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Research Group of Computational Nanoelectronics
NANOCOMP

Molecular dynamics simulation of the full operation cycle of a HfO2-based RRAM cell

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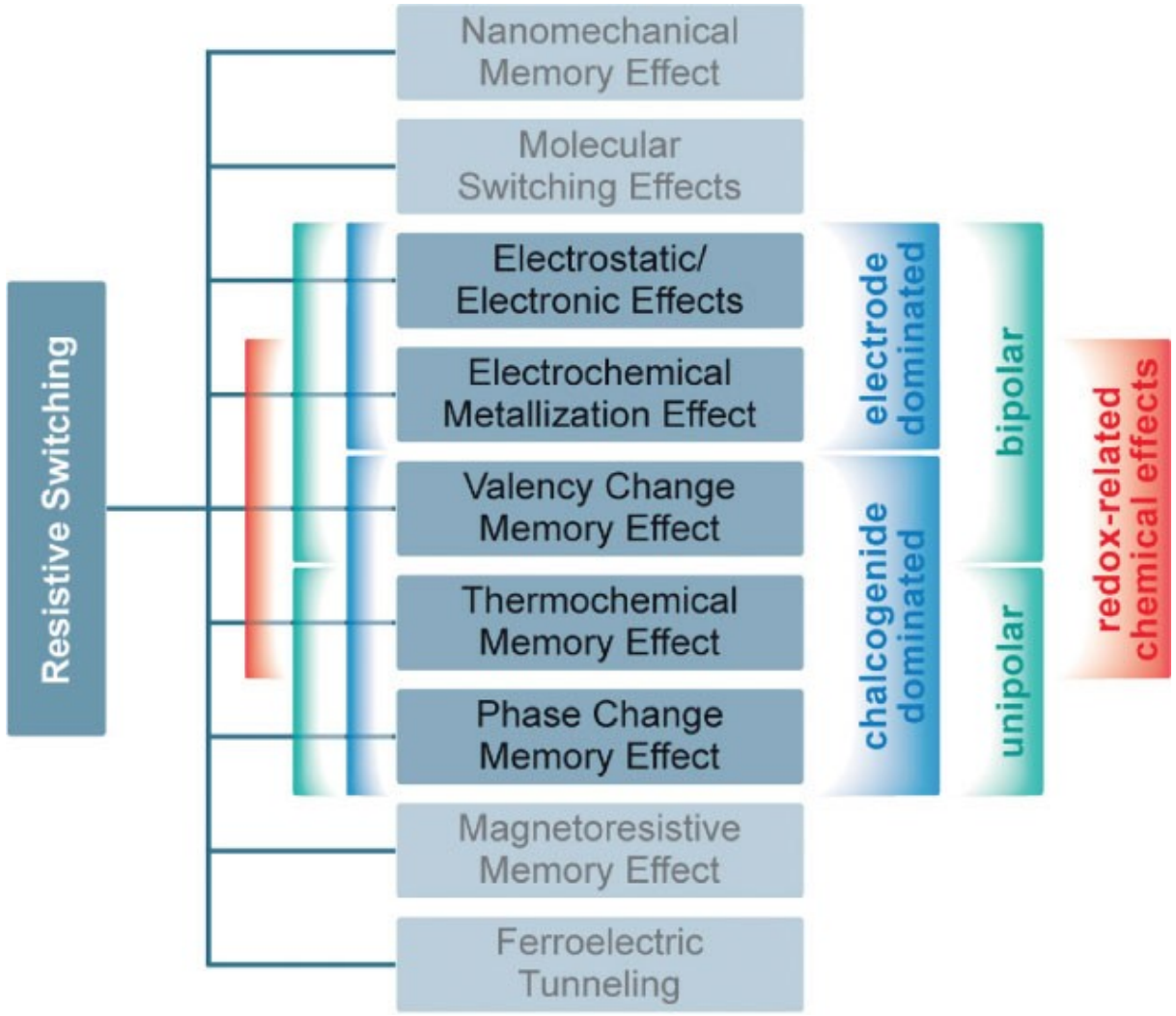
Resistive switching (RS) phenomena

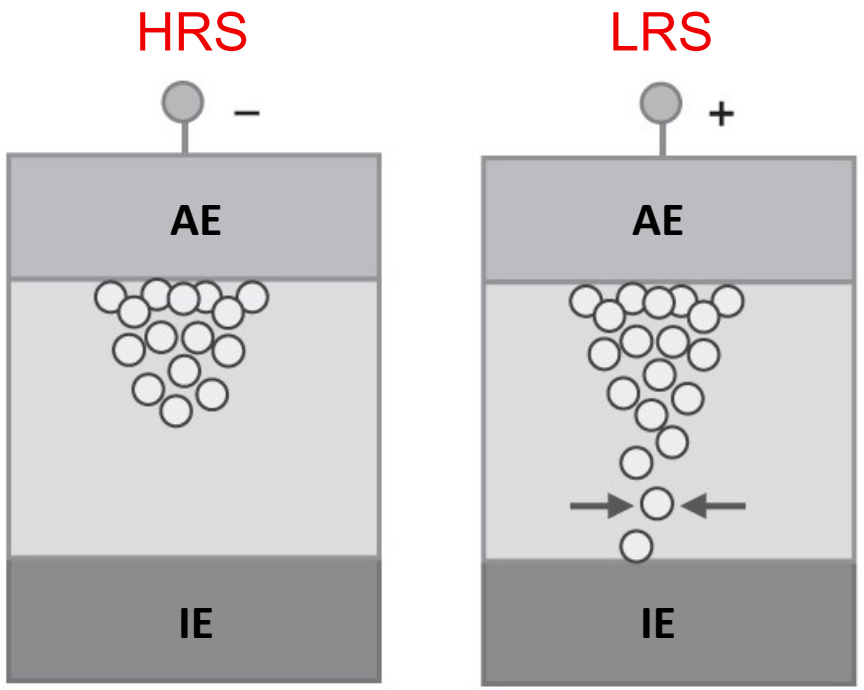
- **RRAM** devices **store bits by switching** memory cells between high resistance states (HRS) and low resistance states (LRS).

- The transition from HRS to LRS can be used to implement **artificial synapses** for **neuromorphic computing** or FPAAs.



Rainer Waser et. al., Adv. Mater. 2009, 21, 2632–2663

General mechanism of filamentary RS



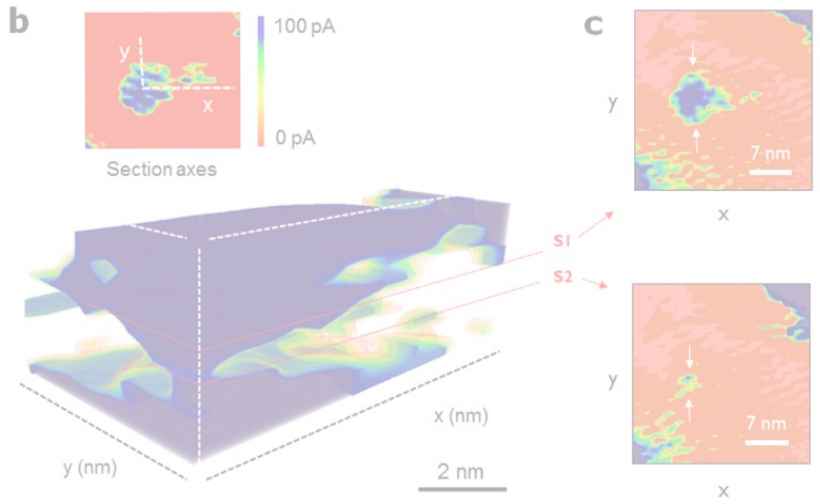
AE: active electrode
IE: inert electrode

- **Electrochemical metallization memories (ECM):** where the CF consists of metallic atoms injected from an active electrode into the dielectric.
- **Valence change memories (VCM or OxRAM):** associated to the valence change of the cations in the oxide produced by the clusterization of oxygen vacancies.

Experimental and theoretical evidence of filamentary conduction in OxRAM devices

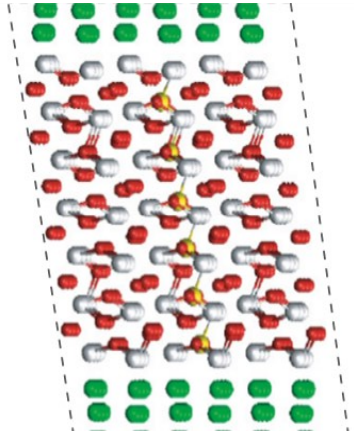
- AFM **three-dimensional** reconstructed **image of conductive channel** in oxide-based resistive switching memory

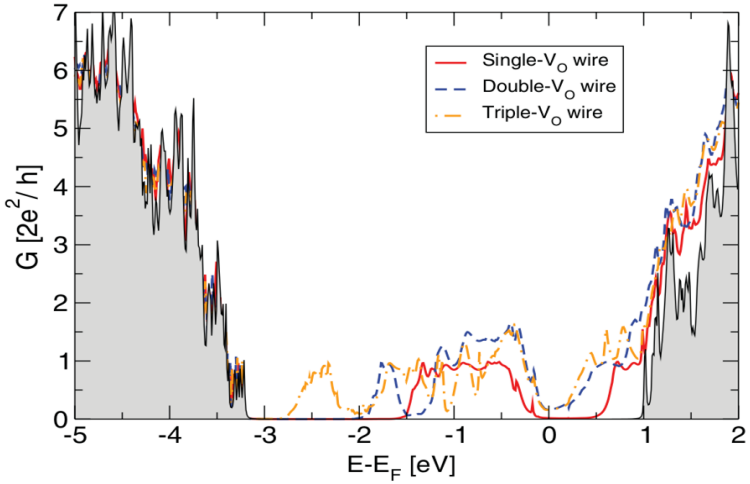
Umberto Celano et. al., Nano Lett. 2015, 15, 7970−7975.



- **Transport properties of oxygen vacancy filaments** in metal/HfO_2/metal structures calculated with NEGF DFT

Cartoixà et. al. Phys. Rev. B, **86** (2012) 165445

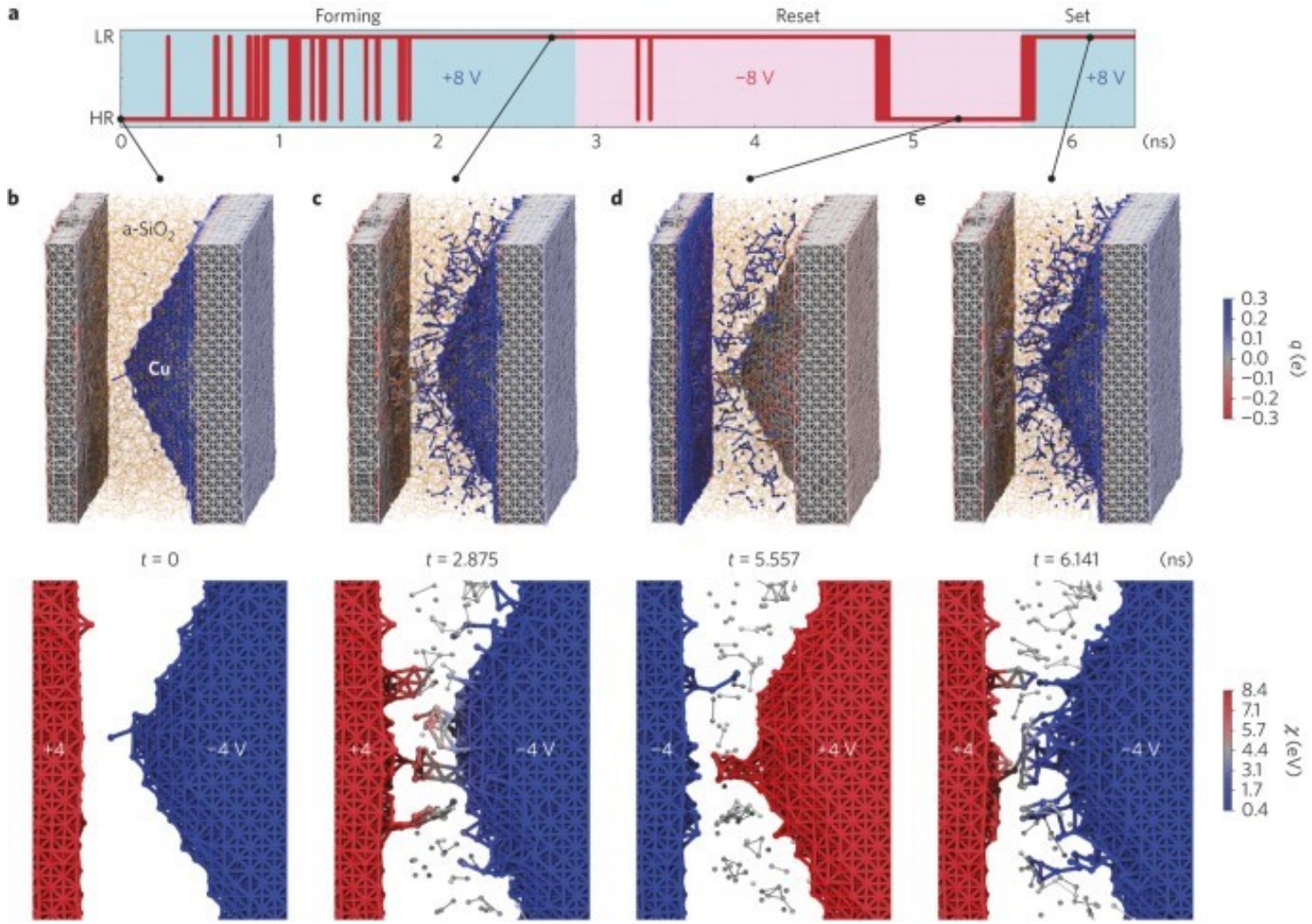




Molecular dynamics (MD) using EChemDID method allowed to simulate the operation of ECM

- EChemDID alters the electronegativities of the electrodes according to the supplied voltage:
  $\chi \rightarrow \chi \pm \varphi/2$

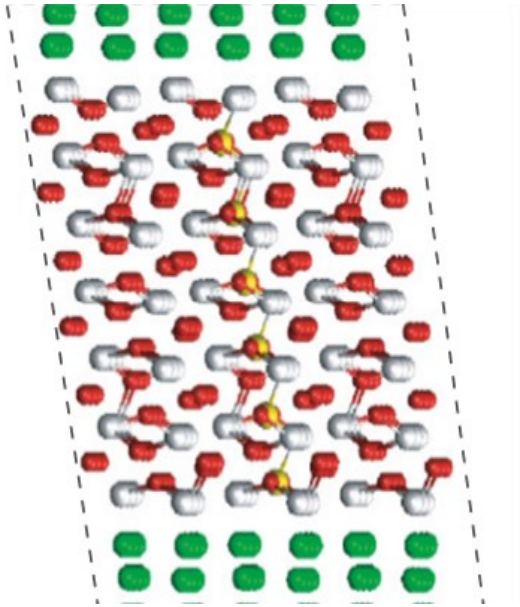
- Metallic atoms in contact with one electrode are given the corresponding χ alteration.
- Isolated metallic atoms or clusters contacting both electrodes are assigned a linear interpolation.



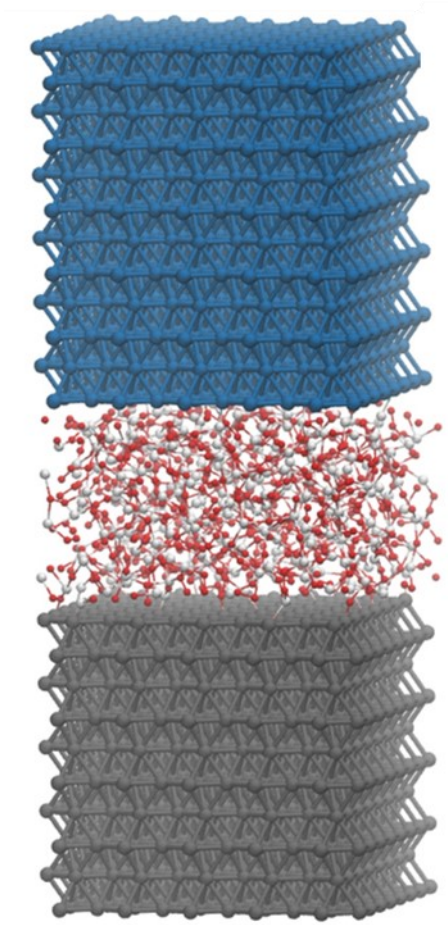
Onofrio et. al Nature Mater **14,** (2015) 440–446.

How do we define an oxygen vacancy filament in VCM cells?

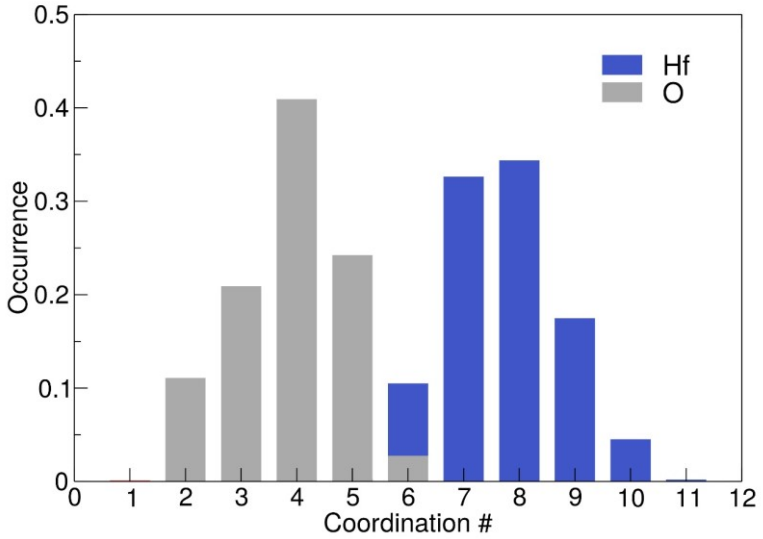
Conductive filament in **monoclinic HfO_2**



CF of Hf atoms bridging two oxygen vacancies (oxygen coordination = 5)



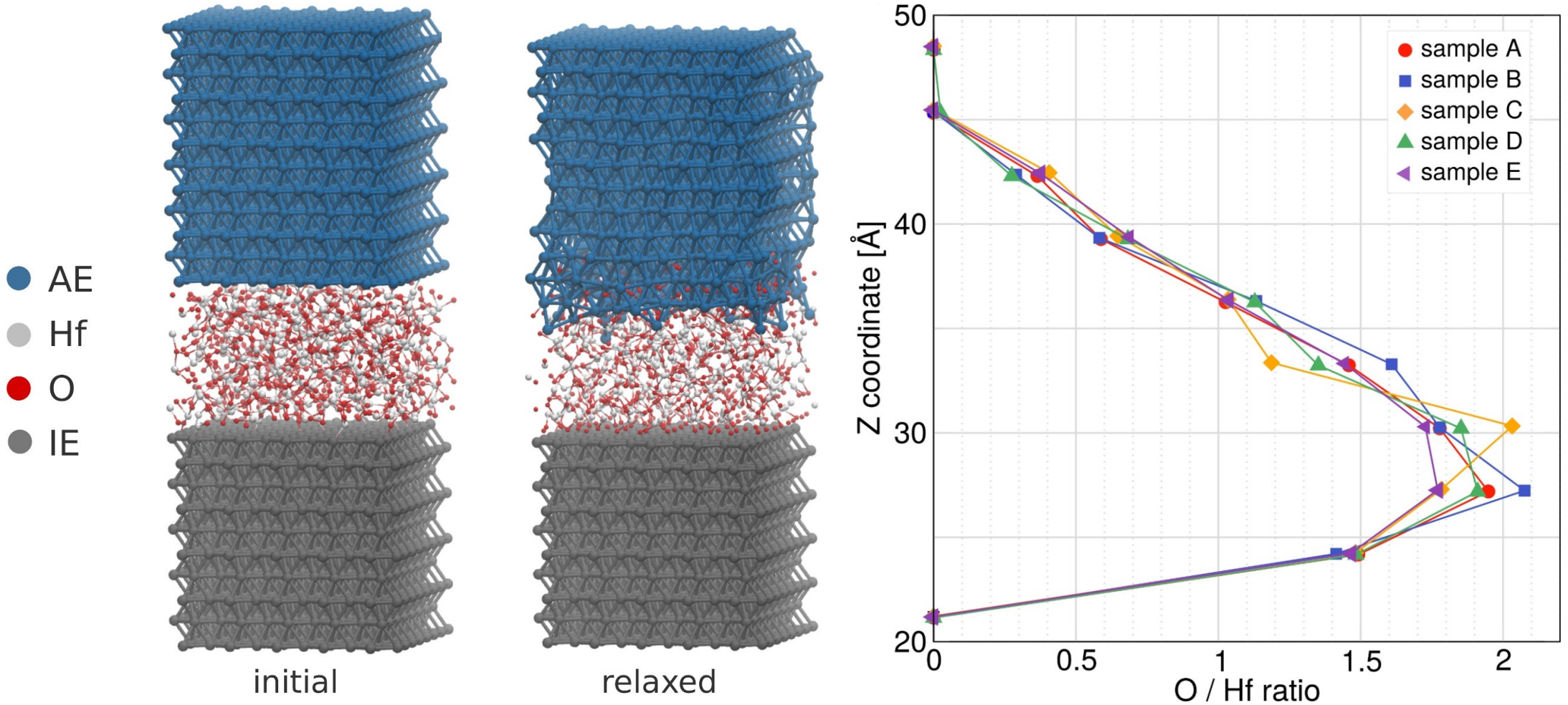
Coordination distribution in **amorphous HfO_2**



In our model, metallic Hf are described by Hf atoms with oxygen coordination ≤ 5.

Cartoixà et. al. Phys. Rev. B, **86** (2012) 165445

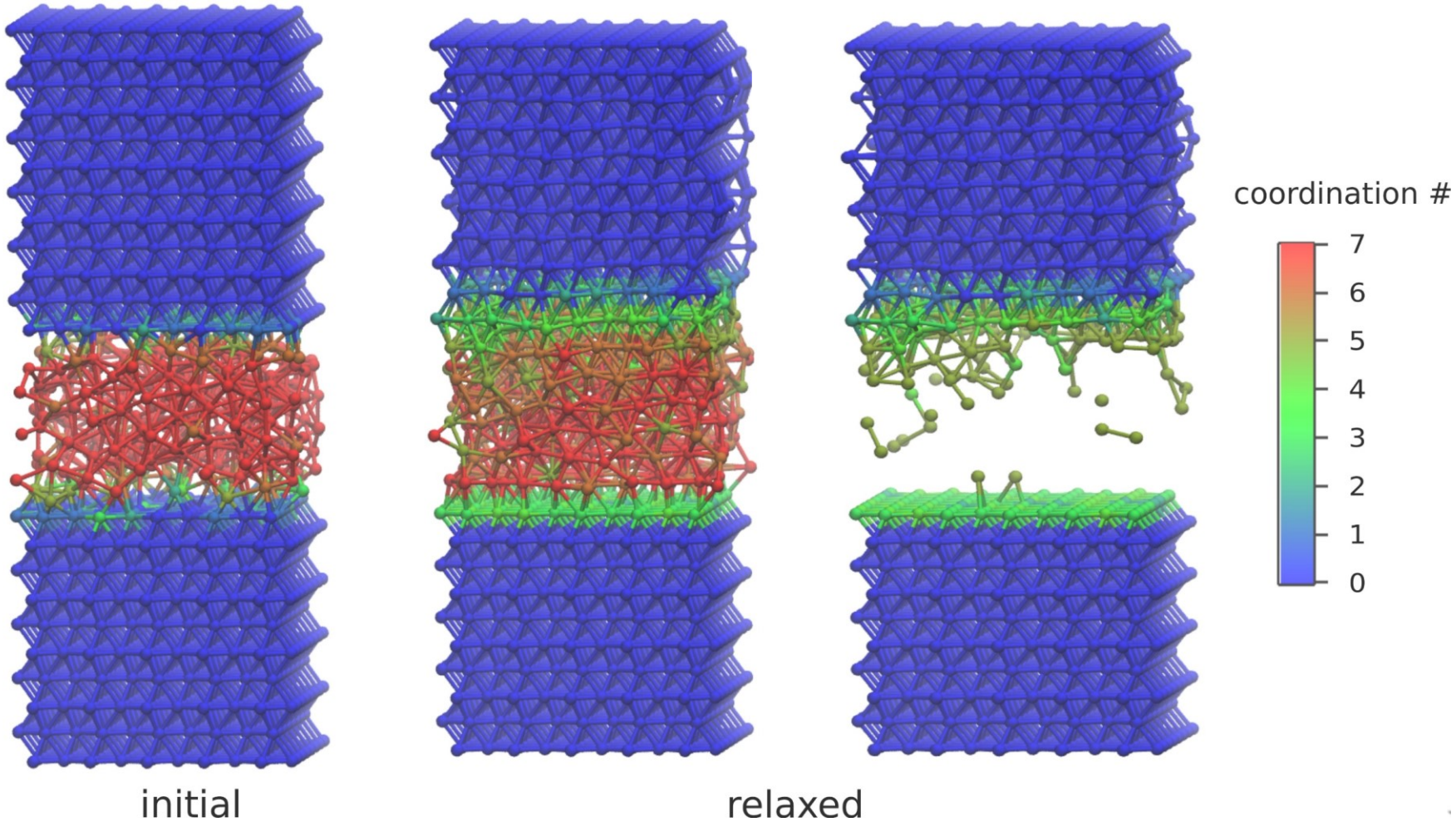
Hf/HfO2 interface relaxation



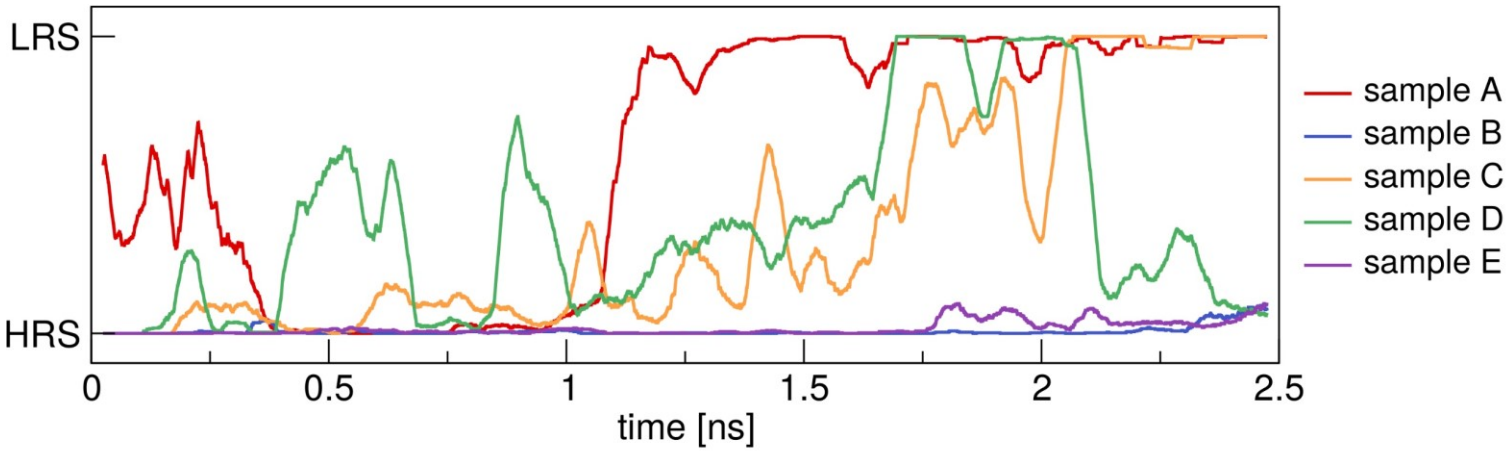
- **MD relaxation at 300 K and 1 atm** (allowing volume change along z).
- The time considered of 100 ps is long enough to ensure no more O atoms migrate towards active electrode.

Relaxation process

- The redox process induces an increase of oxygen vacancies in the oxide layer.
- Relaxation does not induce the formation of the conducting filament.
- From now on we only plot undercoordinated metal atoms. Lines connect atoms below a 3.9Å threshold.

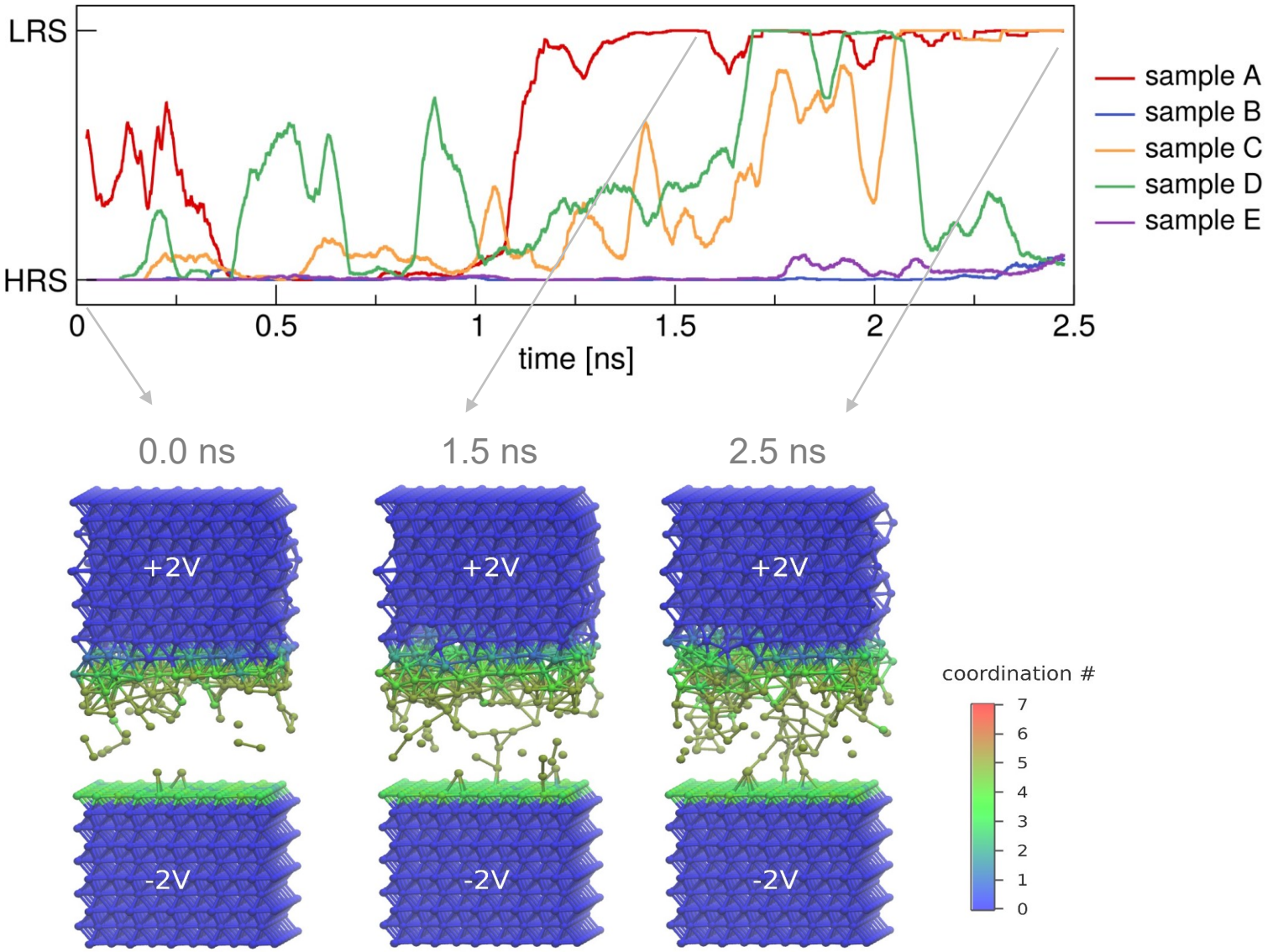


Forming

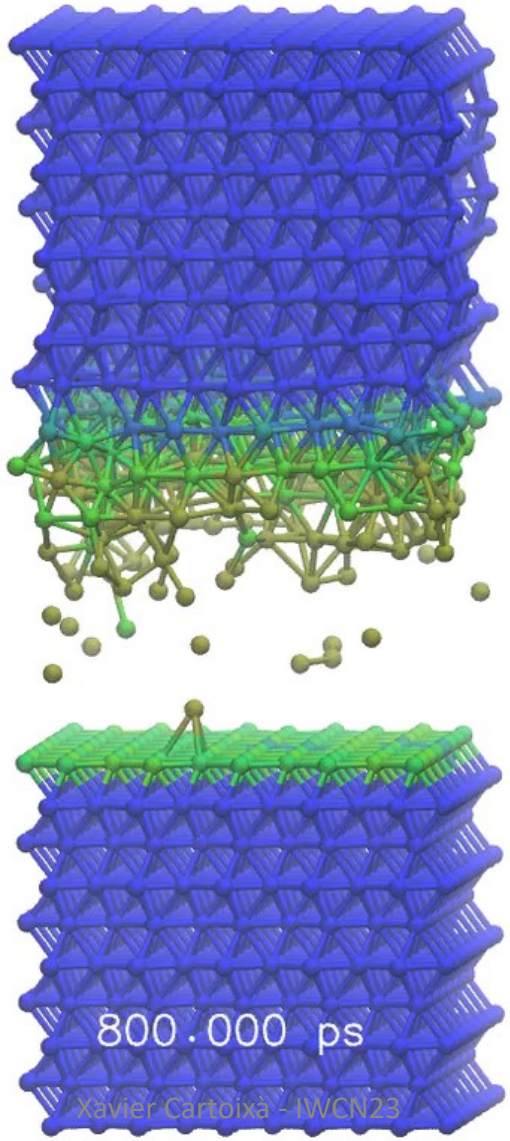


Relatively low forming probability due to the small cross section of the simulated devices

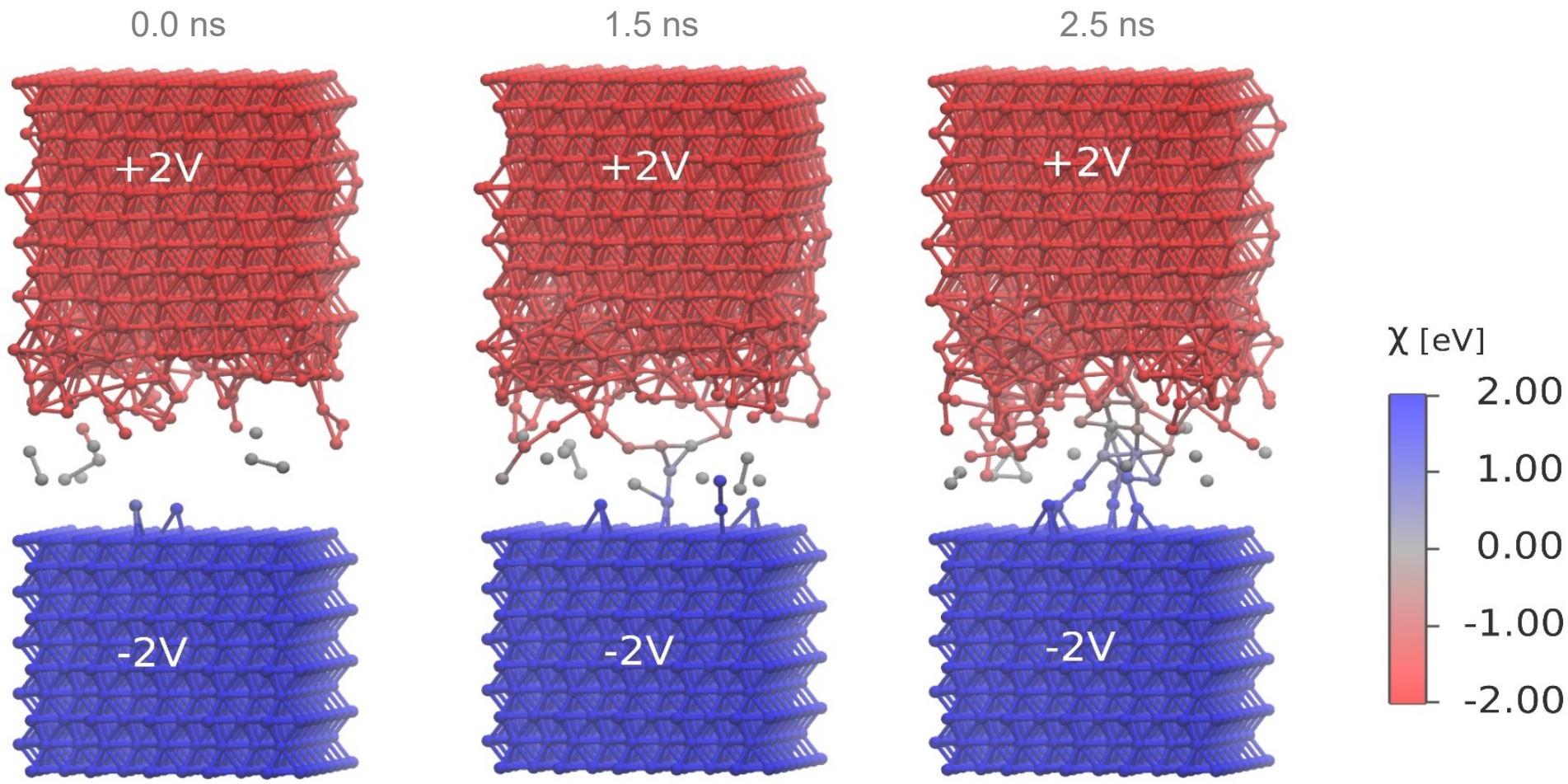
Forming


LRS
HRS
0
0.5
1
1.5
2
2.5
time [ns]
sample A
sample B
sample C
sample D
sample E
0.0 ns
1.5 ns
2.5 ns
+2V
+2V
+2V
-2V
-2V
-2V
coordination #
7
6
5
4
3
2
1
0

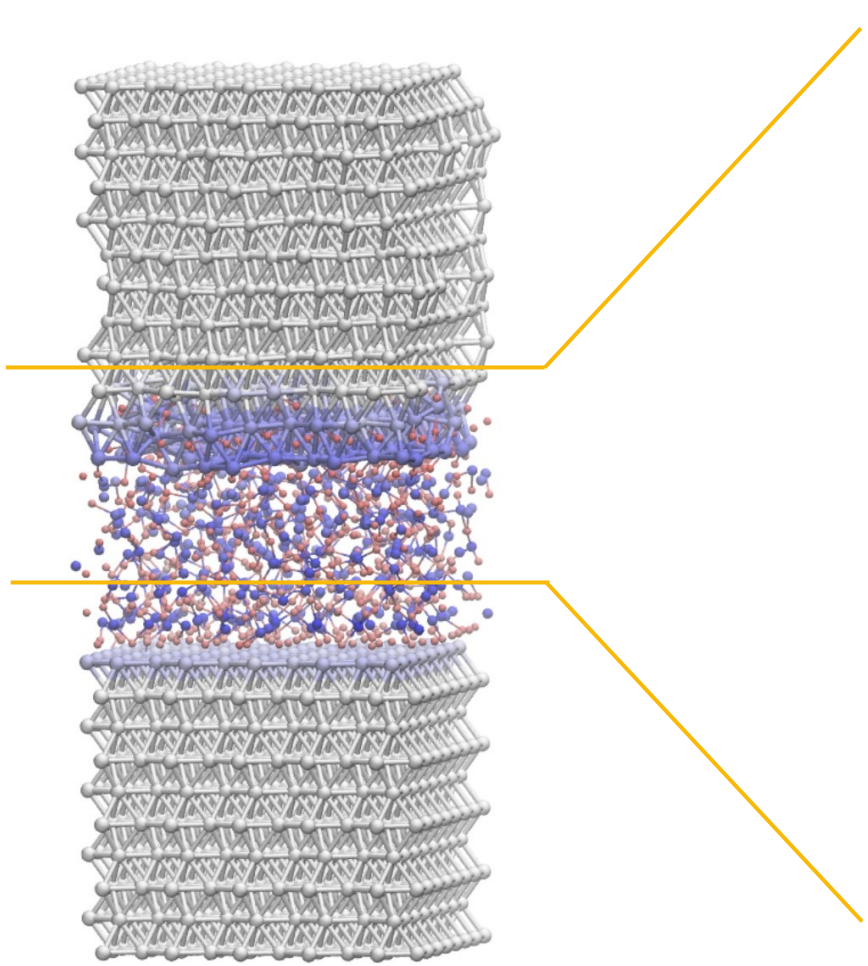
Forming dynamics

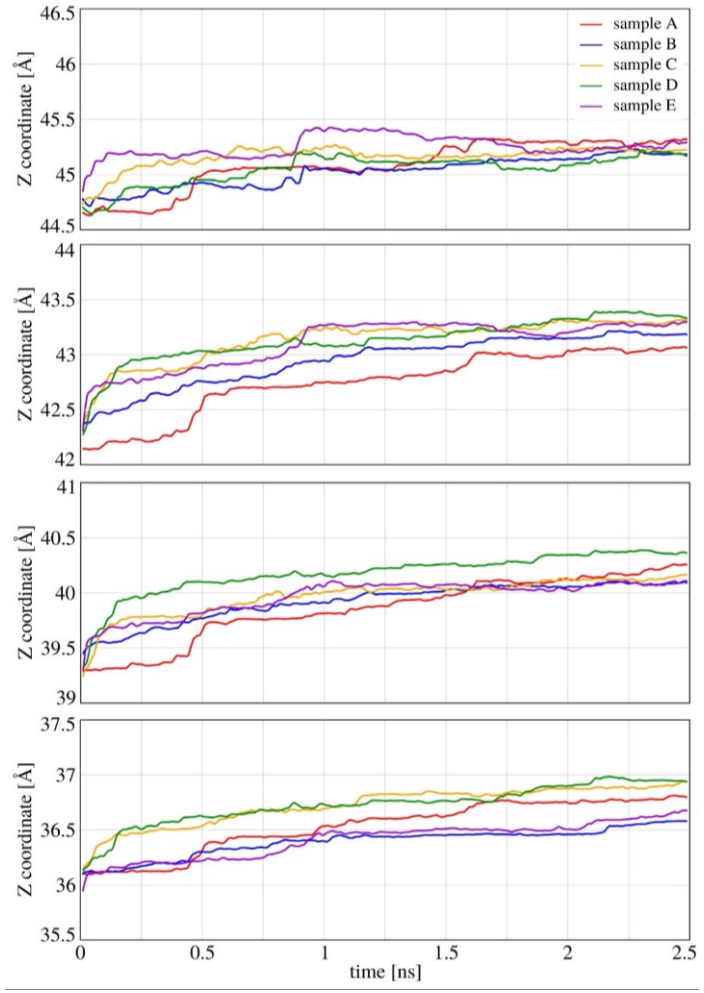


Electronegativity propagates dynamically as the conductive filament forms

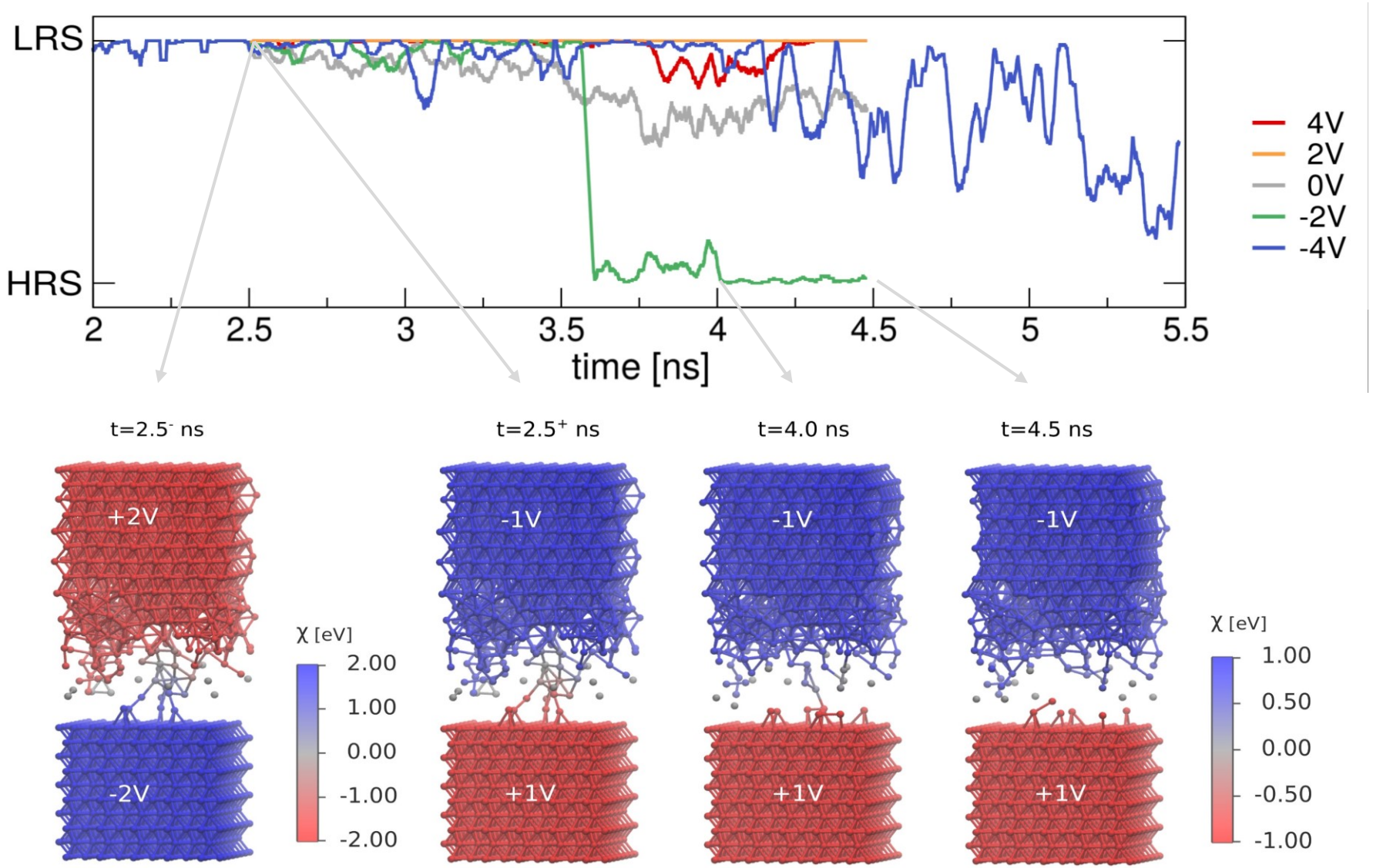


Forming mechanism involves cascade of oxygen displacements towards AE

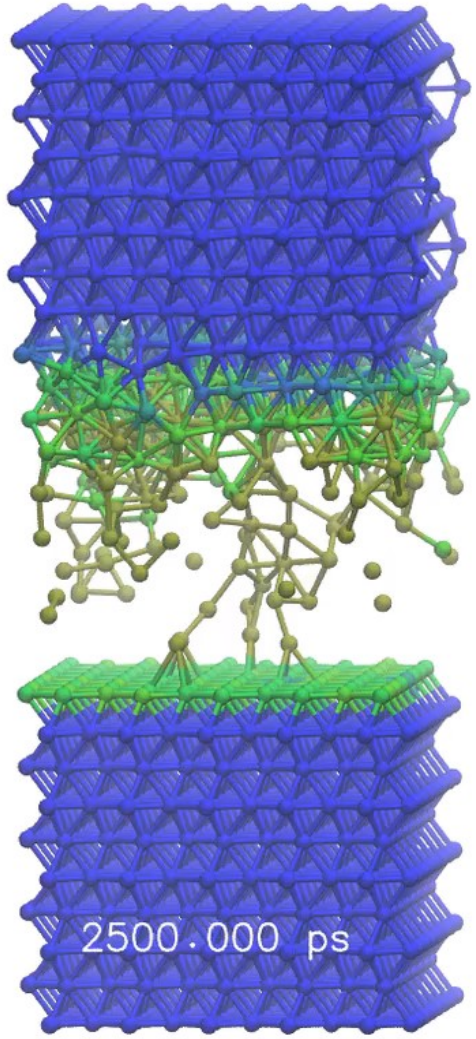




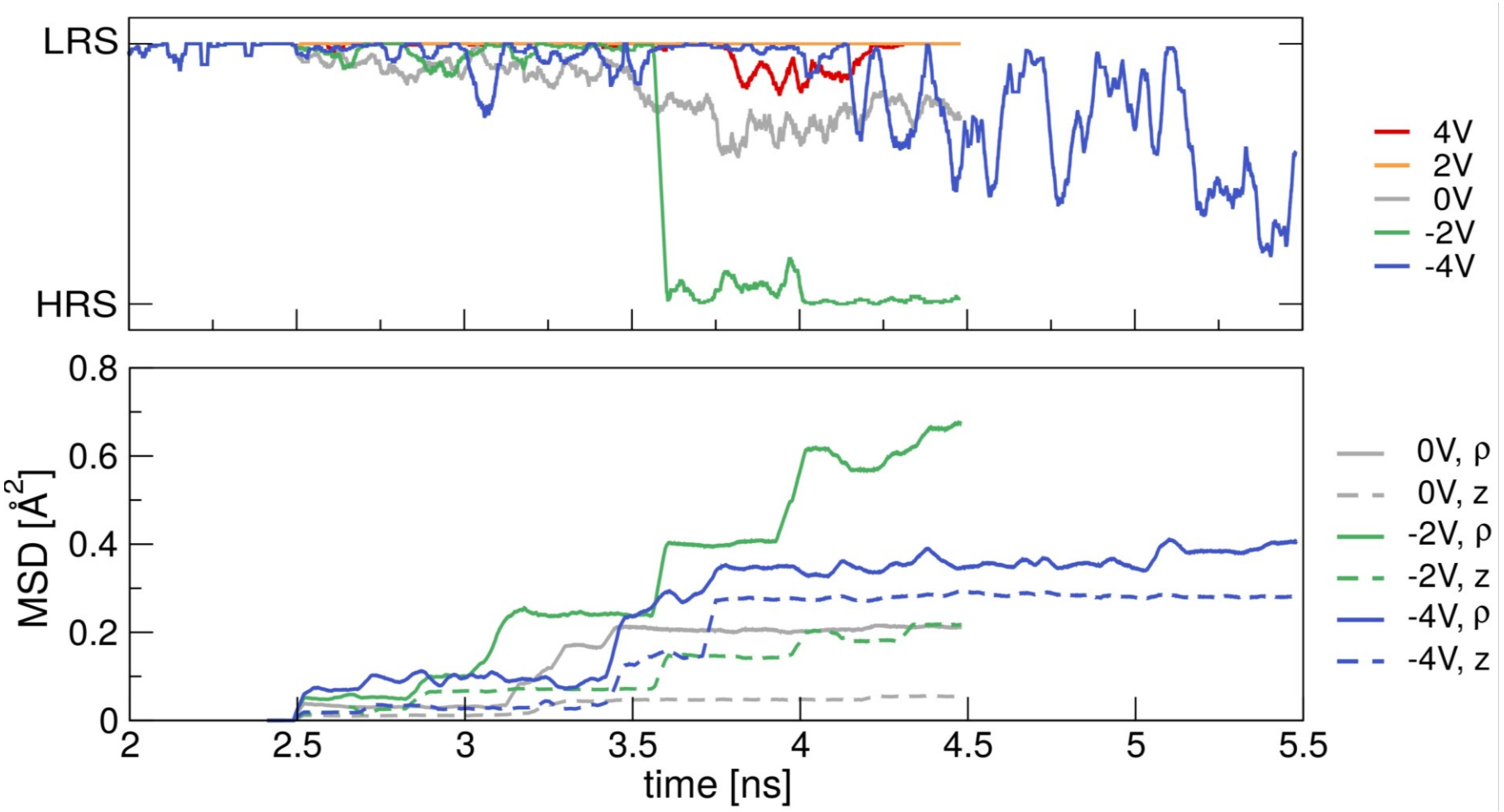
Filament stability at different applied bias



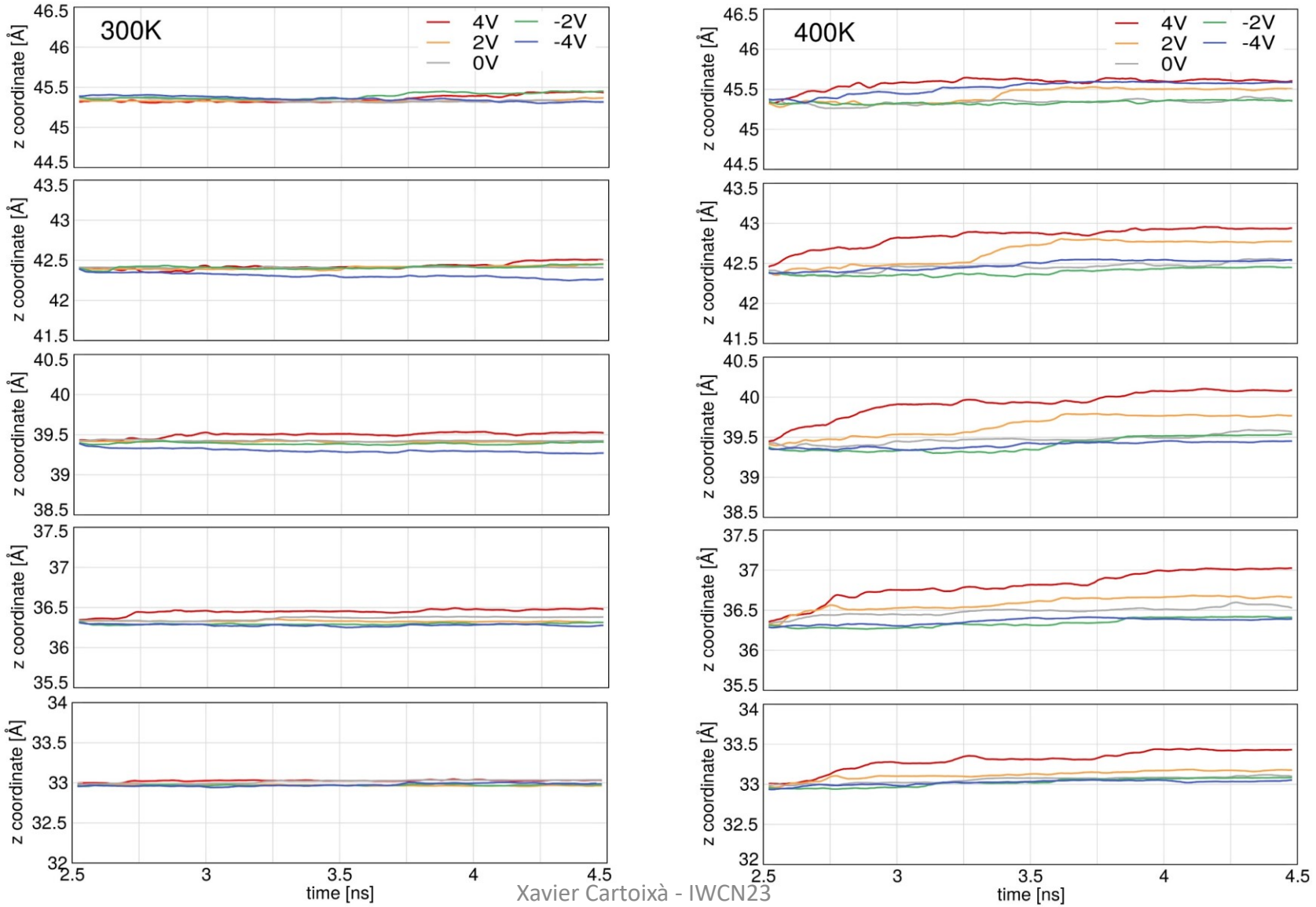
Reset dynamics



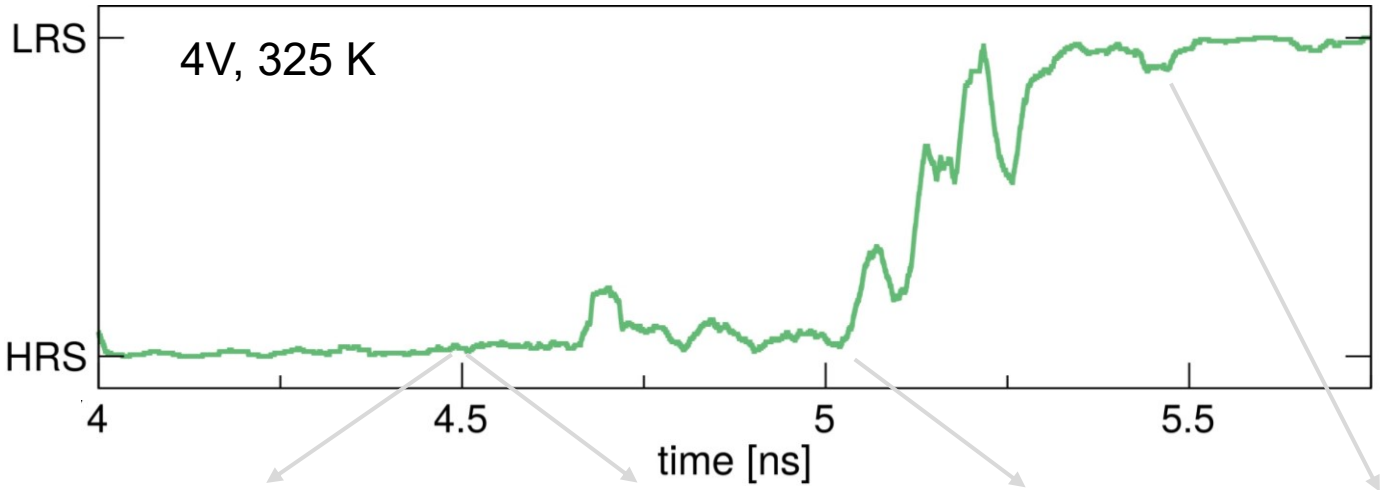
Reset produced by oxygen diffusion in the xy plane



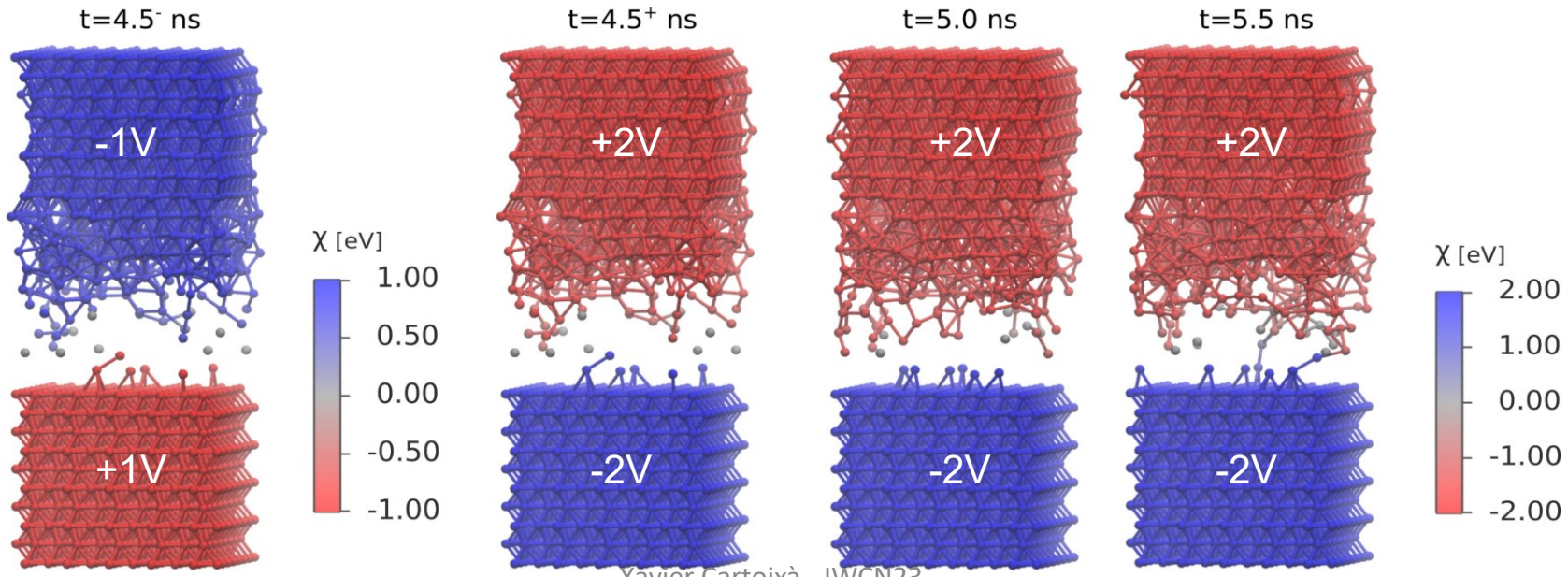
Oxygen diffusion during reset



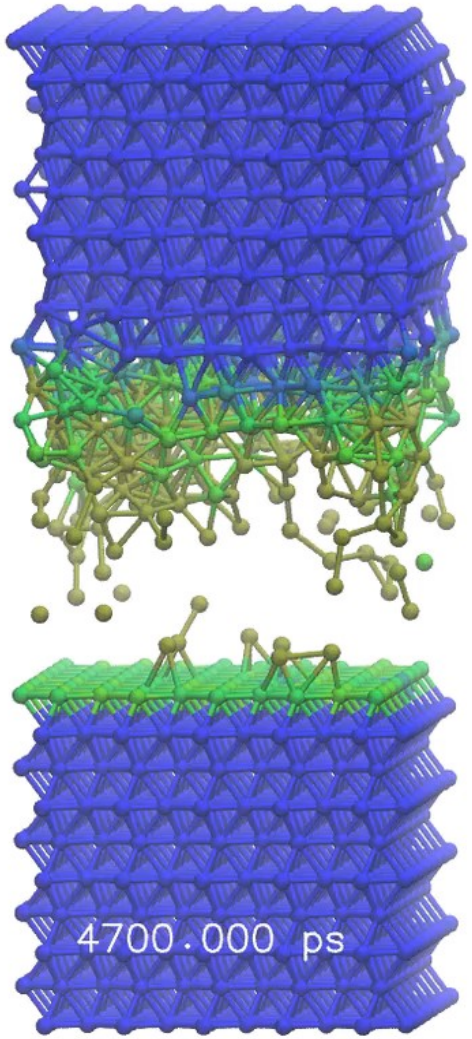
Set process



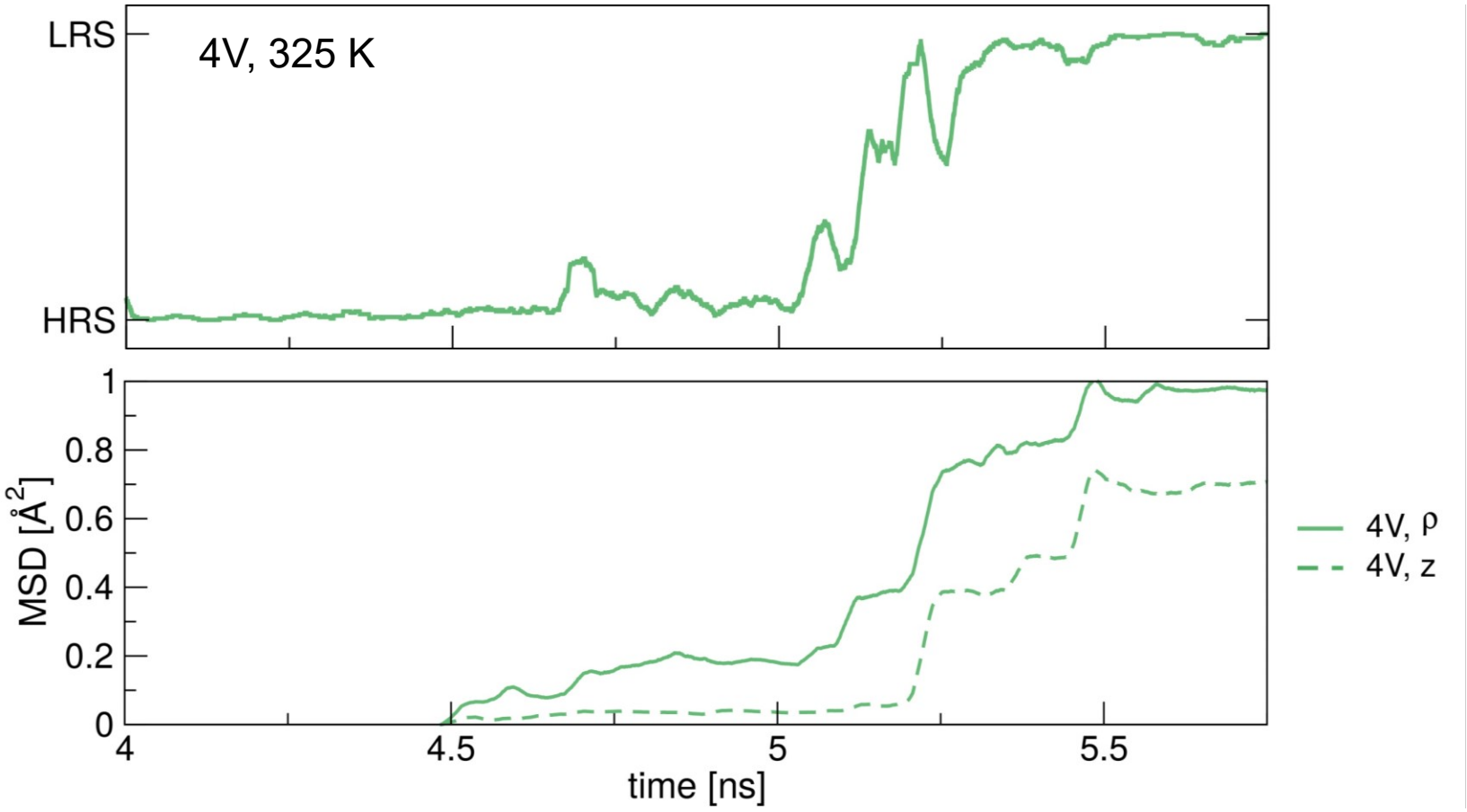
Temperature increased slightly to favour CF formation within shorter times



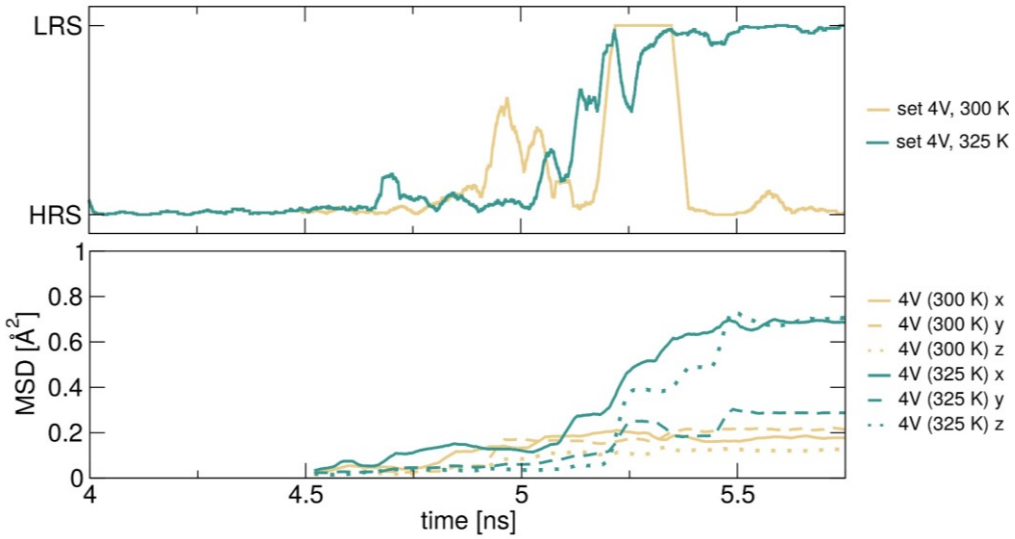
Set dynamics

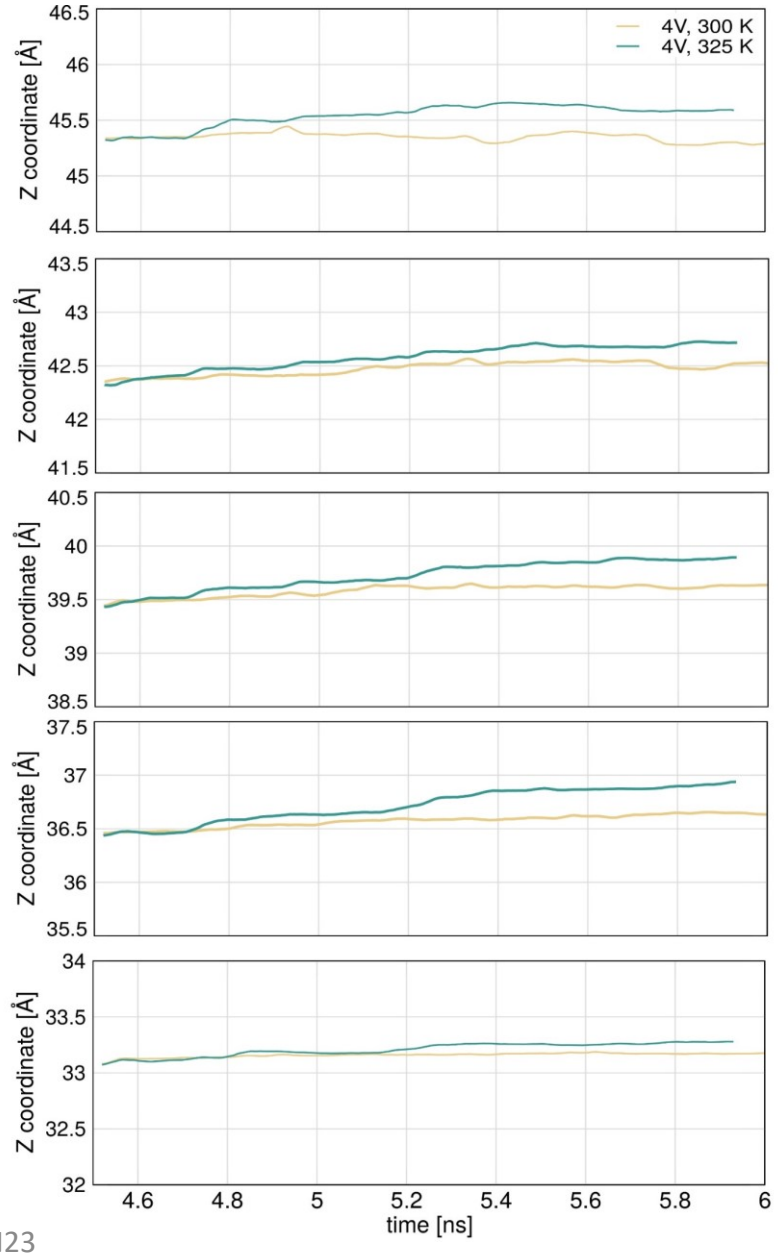


Set produced by oxygen diffusion in the xy plane, rather than vertical migration



Oxygen diffusion during set





Take home messages

- In amorphous oxides an **oxygen vacancy** should be thought of a proxy for an **undercoordinated metallic atom**.

- Strong indications that **lateral diffusion is responsible for RESET and SET** events.

Acknowledgments

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  - RTI2018-097876-B-C21
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