Influence of thickness and surface composition on the stability of ferroelectric polarization in HfO_2

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MRS Spring Meeting,
May 10^{th}, 2022

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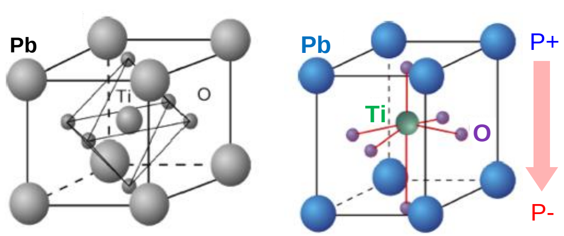
Structural Origin of Ferroelectricity

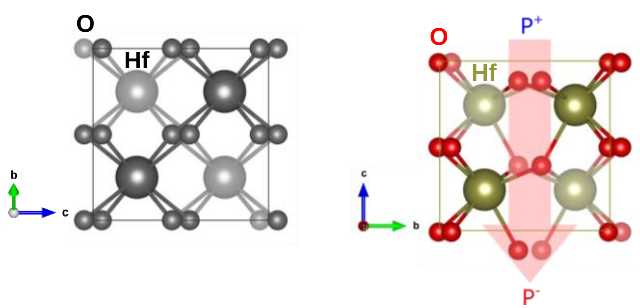
Comparing perovskites to fluorite ferroelectrics

Examples

PbTiO$_3$

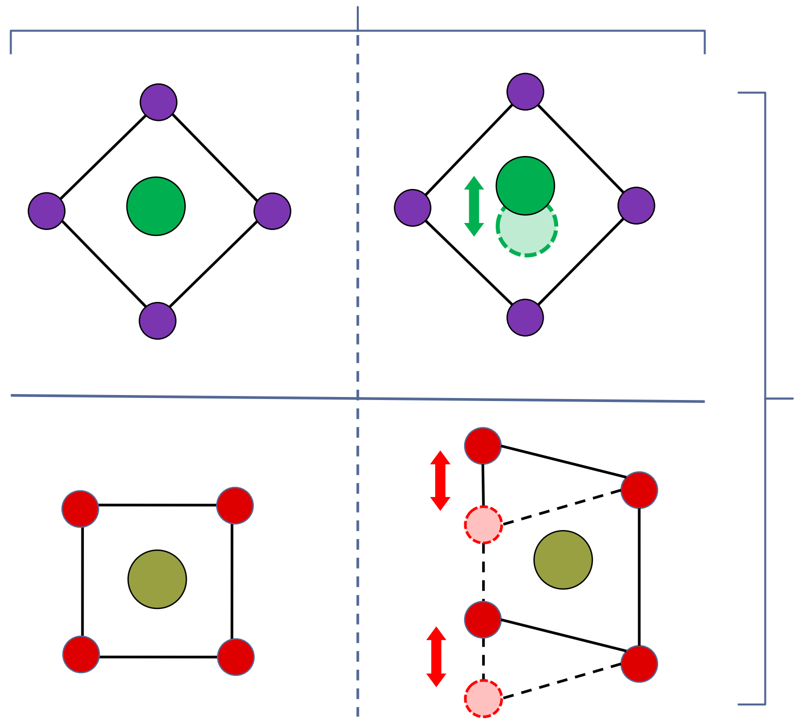


HfO$_2$



parent nonpolar phase

polar phase



Oxygen octahedron in perovskites

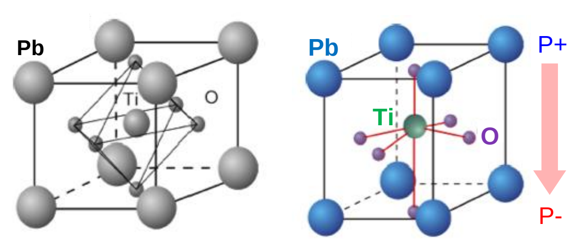
Oxygen hexahedron in fluorites

HfO_2: a superior ferroelectric for nanoscale applications

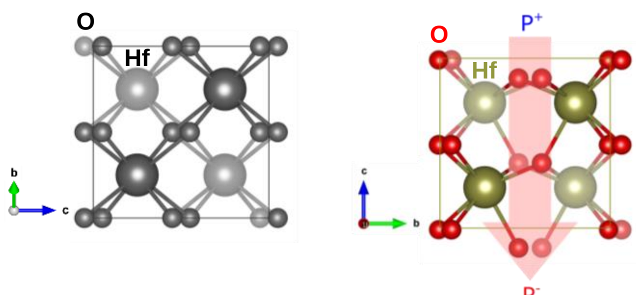
Conventional Perovskite Ferroelectrics

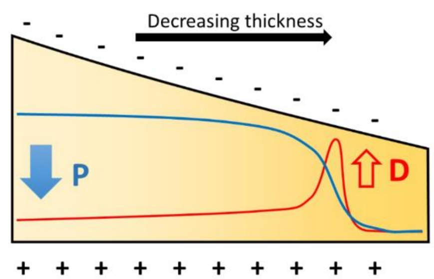
Material	$Pb(Zr, Ti)O_3$	$SrBi_2Ta_2O_9$	$BiFeO_3$	HfO_2-based
P_r ($\mu C/cm^2$)	10-40	5-10	90-95	10-40
E_c (kV/cm)	50-70	30-50	100-1500	2000-5000
ε_0	~400	~200	~50	~25
Minimum film thickness (nm)	**>50**	**>25**	**>10**	**~1**
CMOS compatibility?	**No**	**No**	**No**	**Yes**

$PbTiO_3$



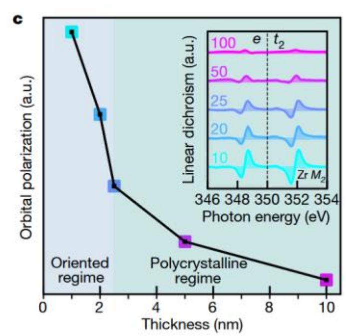
HfO_2





Ferroelectricity is generally unstable at small thickness for perovskites

[1]

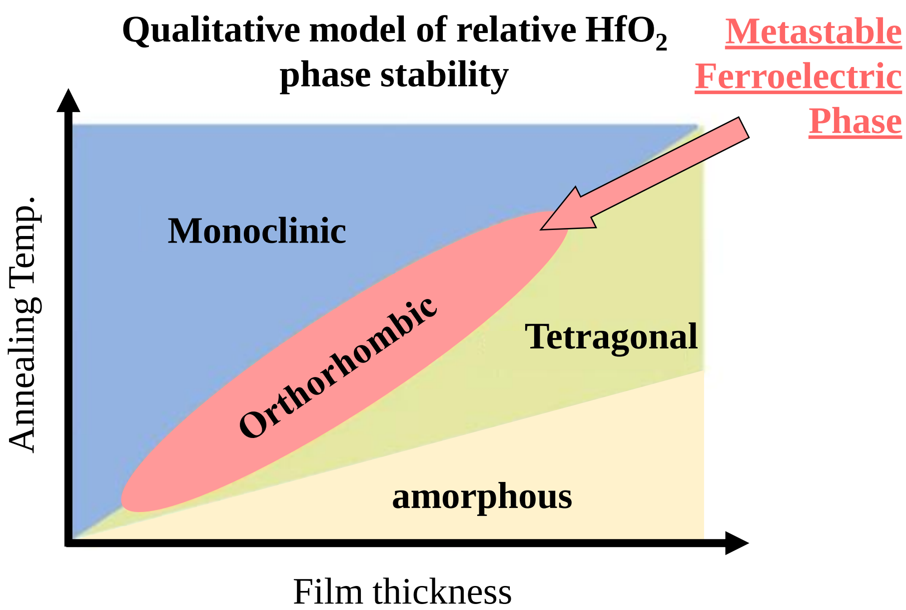


Enhanced polarization in FE-HfO_2 at the nanoscale

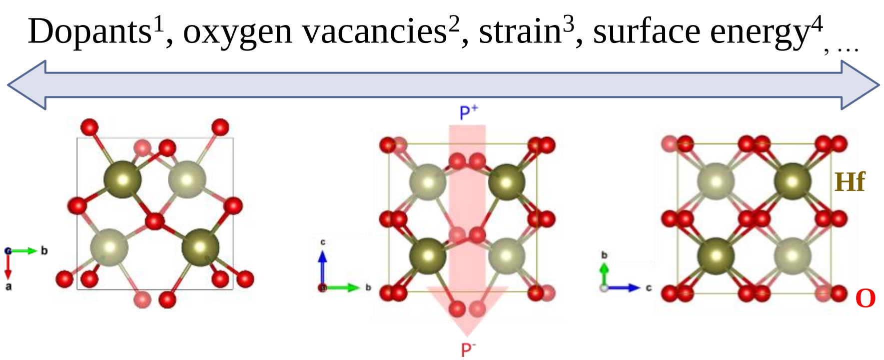
[2]

[1] Östling, Mikael, et al. *Thin solid films* 469 (2004): 444-449.
[2] Cheema, Suraj S., et al. Nature 580.7804 (2020): 478-482.

Challenges with integrating ferroelectric HfO_2



- Generally nonpolar monoclinic phase needs to be kinetically suppressed during crystallization



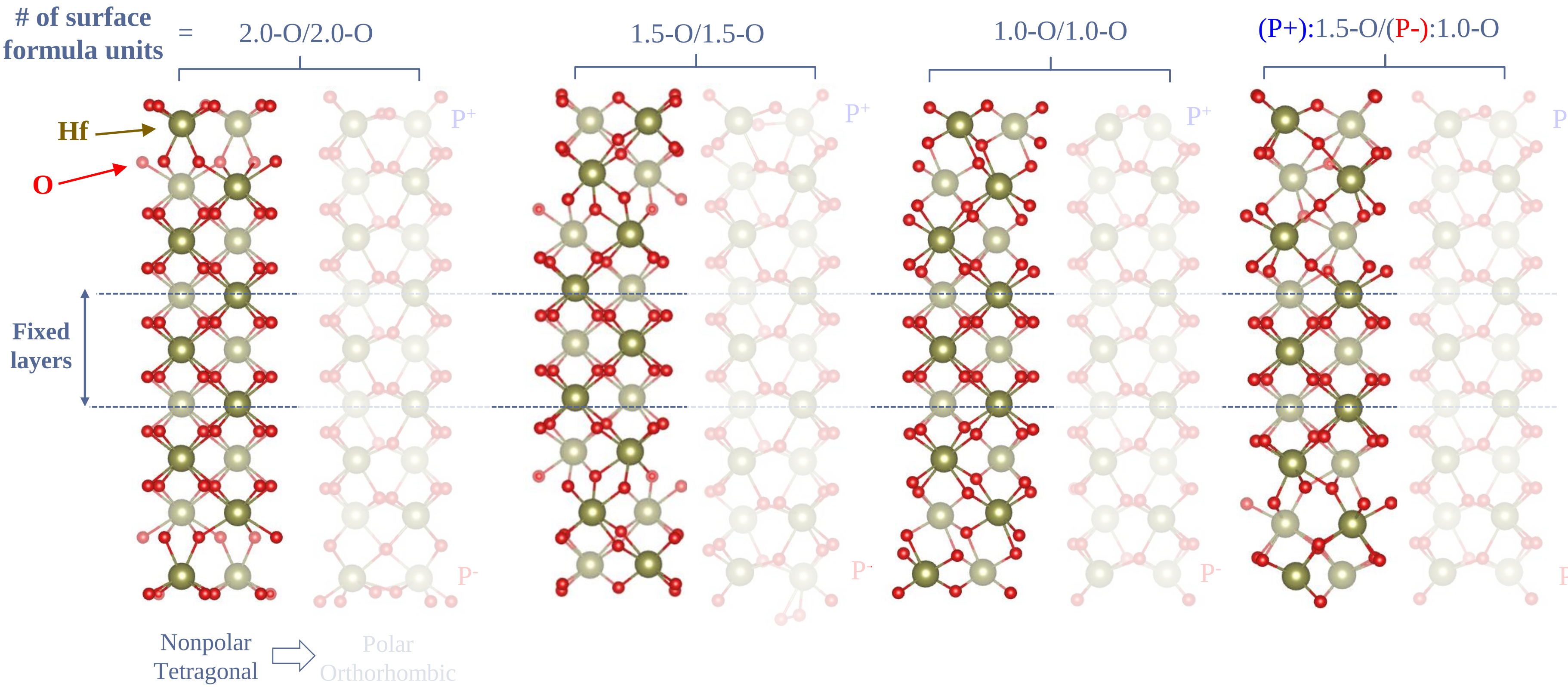
Monoclinic ($P2_1/c$) Orthorhombic ($Pca2_1$) Tetragonal ($P4_2/nmc$)

- Many other factors can contribute to stability of polar orthorhombic phase

[1] Batra, Rohit, et al. *Chem. Mater.* 29.21 (2017): 9102-9109;
[2] Zhou, Y., et al. *Comput. Mater. Sci.* 167 (2019): 143-150.
[3] Batra, Rohit, et al. *J. Phys. Chem* 121.8 (2017): 4139-4145;
[4] Batra, Rohit, Huan Doan Tran, and Rampi Ramprasad. *Appl. Phys. Lett.* 108.17 (2016): 172902

How does ferroelectric polarization influence surface stability?

DFT-PAW-PBE
Kinetic energy cutoff: 800 eV
k-points: 4x4x1
Atomic forces < 0.01 eV/Å
Total energy <1 meV



It is necessary to decouple the influence of surface composition & ferroelectric polarization on the surface stability

Acosta, A., Martirez, J.M.P., Lim, N., Chang, J.P. and Carter, E.A., 2021. *Phys. Rev. Mater.*, 5(12), p.124417.

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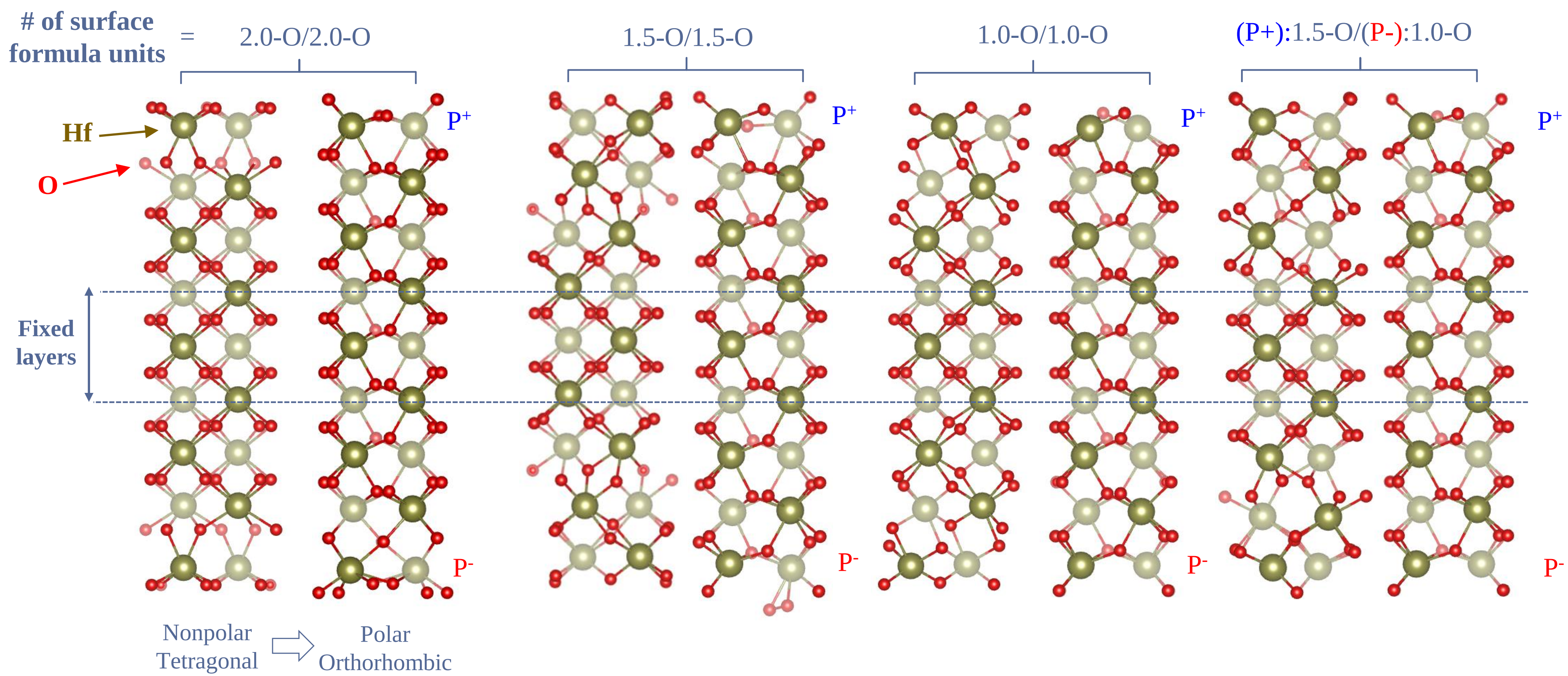

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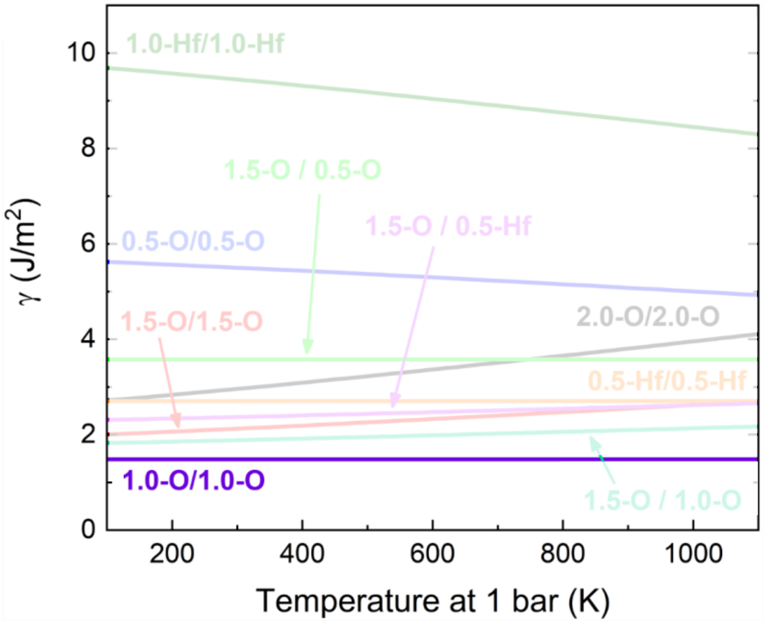
Surface Energy of Nonpolar Tetragonal HfO_2



Calculating average surface free energy:

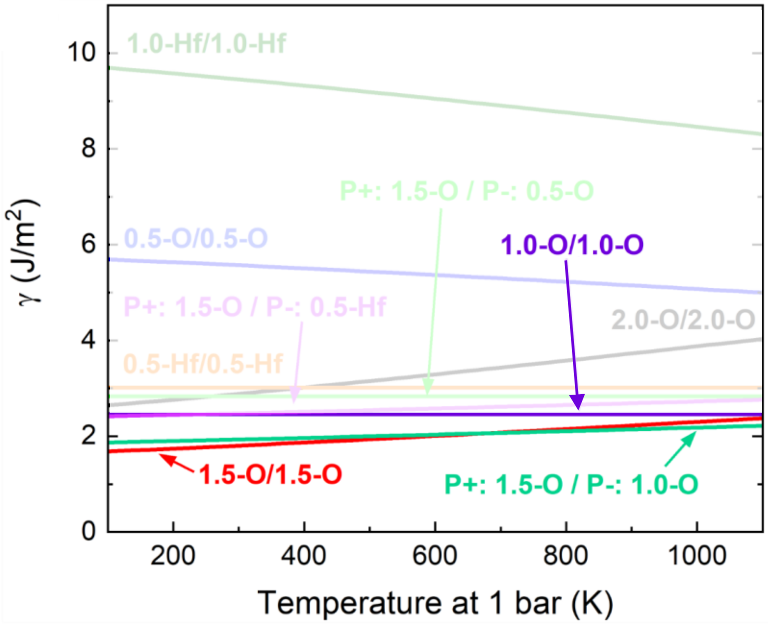
$$\gamma_{avg} = \frac{1}{2A}\begin{pmatrix} G_{slab}(T,P,N_{Hf},N_O) \\ -N_{Hf}\, g^{bulk}_{HfO_2}(T,P) \\ +(2N_{Hf} - N_O)\mu_O(T,P) \end{pmatrix}$$

$$\mu_O(T,p) = \mu_O(T,p^\circ) + \frac{1}{2}kT\ln\left(\frac{p}{p^\circ}\right)$$

Most thermodynamically stable surface composition for a nonpolar slab is **1.0-O/1.0-O**, which corresponds to a stoichiometric slab

Acosta, A., Martirez, J.M.P., Lim, N., Chang, J.P. and Carter, E.A., 2021. *Phys. Rev. Mater.*, 5(12), p.124417.

Surface Energy of Polar Orthorhombic HfO_2



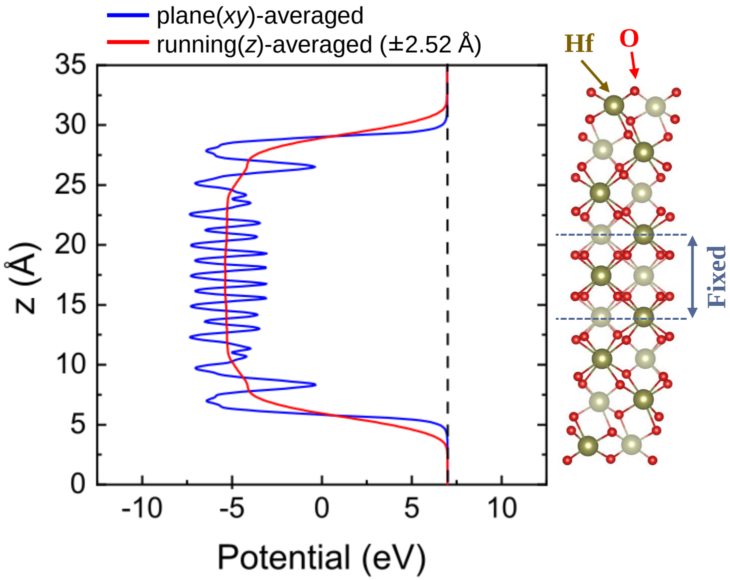
The **1.0-O/1.0-O** surface composition is destabilized when ferroelectric polarization is introduced

Most thermodynamically stable surface composition for a polar slab at high temperature is **P+:1.5-O/P-:1.0-O**

Acosta, A., Martirez, J.M.P., Lim, N., Chang, J.P. and Carter, E.A., 2021. *Phys. Rev. Mater.*, 5(12), p.124417.

Electrostatic potential profiles provide insights into surface stability

Nonpolar Tetragonal
1.0-O/1.0-O



Polar Orthorhombic
P^+:1.0-O/P^-:1.0-O

Polar Orthorhombic
P^+:1.5-O/P^-: 1.0-O

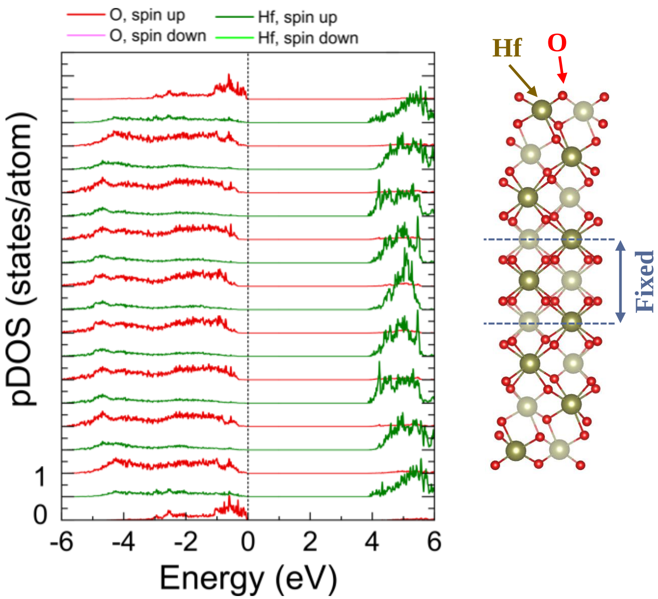
Ferroelectric polarization in the bulk induces electrostatic potential ramp across the slab → asymmetric work function

Addition of O to P+ surface sufficient to screen electrostatic potential

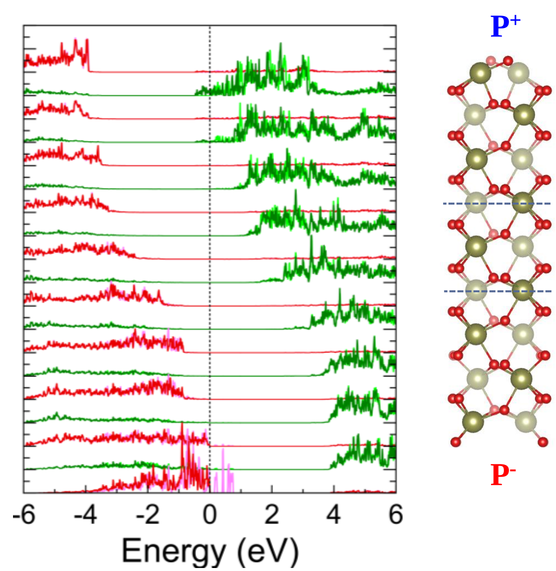
Acosta, A., Martirez, J.M.P., Lim, N., Chang, J.P. and Carter, E.A., 2021. *Phys. Rev. Mater.*, 5(12), p.124417.

Ionic screening of electrostatic potential alleviates band bending

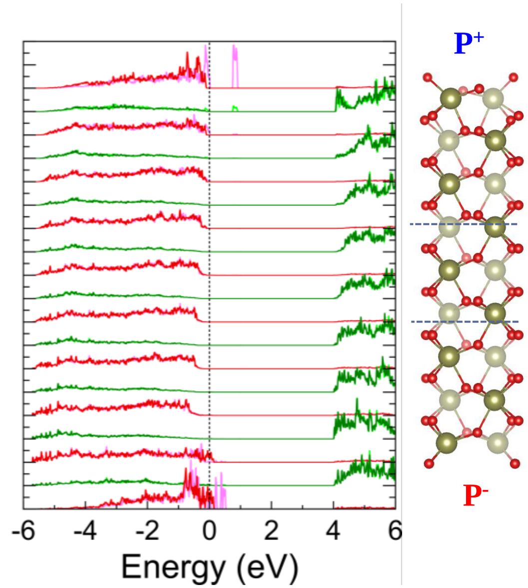
Nonpolar Tetragonal
1.0-O/1.0-O



Polar Orthorhombic
P^+:1.0-O/P^-:1.0-O



Polar Orthorhombic
P^+:1.5-O/P^-: 1.0-O

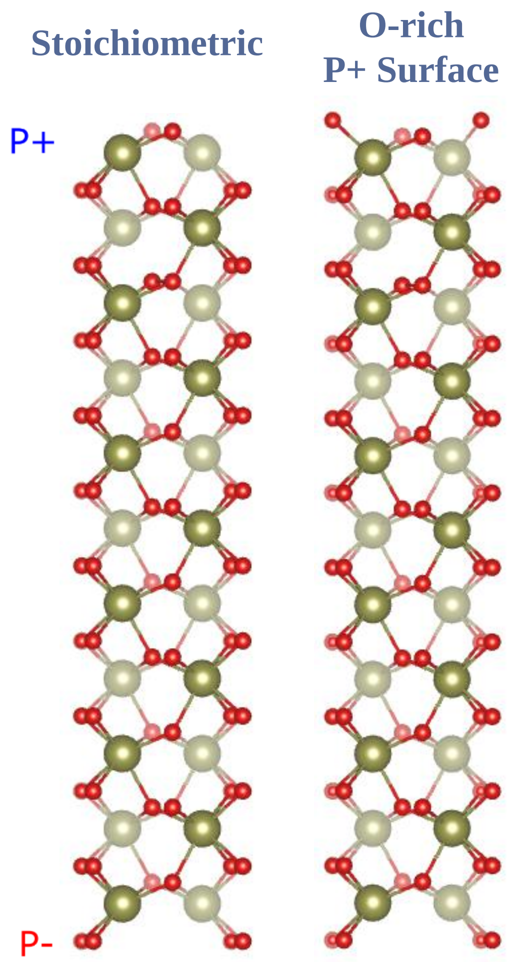


Surface metallization after dielectric breakdown due to electrostatic potential

Charge compensation from additional O on P+ surface screens electrostatic potential to avoid dielectric breakdown

Acosta, A., Martirez, J.M.P., Lim, N., Chang, J.P. and Carter, E.A., 2021. *Phys. Rev. Mater.*, 5(12), p.124417.

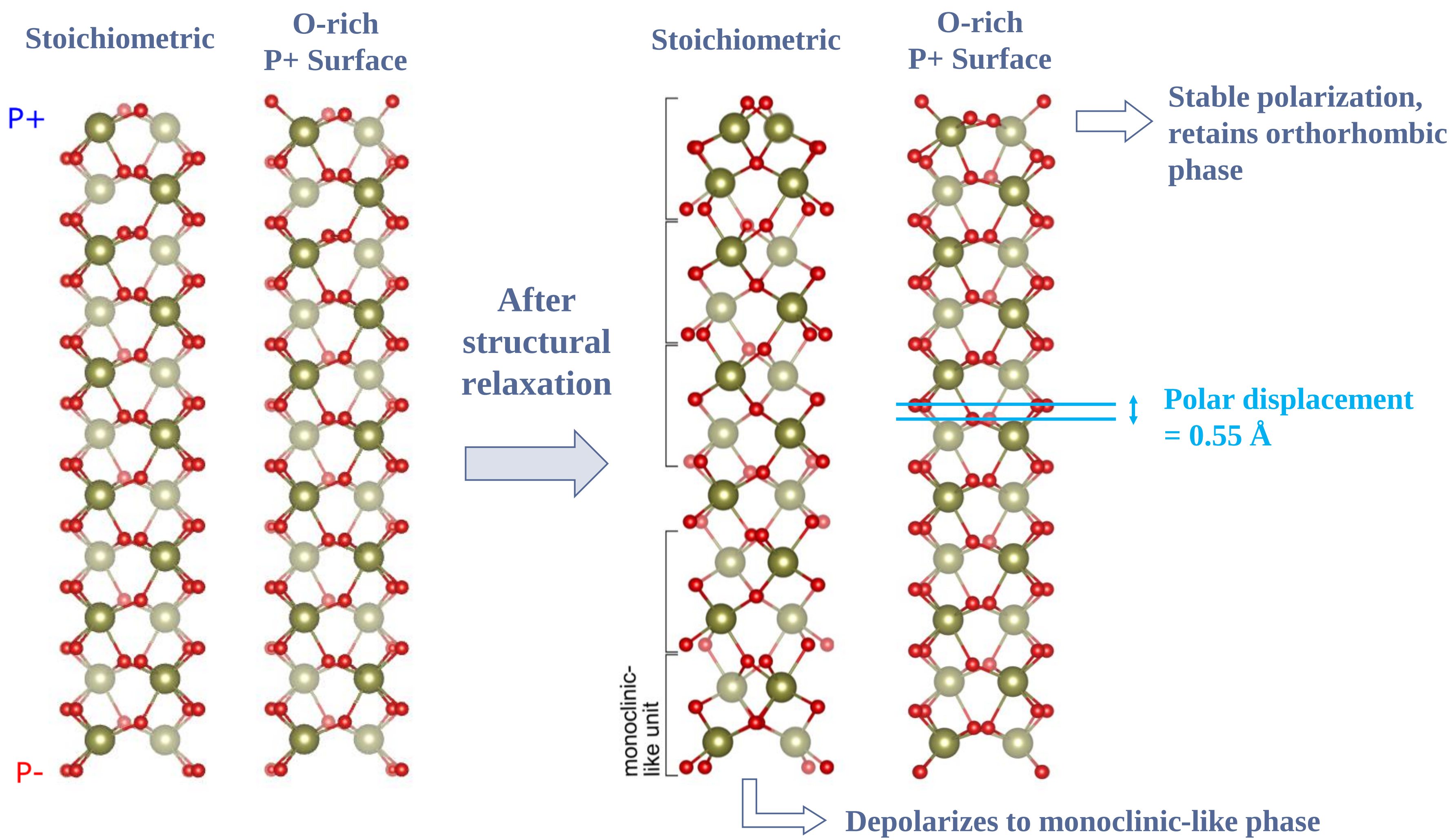
Effect of Surf. Comp. on HfO_2 Ferroelectric Stability



How does the surface composition influence the ferroelectric stability of HfO_2?

Acosta, A., Martirez, J.M.P., Lim, N., Chang, J.P. and Carter, E.A., 2023. *Phys. Rev. Mater.*, 7(11)

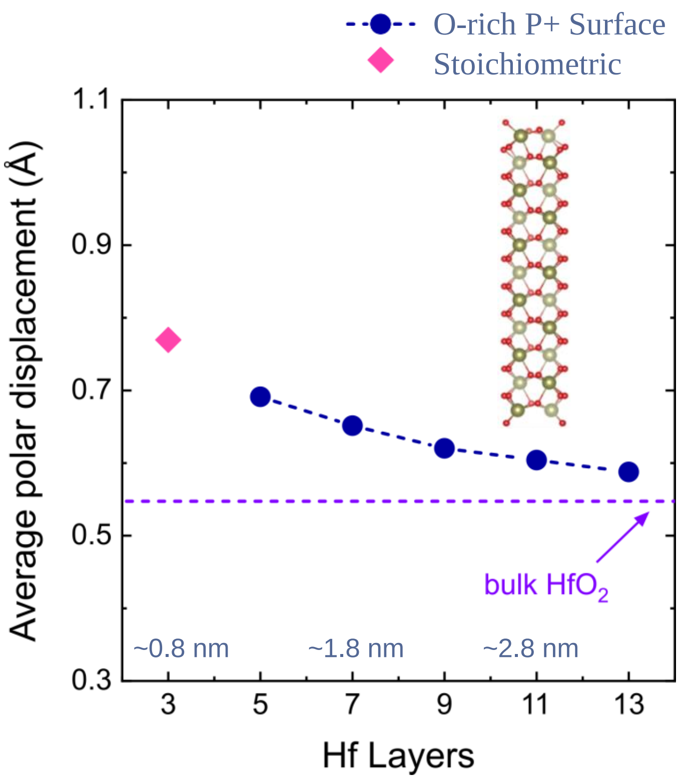
Effect of Surf. Comp. on HfO_2 Ferroelectric Stability



Controlling surface composition can be used to stabilize ferroelectricity in HfO_2

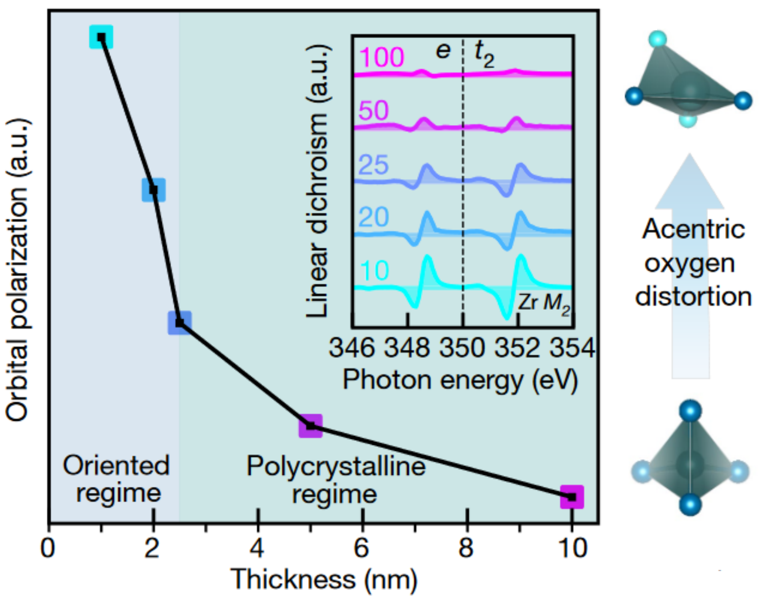
Acosta, A., Martirez, J.M.P., Lim, N., Chang, J.P. and Carter, E.A., 2023. *Phys. Rev. Mater.*, 7(11)

Effect of thickness on polarization of HfO_2



Enhanced ferroelectricity in ultrathin films grown directly on silicon

Nature **580.7804 (2020): 478-482.**



1. No size limit to ferroelectric stability
2. Increased polarization with decreasing thickness
   - Large band gap enables stable, increasing polarization at small thicknesses

Acosta, A., Martirez, J.M.P., Lim, N., Chang, J.P. and Carter, E.A., 2023. *Phys. Rev. Mater.*, 7(11)

Acknowledgements & Funding Support

- Dr. John Mark P. Martirez
- Norleakvisoth Lim
- Prof. Jane P. Chang
- Prof. Emily A. Carter
- IDRE Hoffman2 Computing Cluster

UCLA Samueli School of Engineering

NSF

TANMS