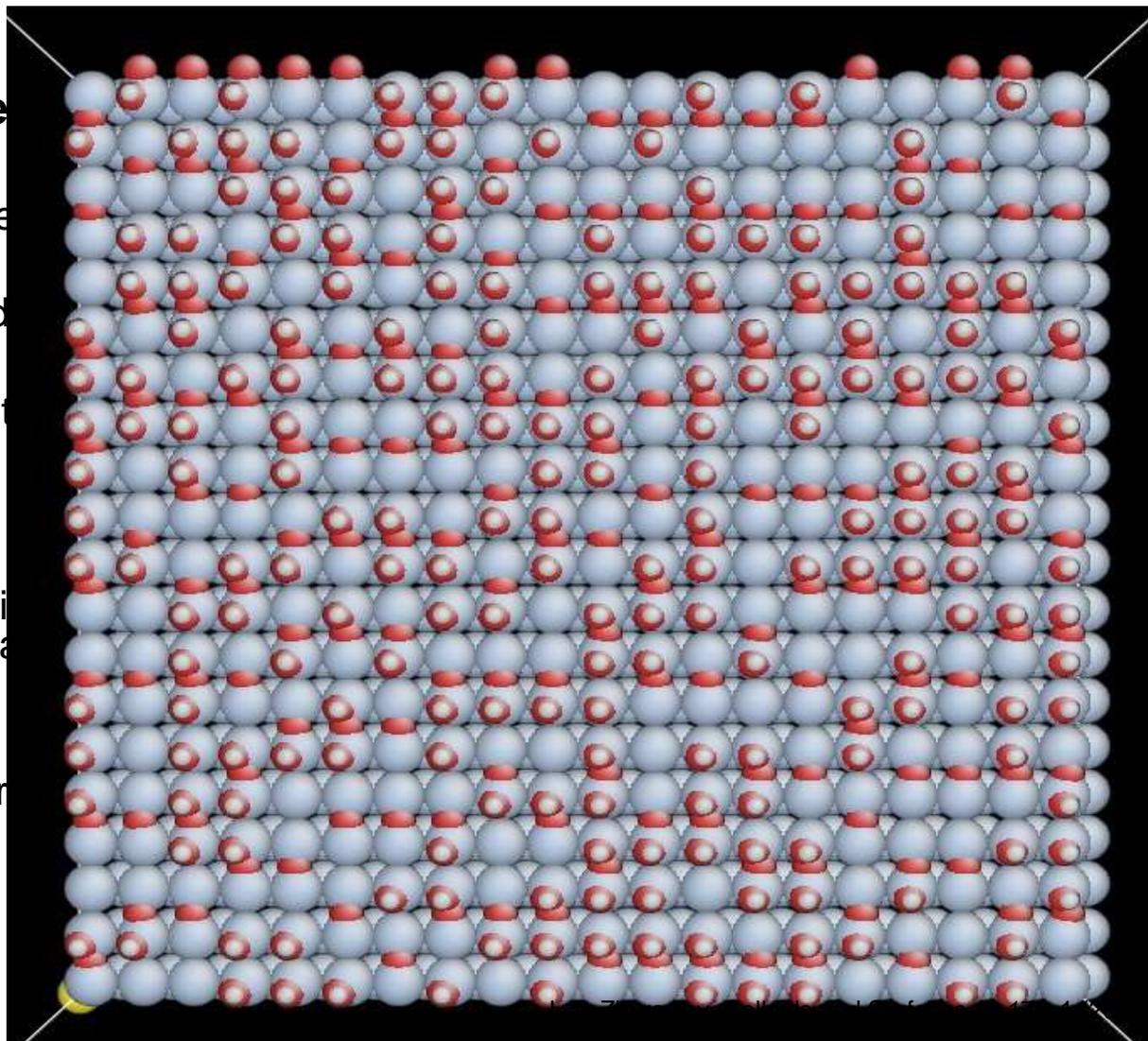
Zhuravlev model = %OH under deposition conditions

Experimental growth conditions

10 first cycles under exper

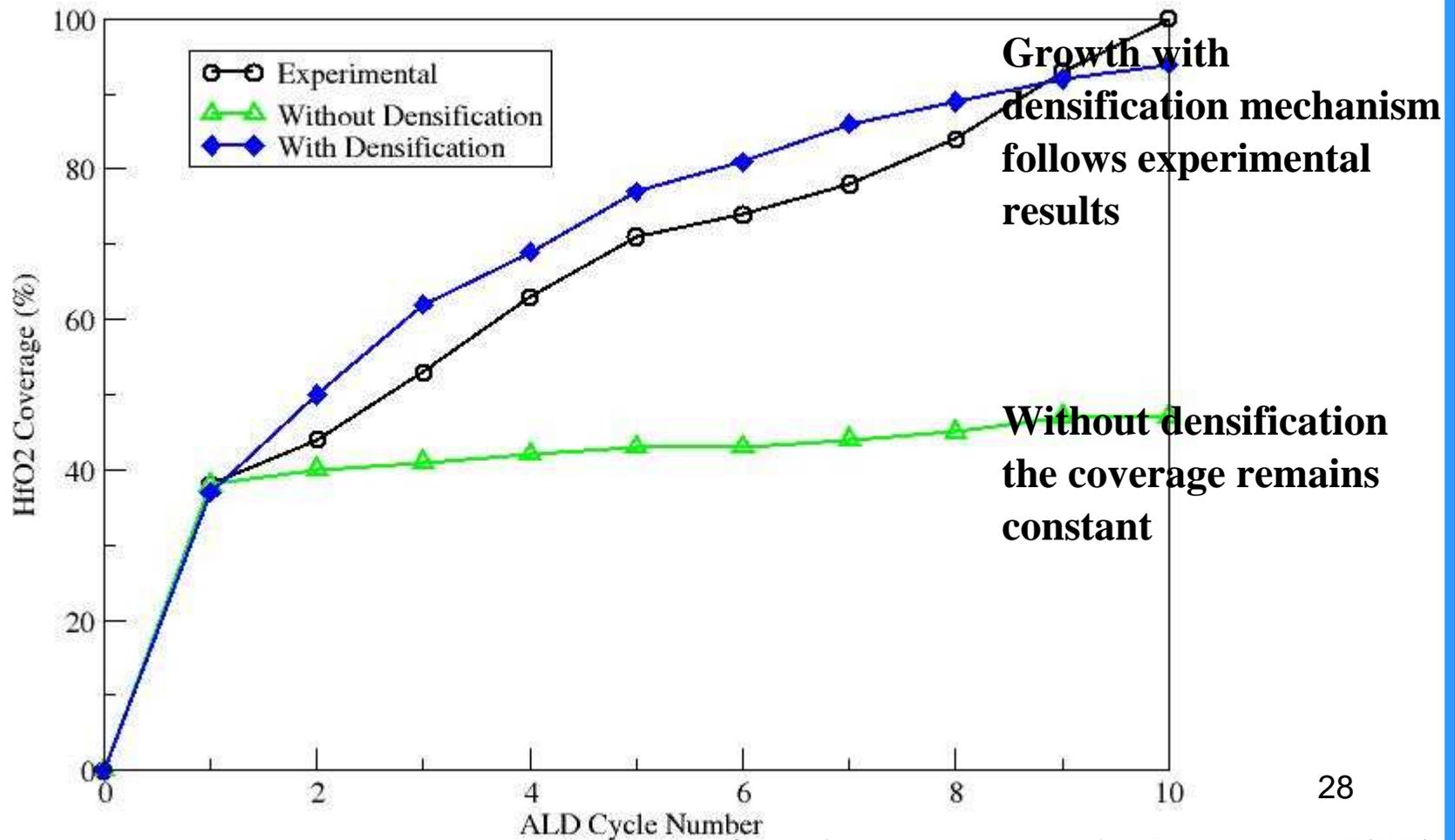
- Temperature 300°C and pre
- Precursor injection phase d
- Water injection phase dura
- Purge phase duration 3.5s
- Substrate 20 x 20 atoms wi
52% OH according to Zhurav

Zhuravlev model = %OH under



Importance of densification mechanisms

➤ *Simulated coverage compared to LEIS experimental measurements*

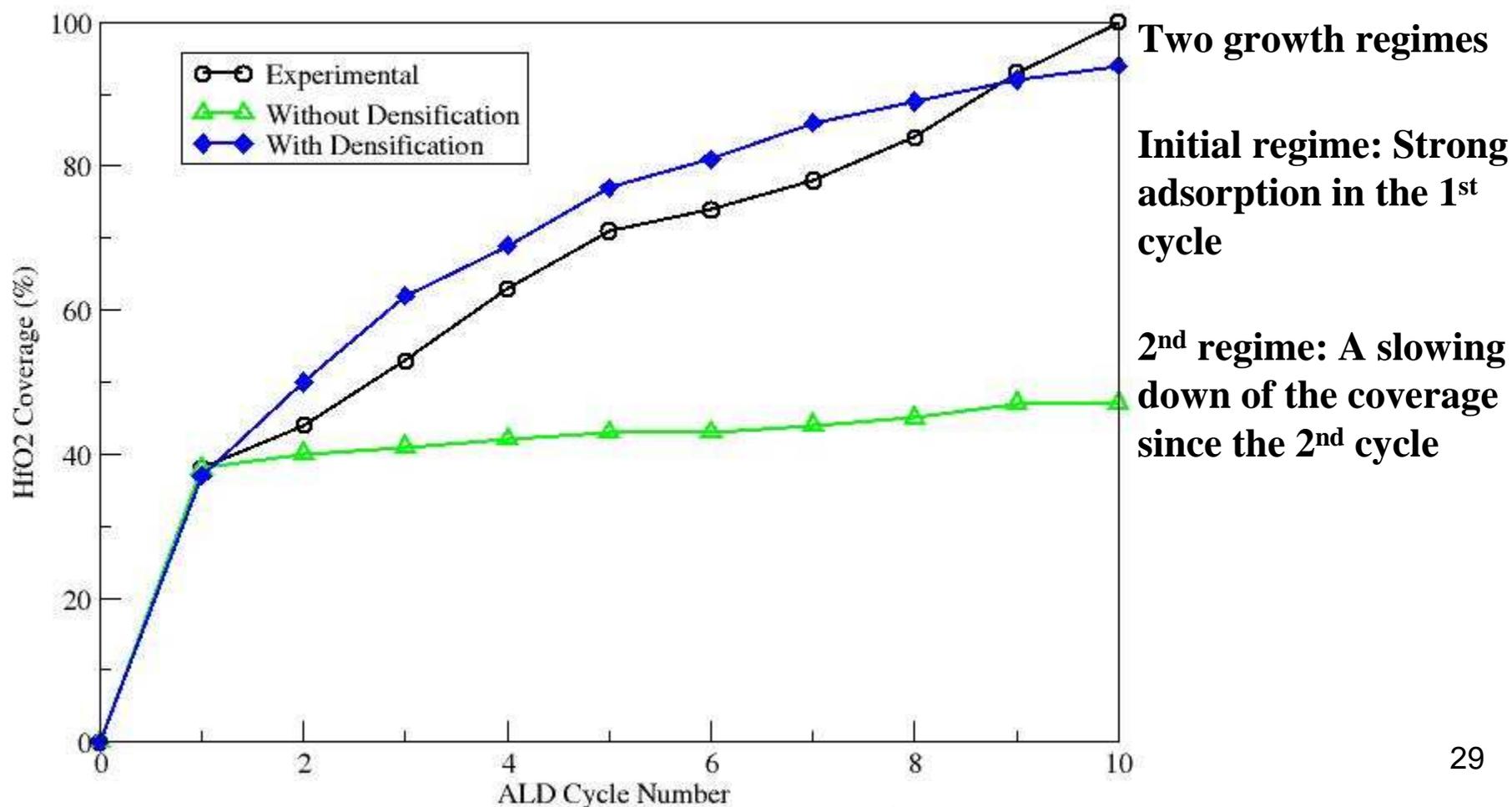


Growth with densification mechanism follows experimental results

Without densification the coverage remains constant

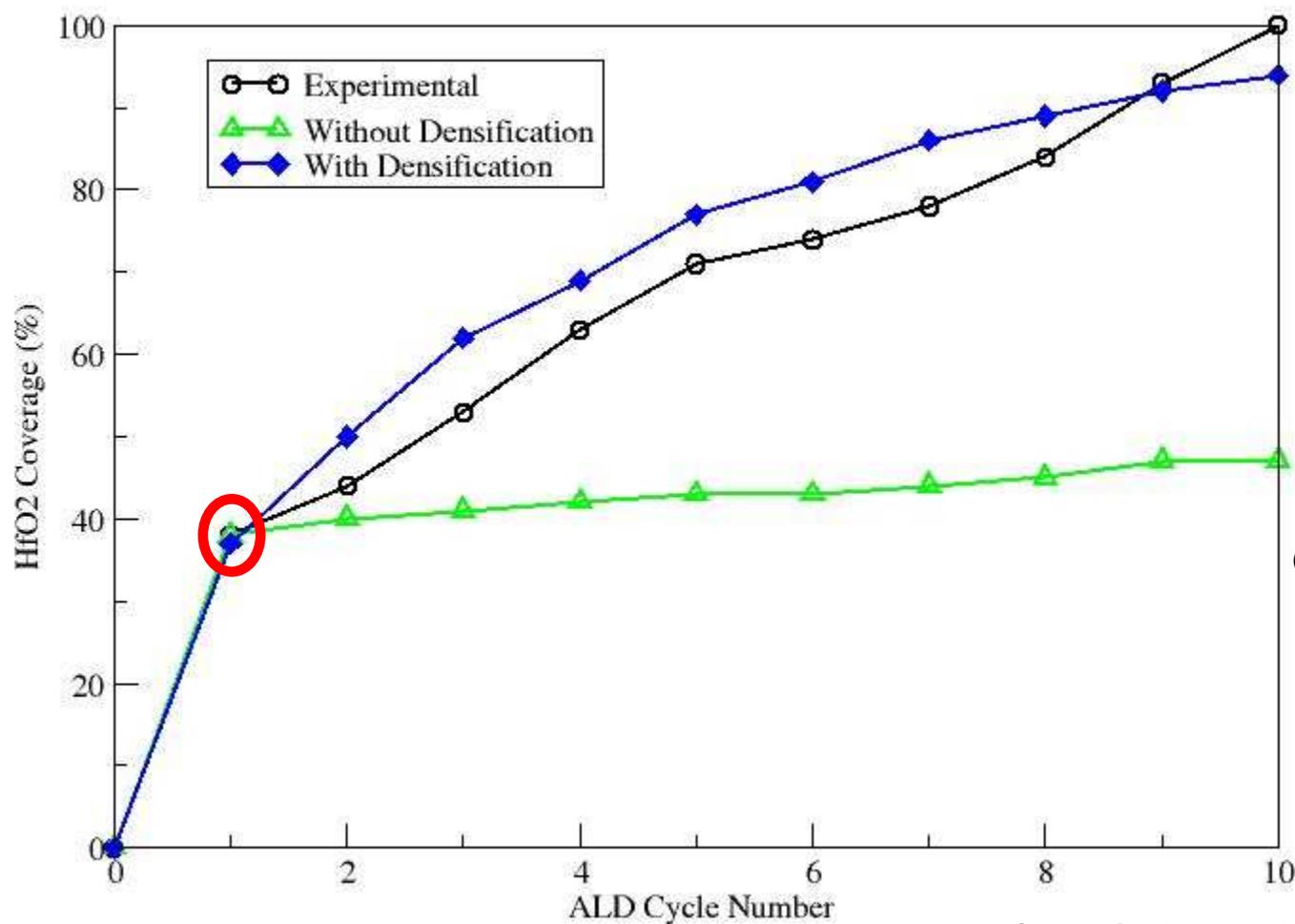
Importance of densification mechanisms

➤ *Simulated coverage compared to LEIS experimental measurements*



Importance of densification mechanisms

➤ *Simulated coverage compared to LEIS experimental measurements*



Initial regime
Perfect agreement
between experience
and simulations

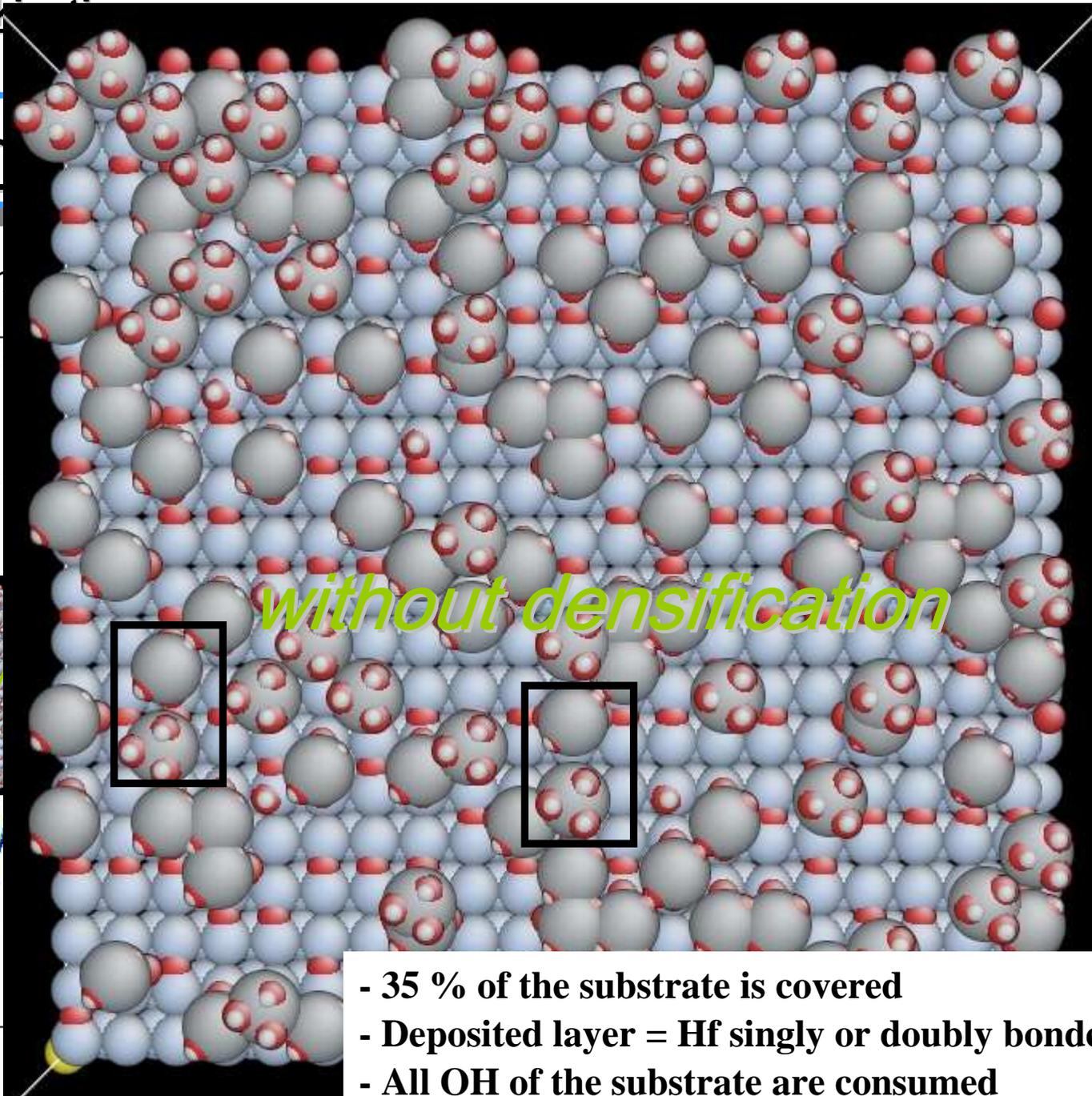
Gas/surface mechanisms
(DFT) are sufficient

Growth Kinetics

In

sms

➤ Sim



without densification

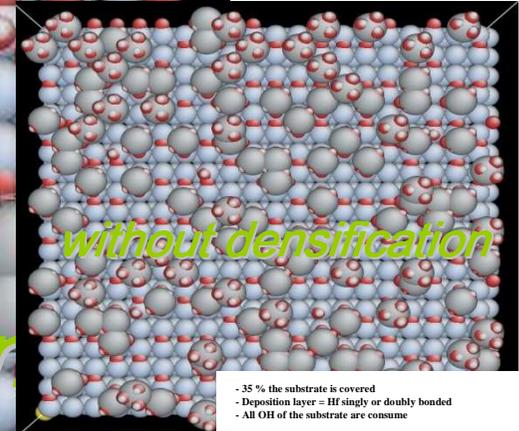
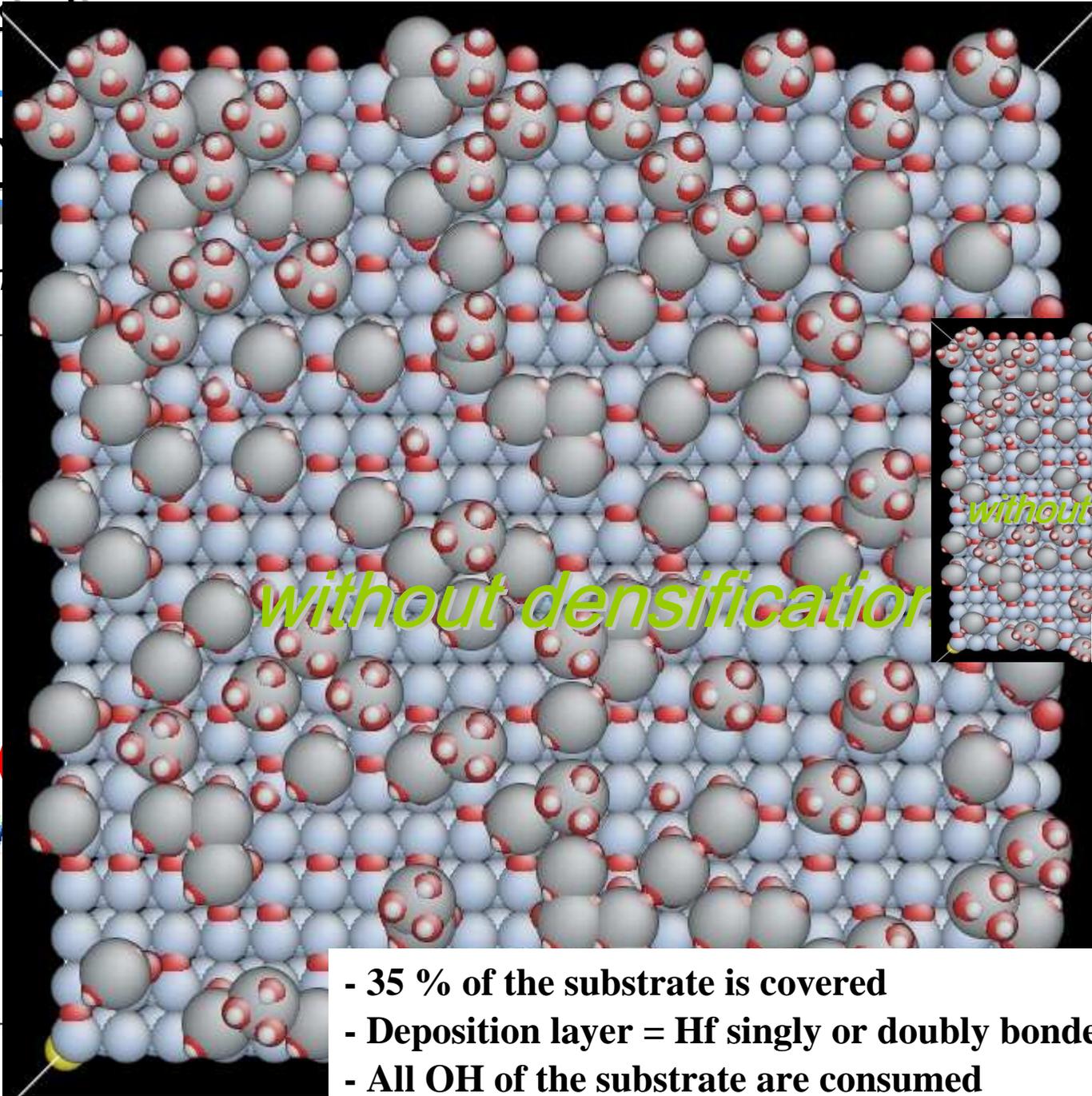
- 35 % of the substrate is covered
- Deposited layer = Hf singly or doubly bonded
- All OH of the substrate are consumed

Growth Kinetics

In

ms

➤ Sim



- 35 % of the substrate is covered
- Deposition layer = Hf singly or doubly bonded
- All OH of the substrate are consumed

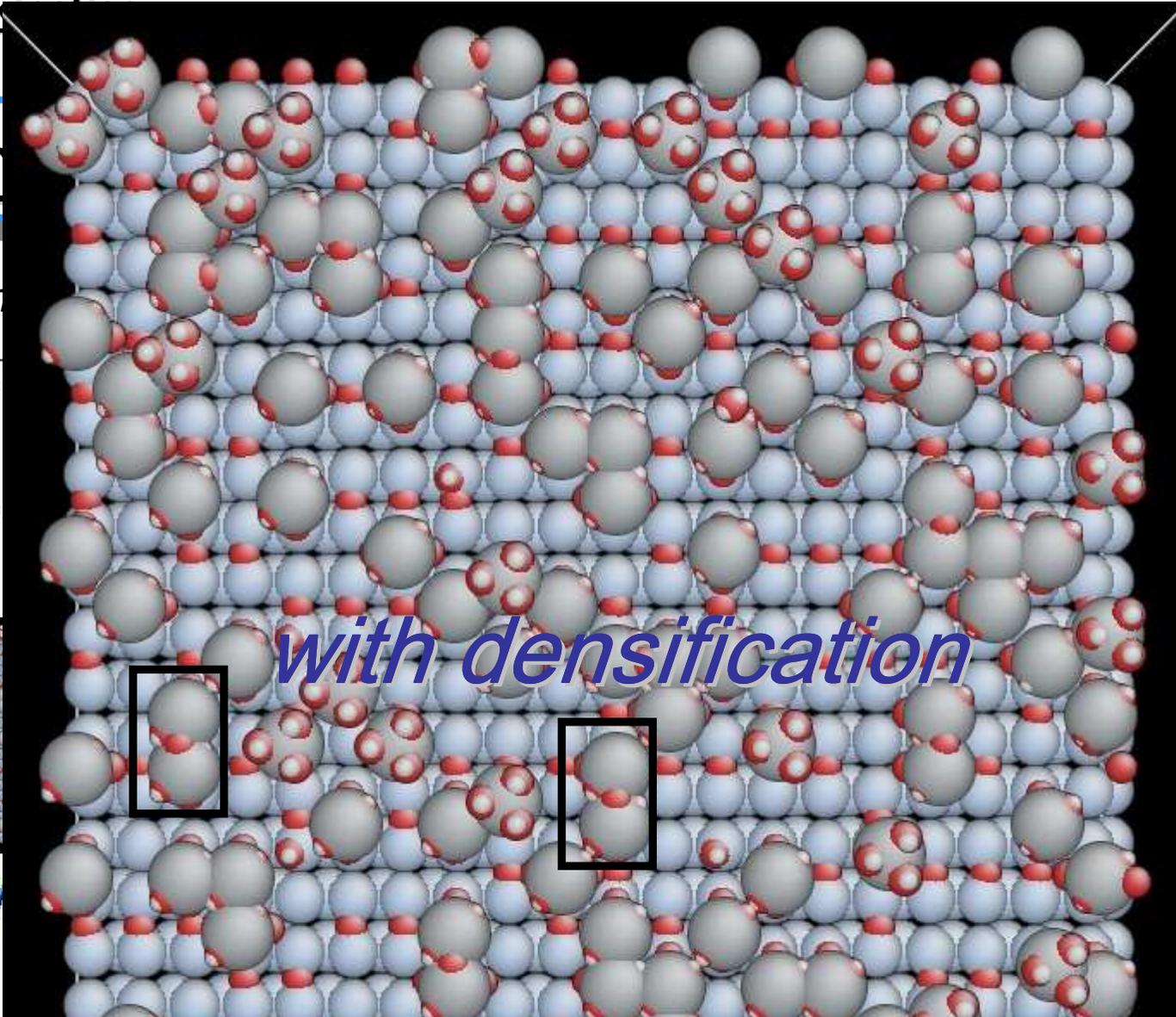
- 35 % the substrate is covered
- Deposition layer = Hf singly or doubly bonded
- All OH of the substrate are consumed

Growth kinetics

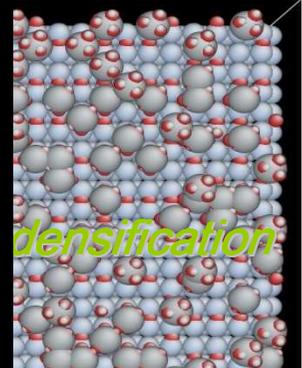
In

ms

➤ Sim



with densification



- 35 % of the substrate is covered
- Deposition layer = Hf singly or doubly bonded
- All OH of the substrate are consumed

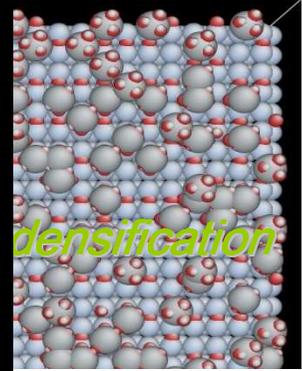
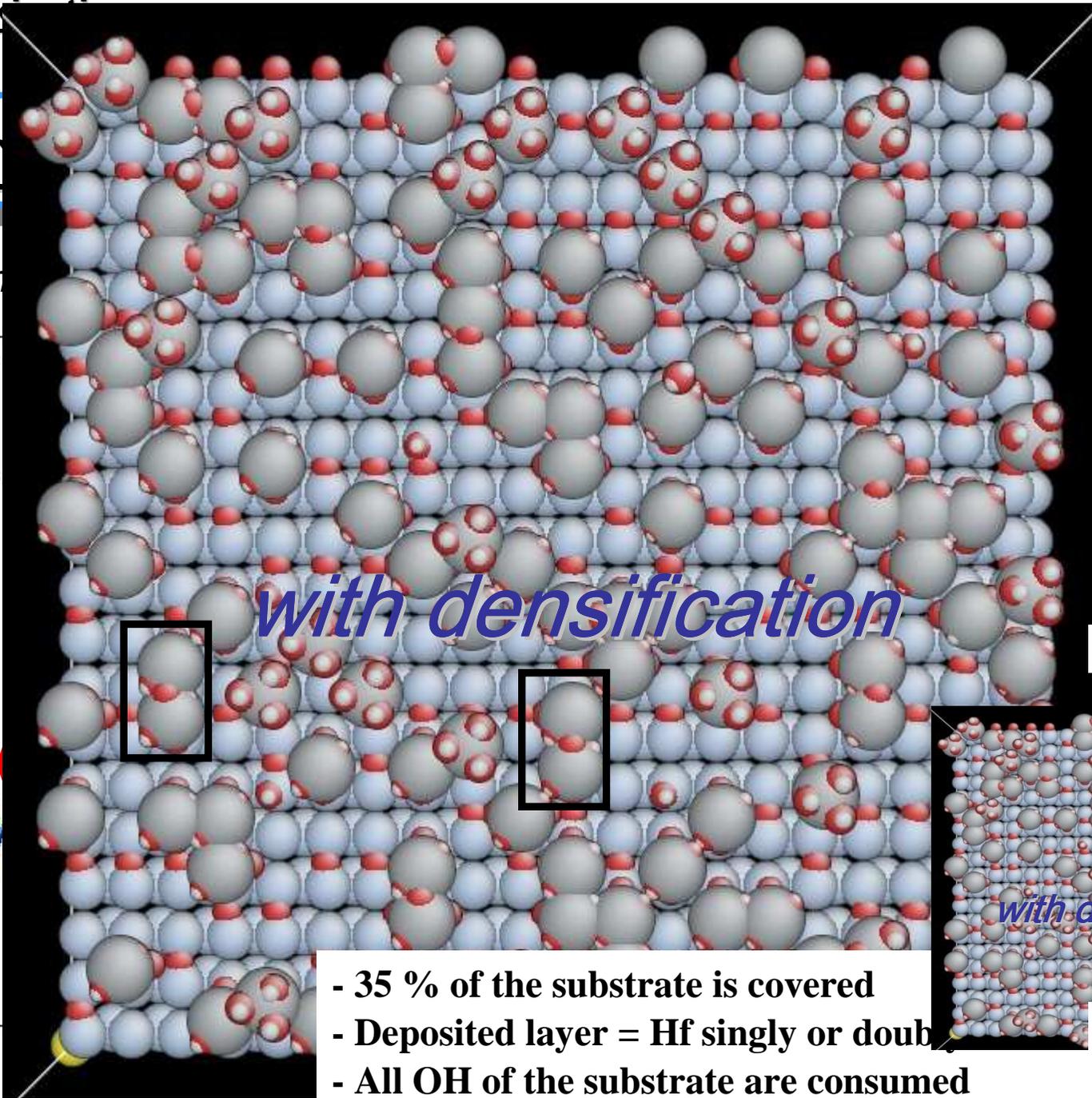
- 35 % of the substrate is covered
- Deposited layer = Hf singly or doubly bonded
- All OH of the substrate are consumed

Growth Kinetics

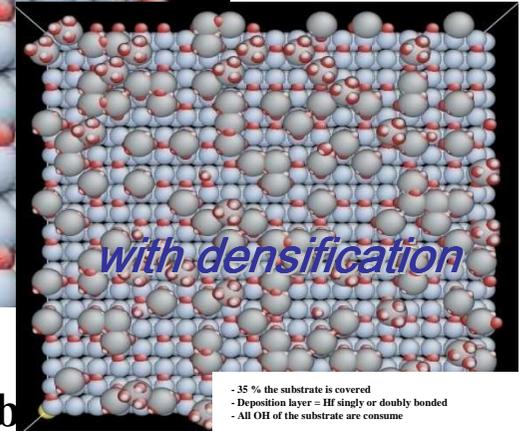
In

ms

➤ Sim



- 35 % the substrate is covered
- Deposition layer = Hf singly or doubly bonded
- All OH of the substrate are consumed

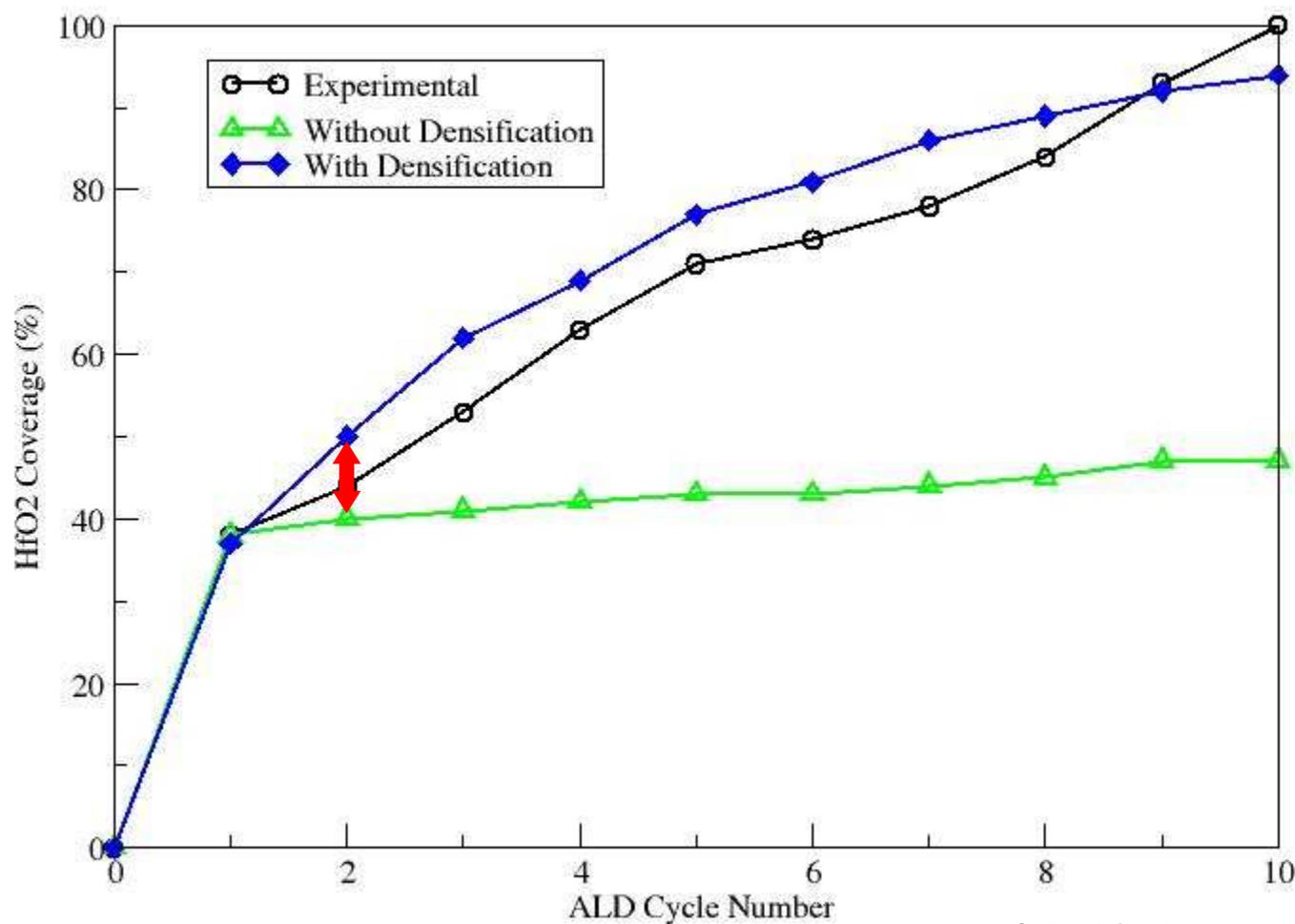


- 35 % the substrate is covered
- Deposition layer = Hf singly or doubly bonded
- All OH of the substrate are consumed

- 35 % of the substrate is covered
- Deposited layer = Hf singly or doubly bonded
- All OH of the substrate are consumed

Importance of densification mechanisms

➤ *Simulated coverage compared to LEIS experimental measurements*



Transition regime

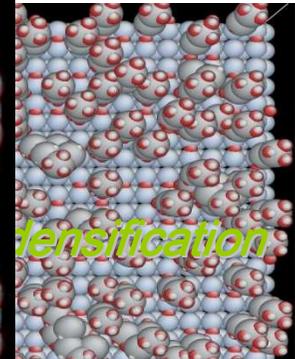
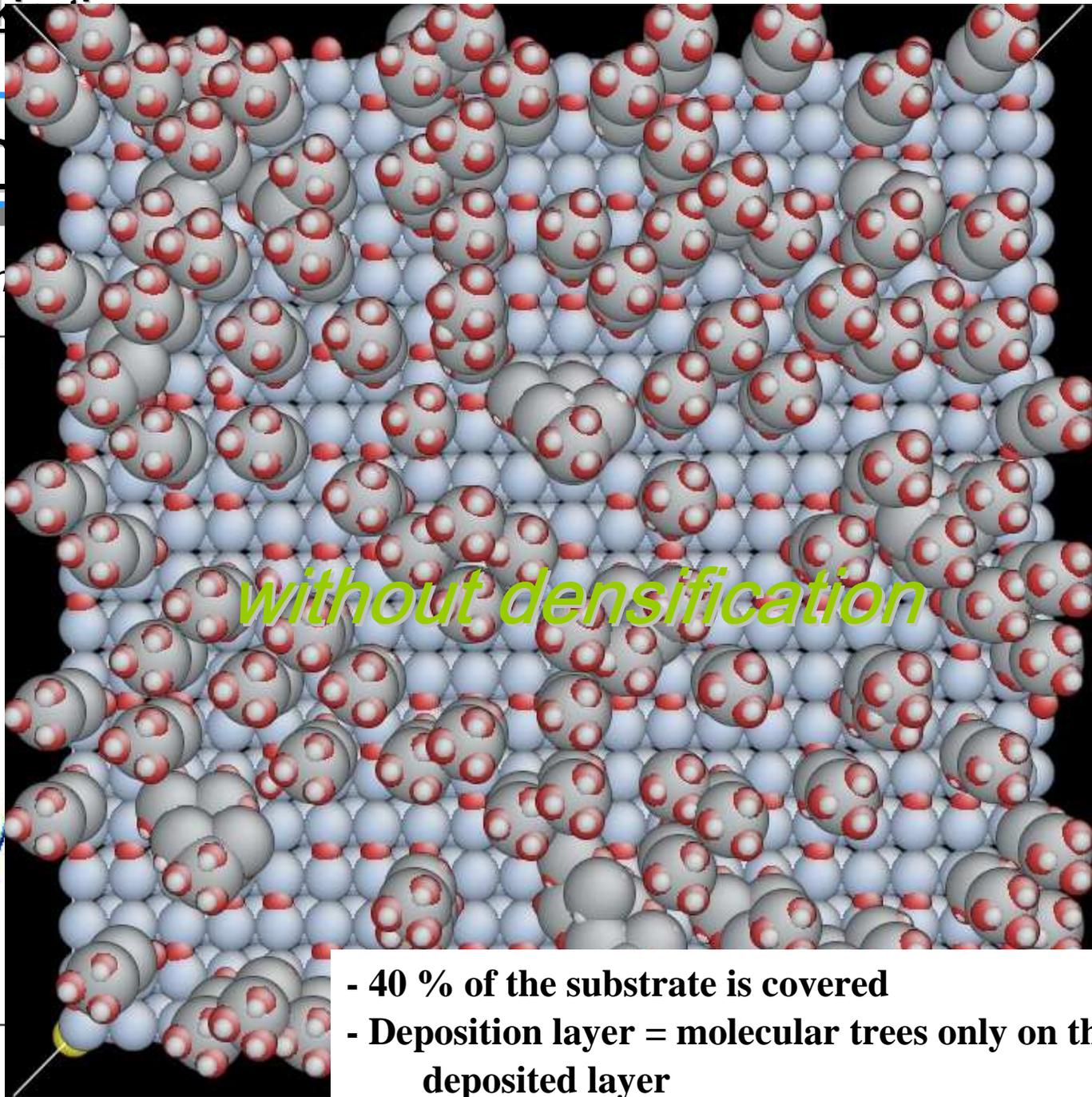
Difference behaviour since the 2nd cycle between simulation with and without densification

Growth kinetics

In

ms

➤ Sim



of the substrate is covered
deposition layer = molecular trees only on the 1st deposited layer

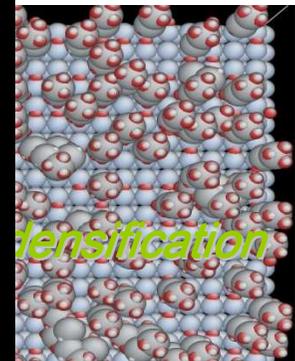
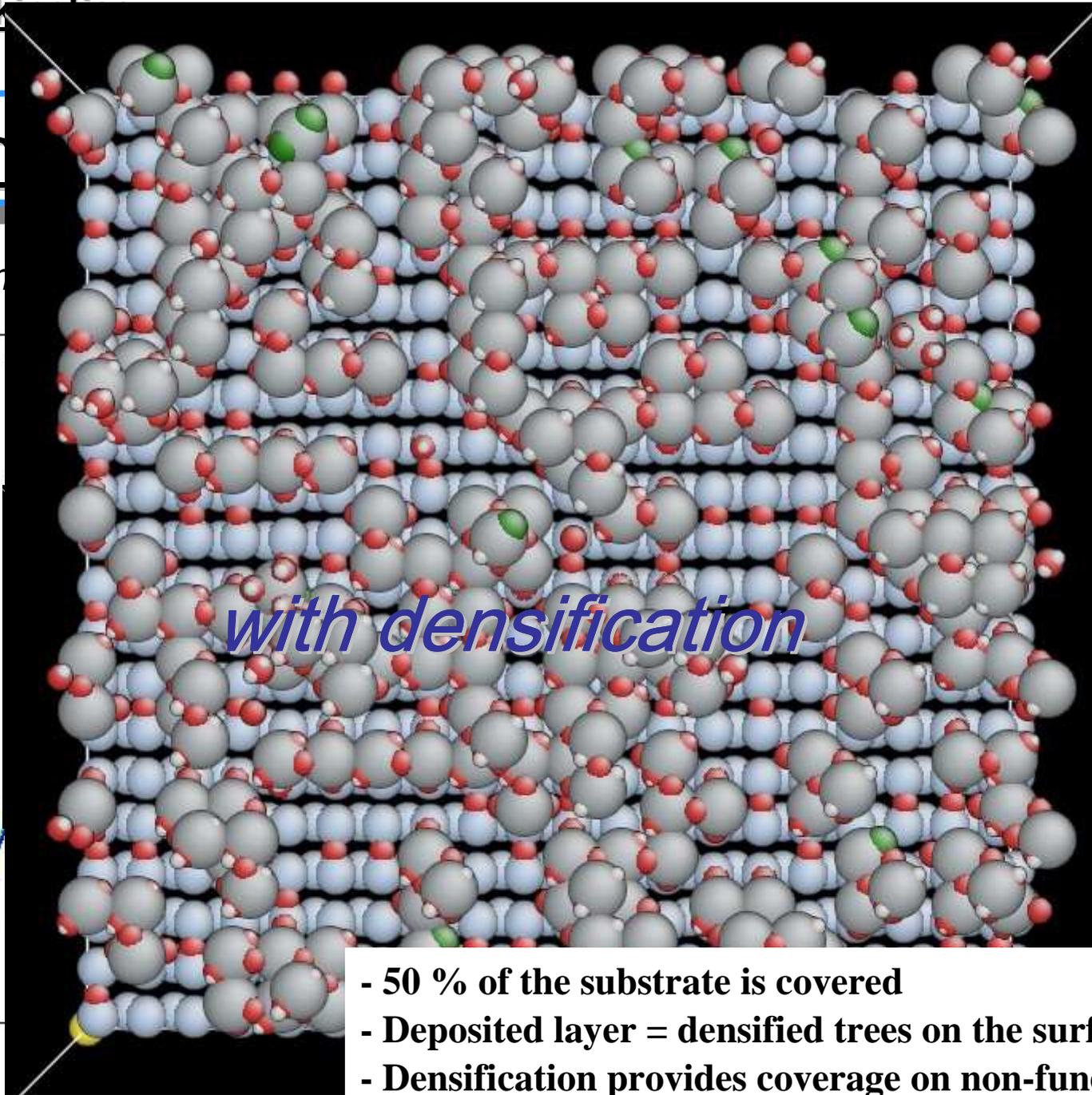
- 40 % of the substrate is covered
- Deposition layer = molecular trees only on the 1st deposited layer

Growth kinetics

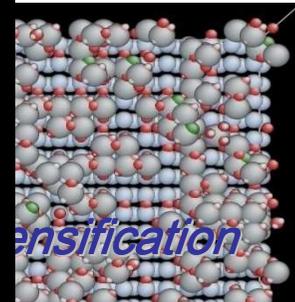
In

ms

➤ Sim



of the substrate is covered
tion layer = molecular trees only on the 1st deposited layer



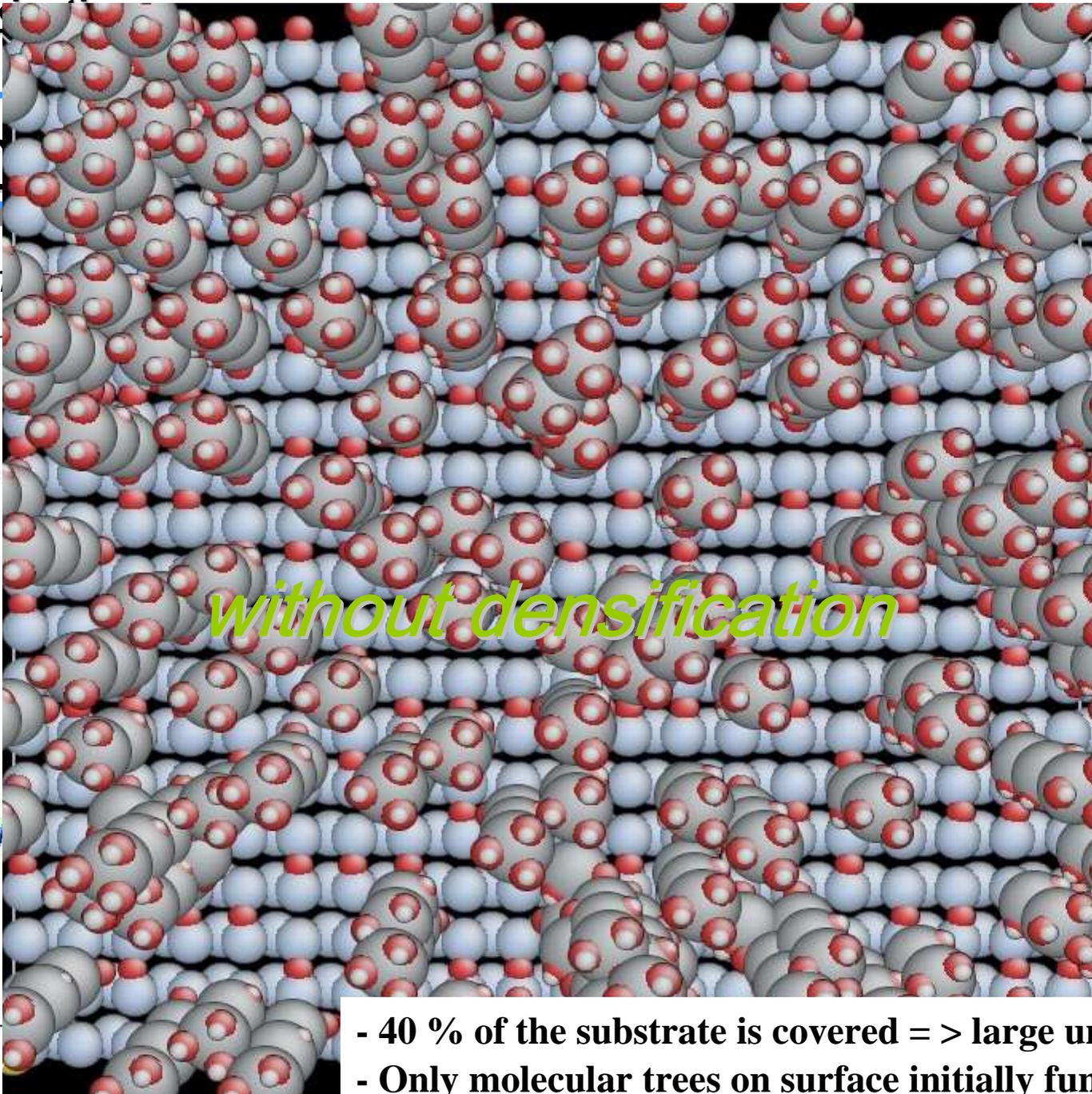
- 50 % of the substrate is covered
- Deposited layer = densified trees on the surface
- Densification provides coverage on non-functionalized Si

Growth kinetics

In

ms

➤ Sim



without densification

for
ted coverage

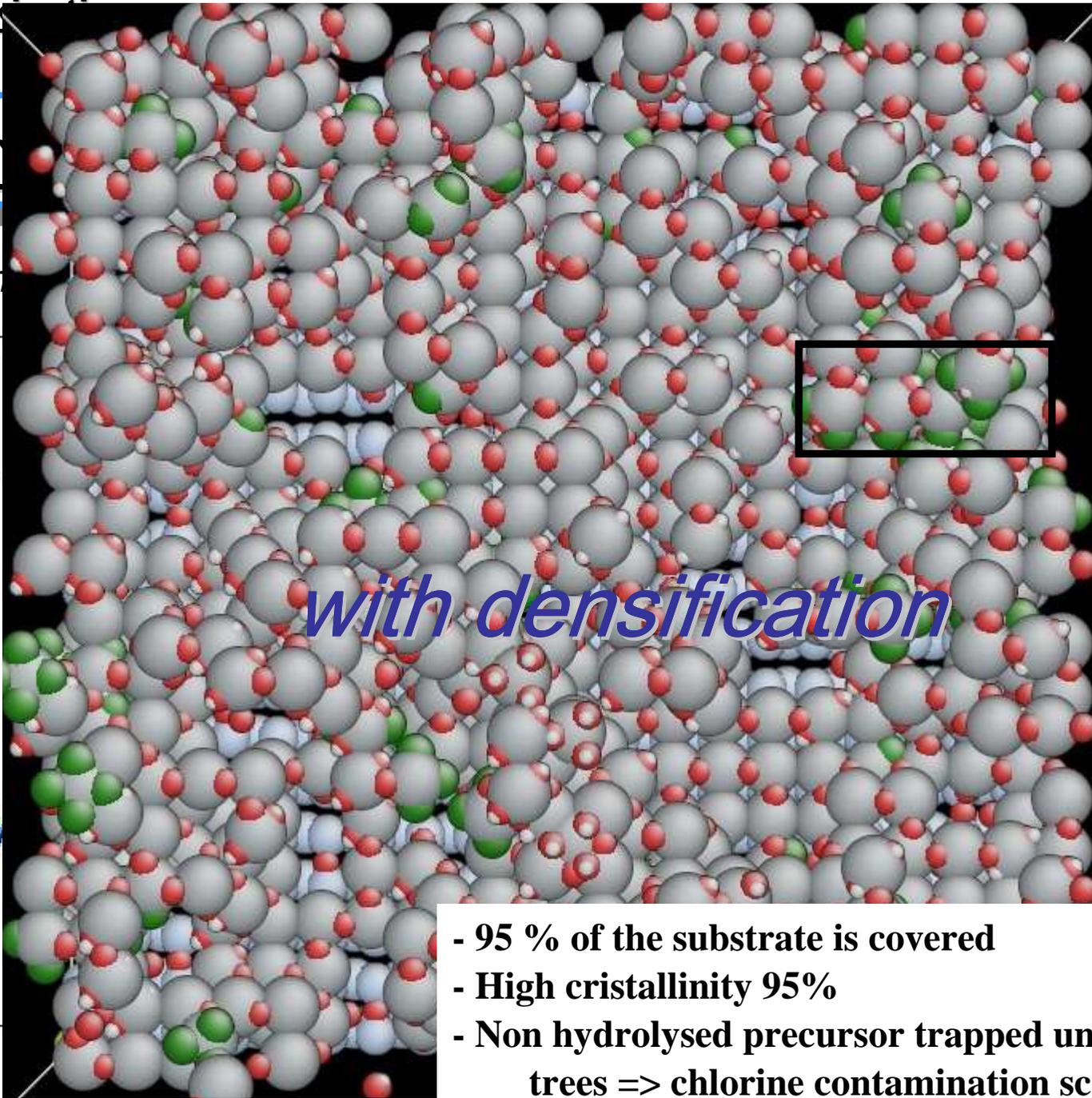
- 40 % of the substrate is covered => large uncovered area
- Only molecular trees on surface initially functionalized

Growth kinetics

In

ms

➤ Sim



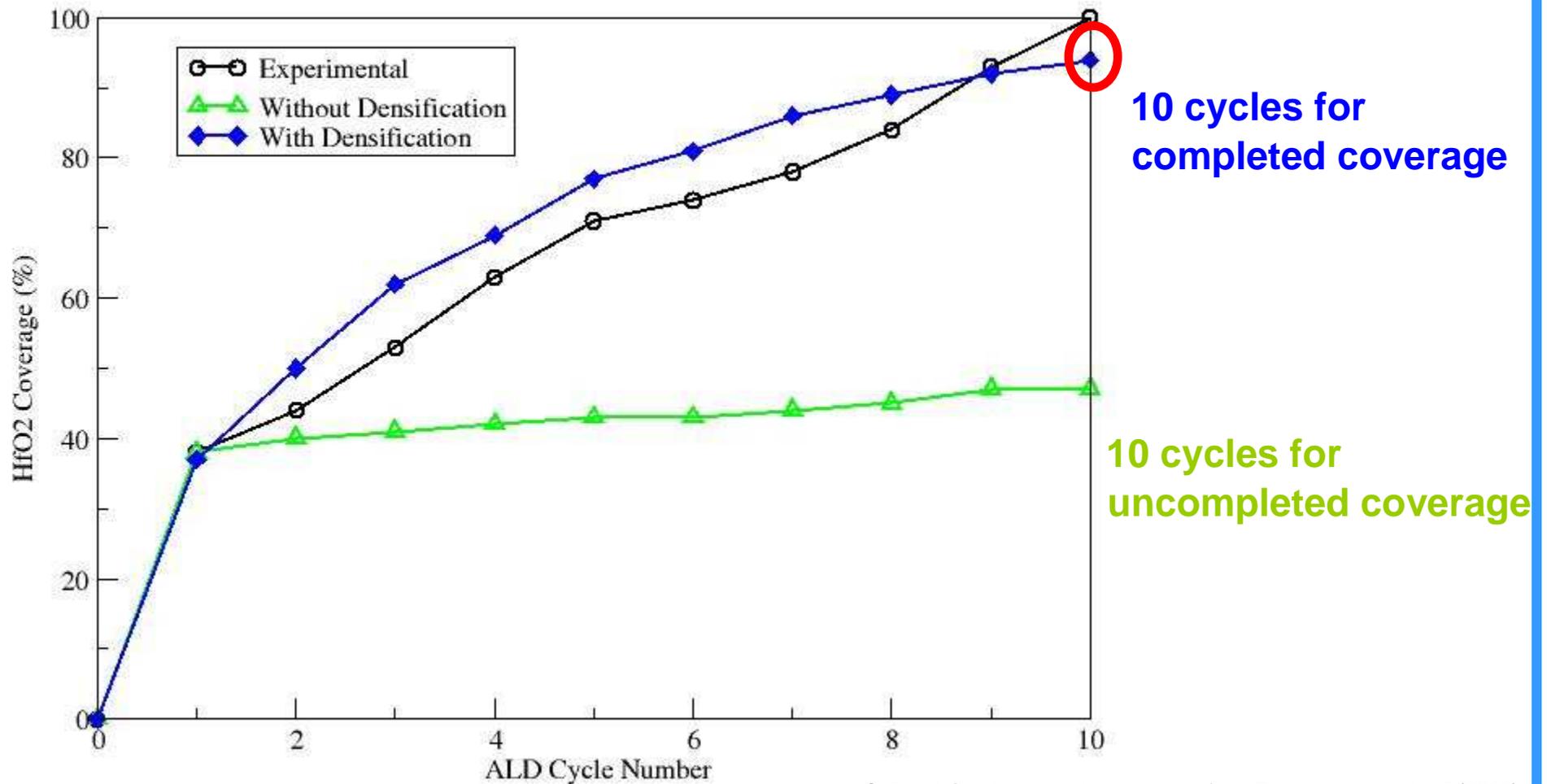
with densification

s for
ed coverage

- 95 % of the substrate is covered
- High cristallinity 95%
- Non hydrolysed precursor trapped under densified trees => chlorine contamination scenario

Importance of densification mechanisms

➤ *Simulated coverage compared to LEIS experimental measurements*

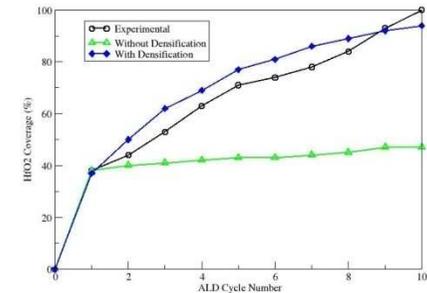


Importance of densification mechanisms

Densification mechanisms are needed to simulate the growth

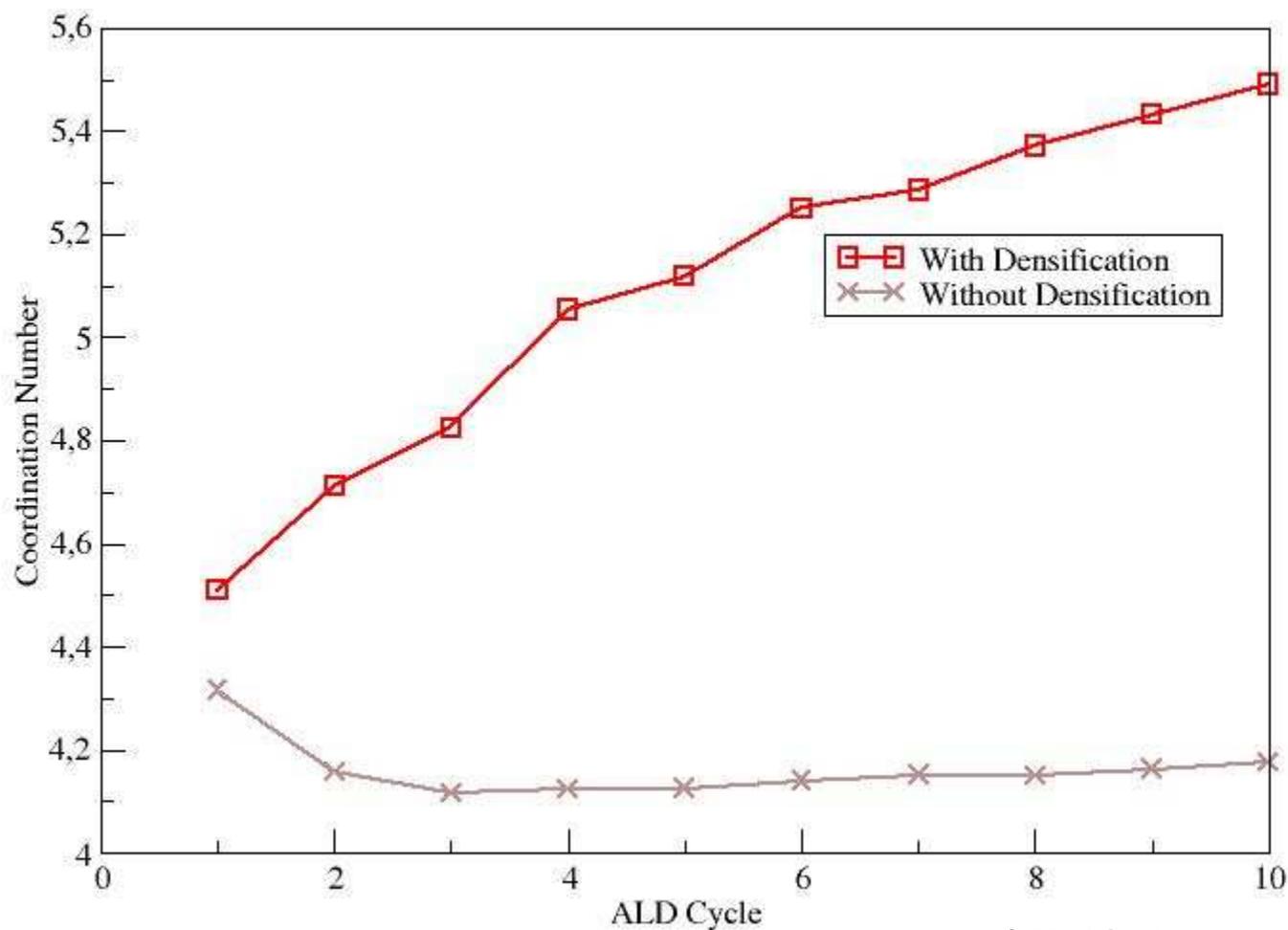
Experimental observation of a slowing down of coverage rate

→ densification mechanisms slower than surface reactions control the growth rate



Importance of densification mechanisms

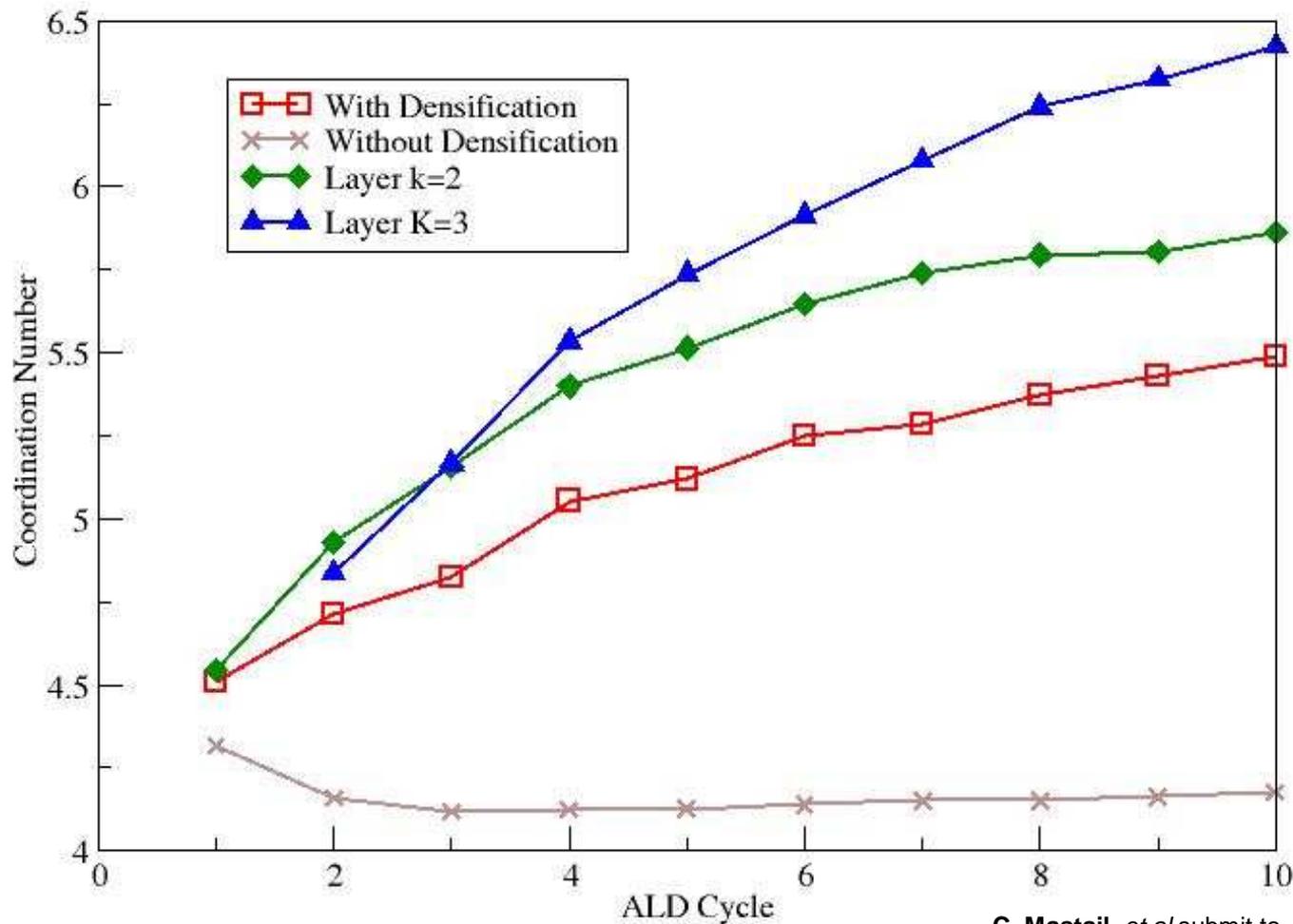
➤ *Hafnium coordination number*



Coordination number increases as a result of densification mechanisms

Discussion of the two growth regimes

➤ *Hafnium coordination number*

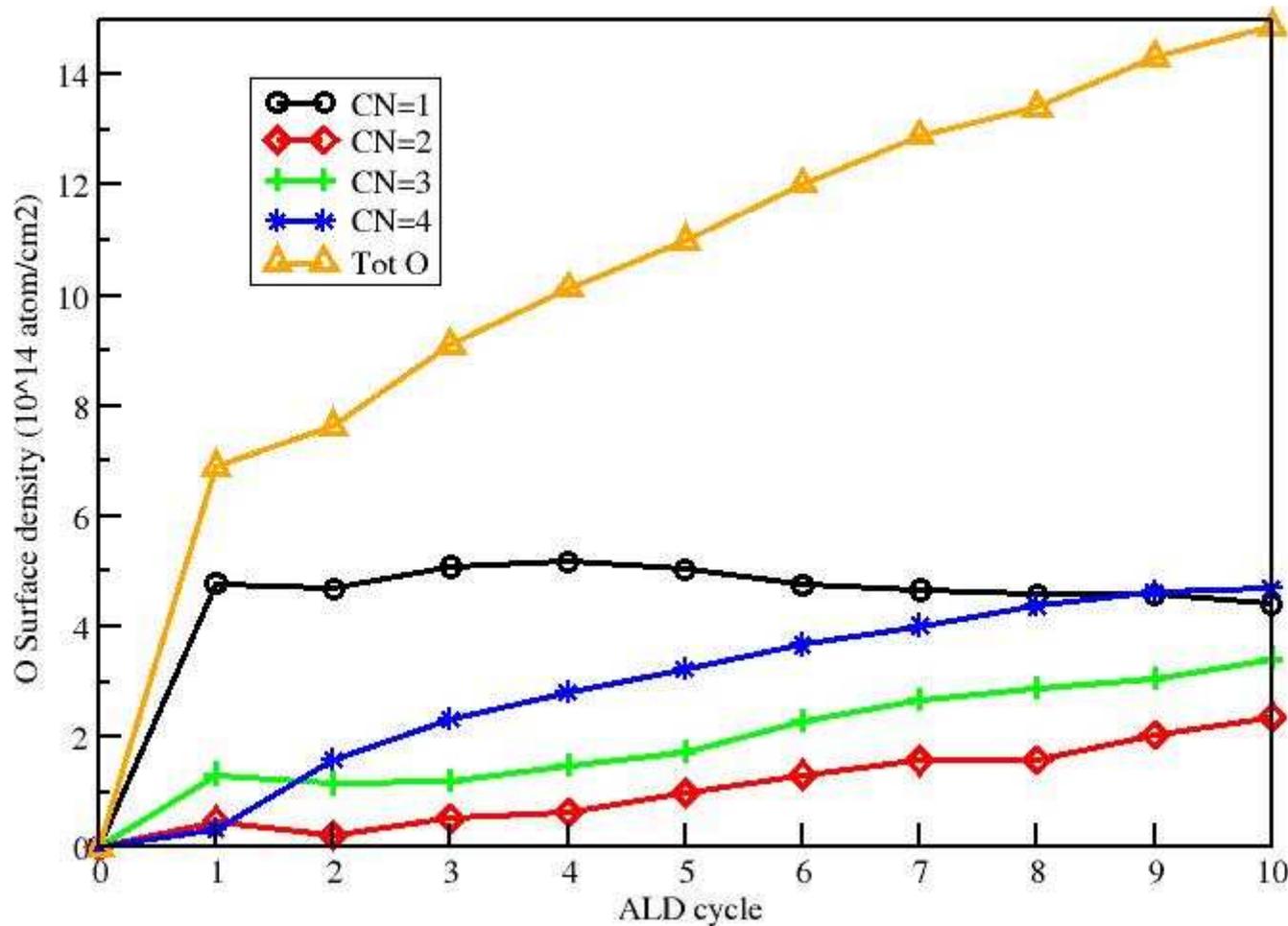


After the first two cycles the coordination number is higher than the average of the 2nd layer

➔ Low coverage of the higher layers
➔ Creation of bridge mechanisms explains the non-stoichiometric interface observed experimentally

Discussion of the two growth regimes

➤ *Oxygen coordination number*

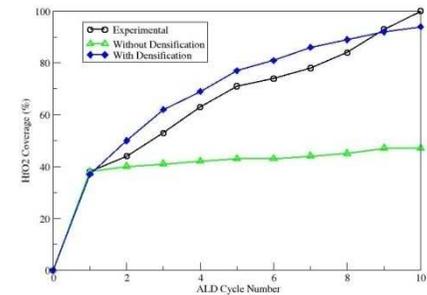


Number of singly bonded oxygen remains constant during the growth

Number of Oxygen with bulk coordination number increases quickly

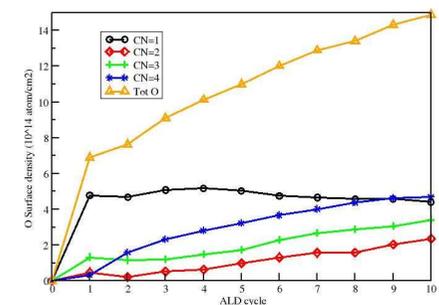
Importance of densification mechanisms

- *Densification mechanisms are needed to simulate the growth*



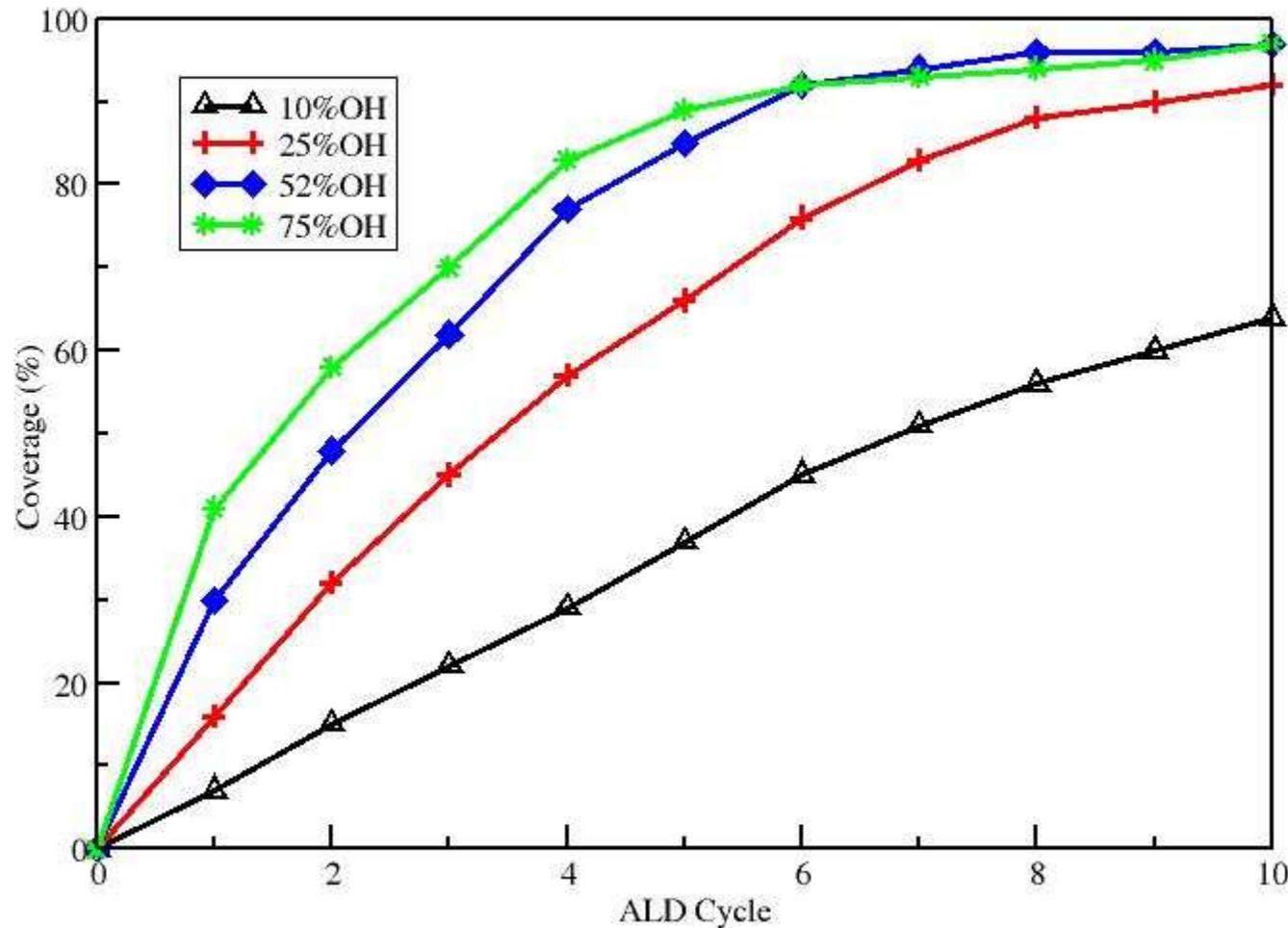
Discussion of the two growth regimes

- *Densification mechanisms build the oxide in the final ionic structure*



Substrate preparation

Temperature 300°C and pressure 1.33 mbar



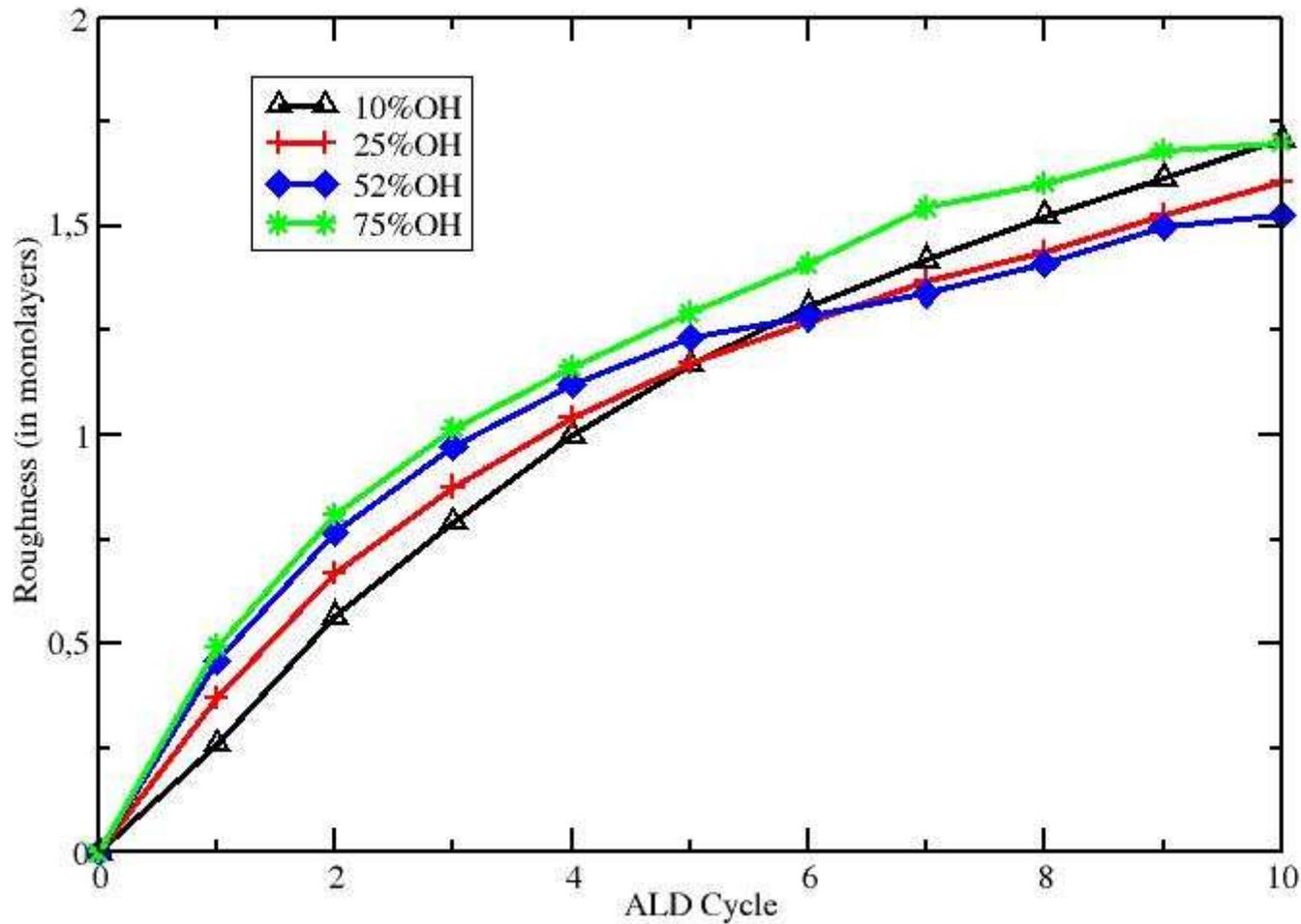
Influence on the initial regime

After same growth rate for all simulations

Growth of HfO₂ layer becomes possible even with low OH density due to densification mechanisms

Substrate preparation

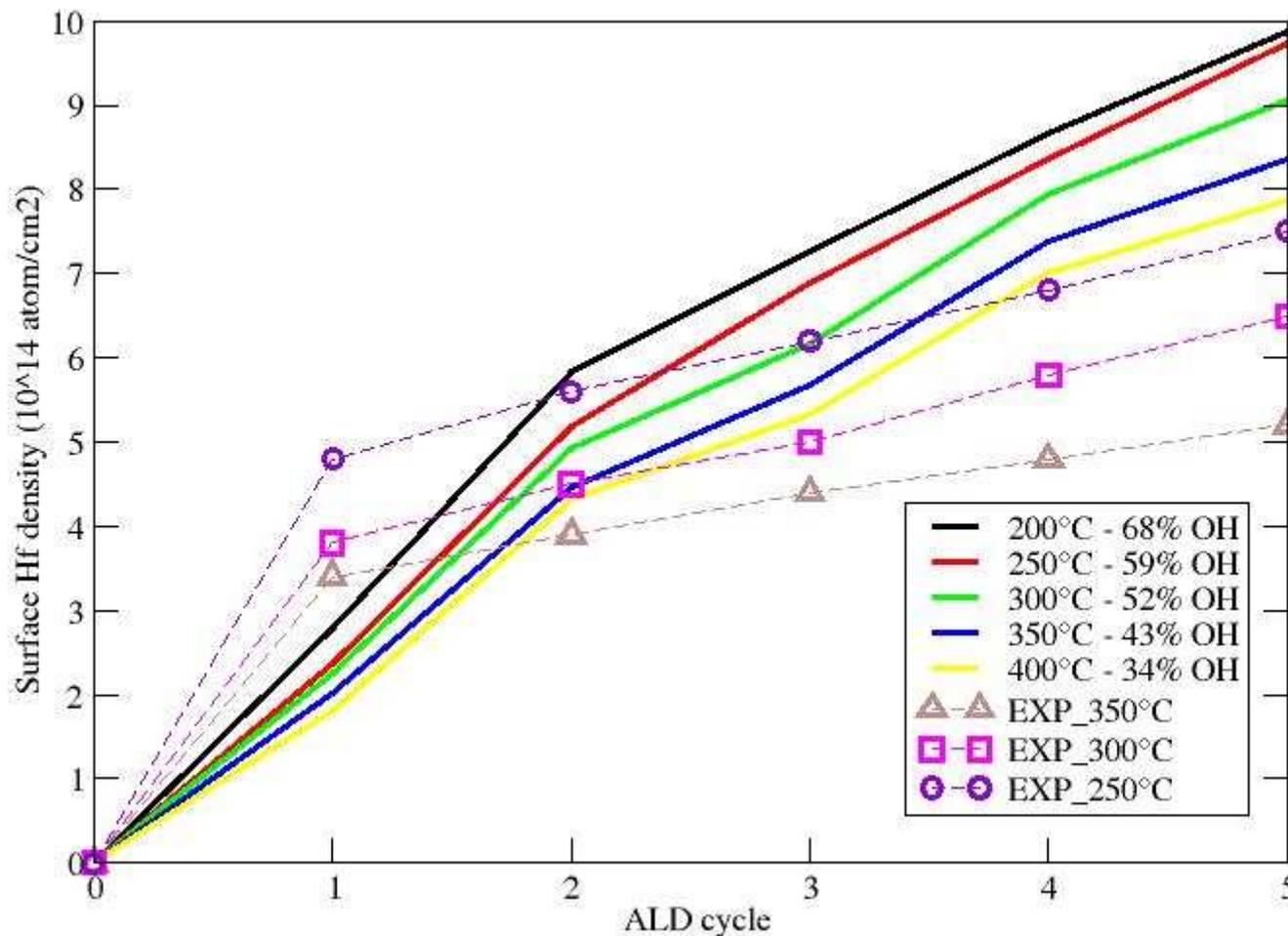
Temperature 300°C and pressure 1.33 mbar



Roughness is lower than 2 monolayers

Temperature and %OH

➤ *Simulated Hf surface density compared to TXRF experimental measurements*



%OH decreases with temperature (Zhuravlev)

Coverage rate increases with %OH

Conclusion

- Validation of the multi-scale strategy
- Development of a KMC simulation package for HfO₂ deposition
- Experimental validation of the implemented mechanisms
“densification is strictly needed for the description of ALD of HfO₂”
- Validation of the software package by comparison with experimental results: predictive nature
 - Growth rate with LEIS
 - Coordination numbers with XPS
 - Influence of growth parameters with TXRF and AFM
 - Densification-mediated surface migration

Perspectives

- Migration mechanism implementation
- Simulate thermal annealing (migrations, crystallisation...)
- Study interfacial SiO_2 re-growth, thanks to another existing kMC tool (Oxcad)
- Sensitivity to dopant migration
- Strain effect: nitrogen introduction
- Extension to multi-layer materials: $\text{HfO}_2/\text{Al}_2\text{O}_3$
- Extension to second generation materials: La_2O_3 ...

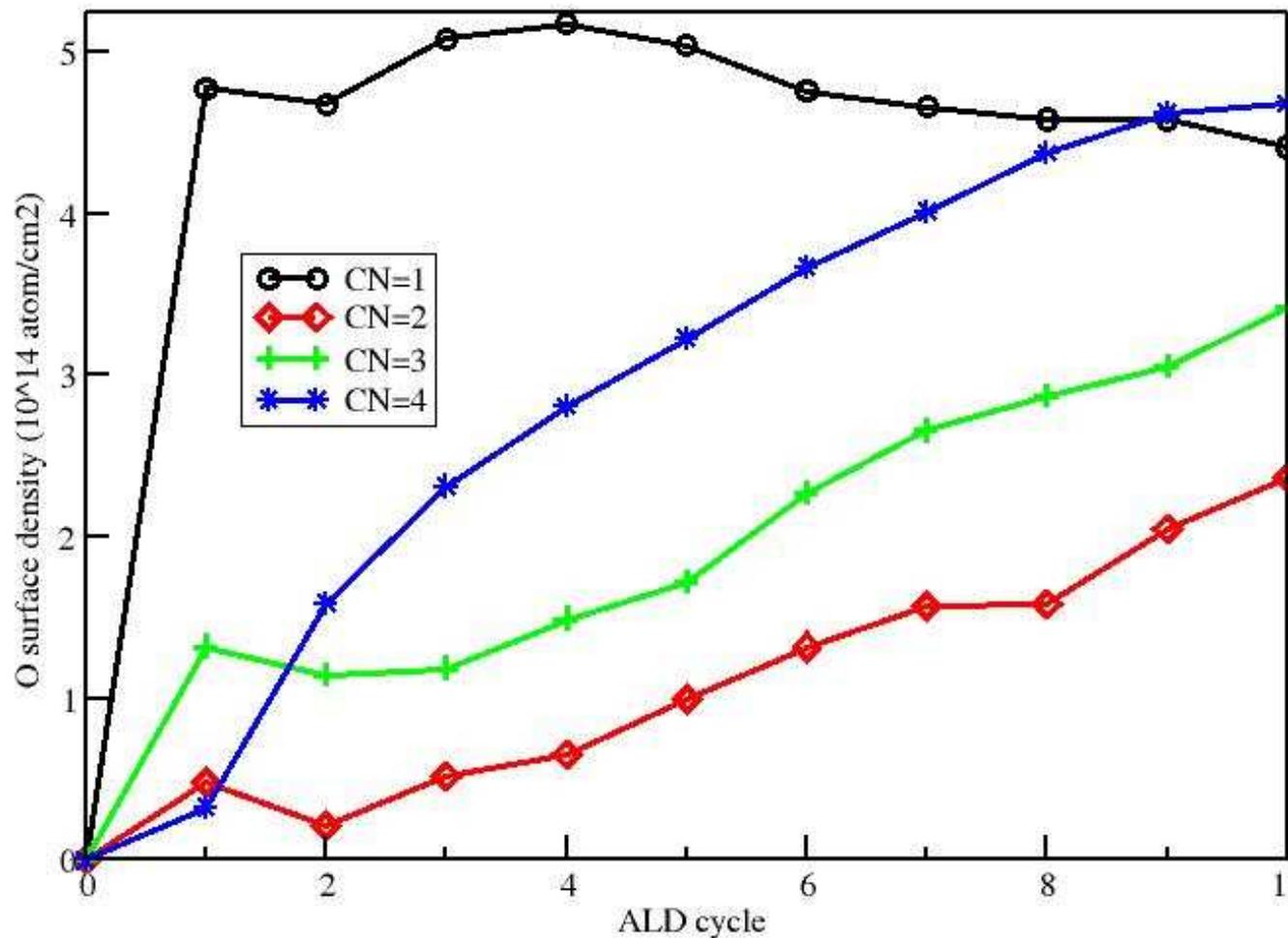
Thank you

Hikad.2 platform

- 'Hikad.2' = simulation (application 'kmc') + analysis (application 'anl')
- Written in Fortran90 ($\approx 10\ 000$ lines)
- Using 'AtomEye', free atomistic configuration viewer
J. Li, Modelling Simul. Mater. Sci. Eng. 11 173 (2003)
- Using 'XMgrace' free graph writer software
- Output compatible with traditional atomistic viewer using xyz files

Discussion of the two growth regimes

➤ *Oxygen coordination number*

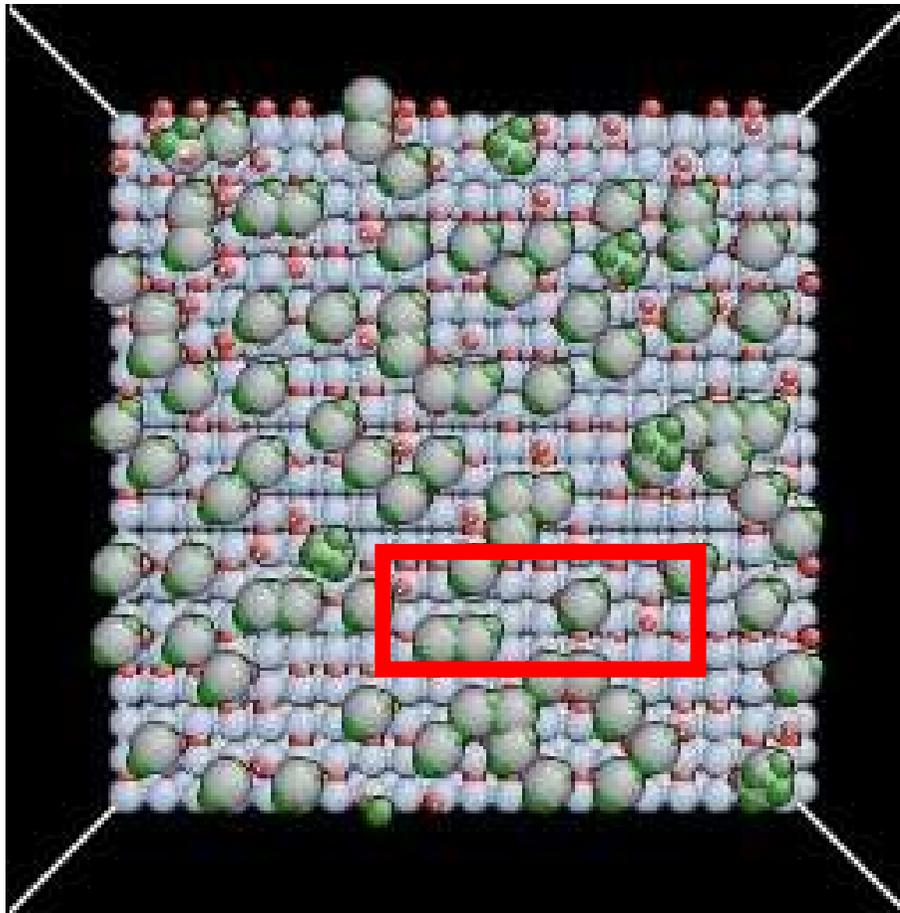


Number of singly bonded oxygen remains constant during the growth

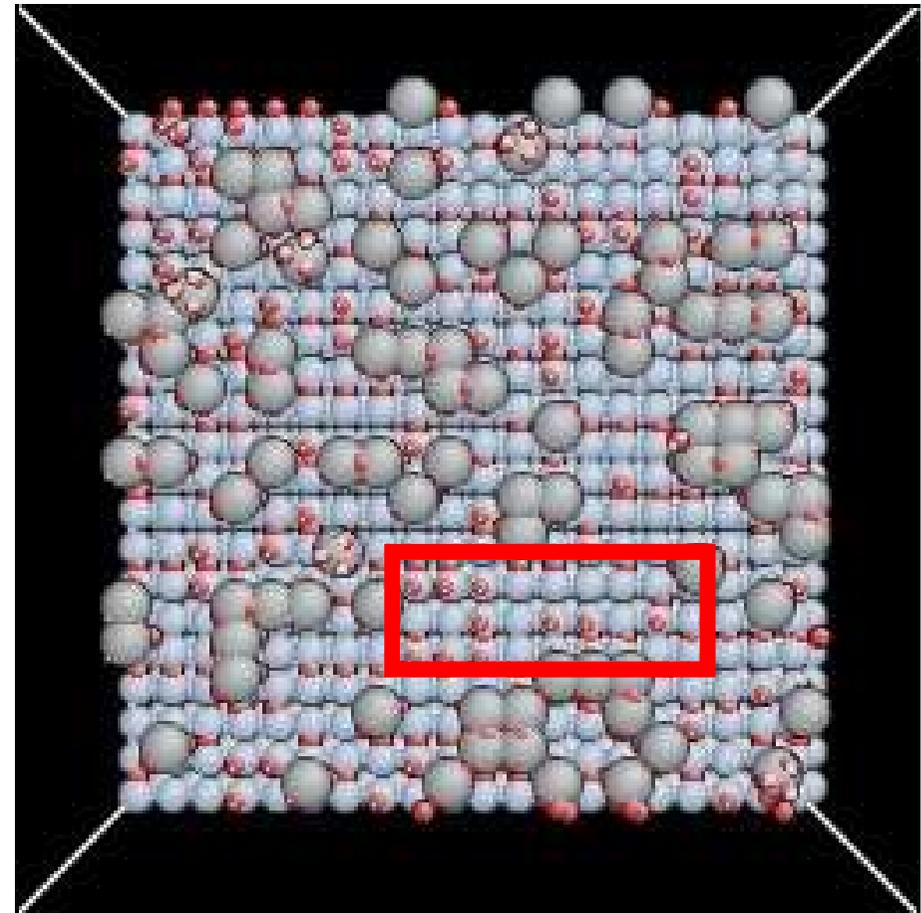
Number of Oxygen with bulk coordination number increases quickly

Migration process

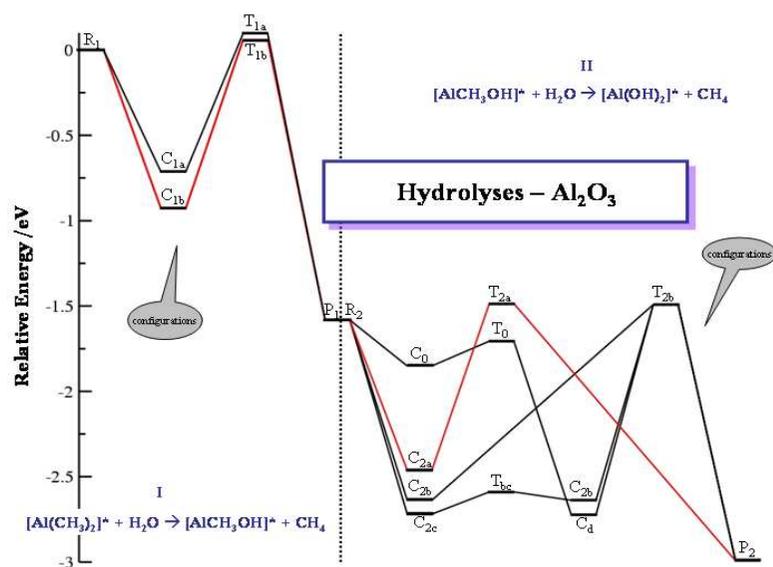
At the beginning of
the hydrolysis phase



At the end of the
hydrolysis phase



Our goals



La connaissance de chemins réactionnels permet d'aboutir à certaines caractéristiques locales. Par exemple, le faible coefficient de collage des précurseurs $ZrCl_4$ et $HfCl_4$ est clairement déduit des enthalpies de réaction et des barrières d'activation (Fig. 1). D'autres mécanismes, comme l'hydrolyse (Fig. 2), présentent des chemins réactionnels trop complexes pour aboutir à une conclusion, même locale. C'est le rôle des simulateurs Monte Carlo de prendre en charge la complexité, mais aussi d'examiner les conséquences plus globales des caractéristiques locales

Outline

Hikad: ALD of HfO_2 , ZrO_2 , Al_2O_3

Success: good description of the first regime

Limitation: saturation of the coverage and atom coordination

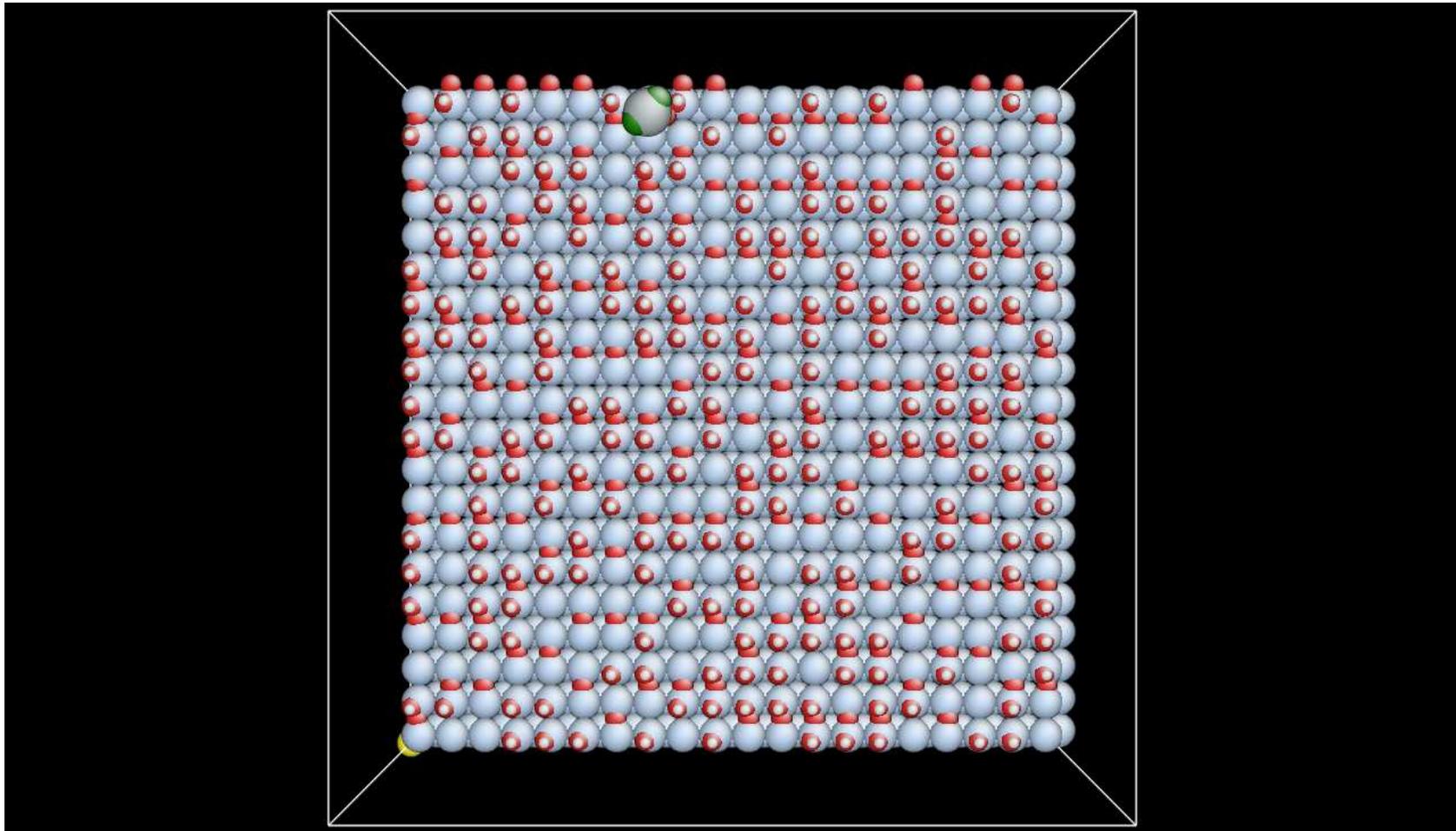
Hikad.2: ALD of HfO_2

Success: good description of the first and second regime

efficient implementation of densification mechanism

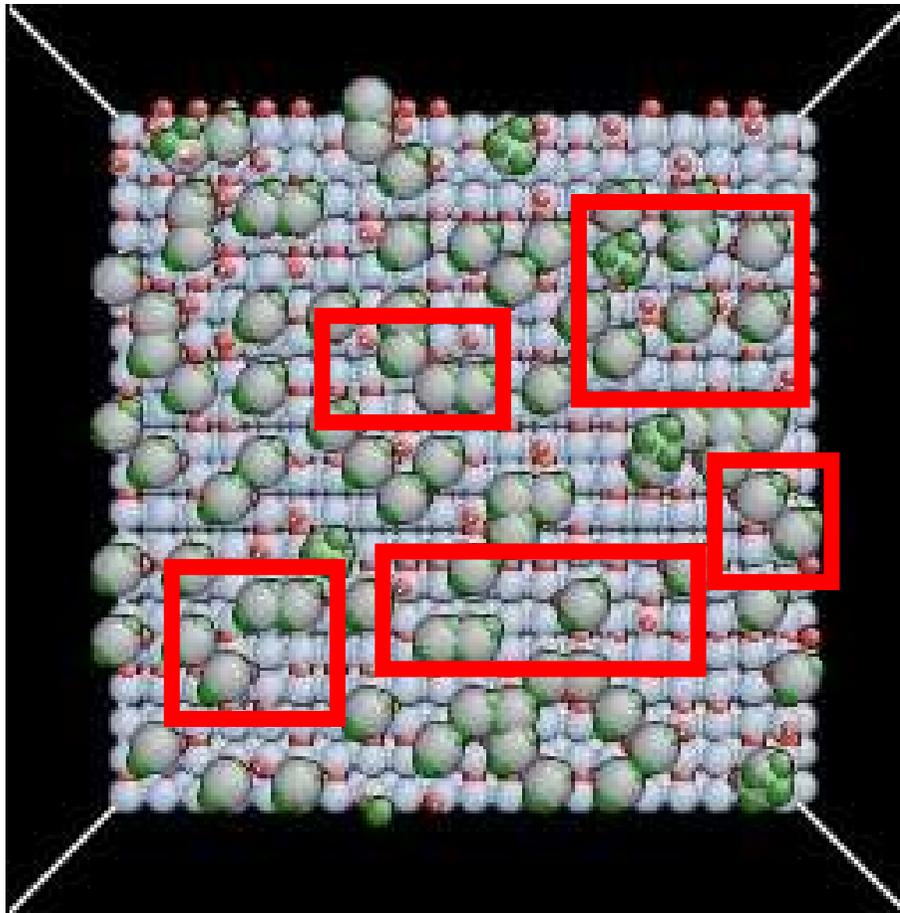
Densification-mediated migration process

12 last millisecond of the first hydrolysis phase



Migration process

At the beginning of
the hydrolysis phase



At the end of the
hydrolysis phase

