Polarity in low dimensions: MgO nano-ribbons on Au(111)

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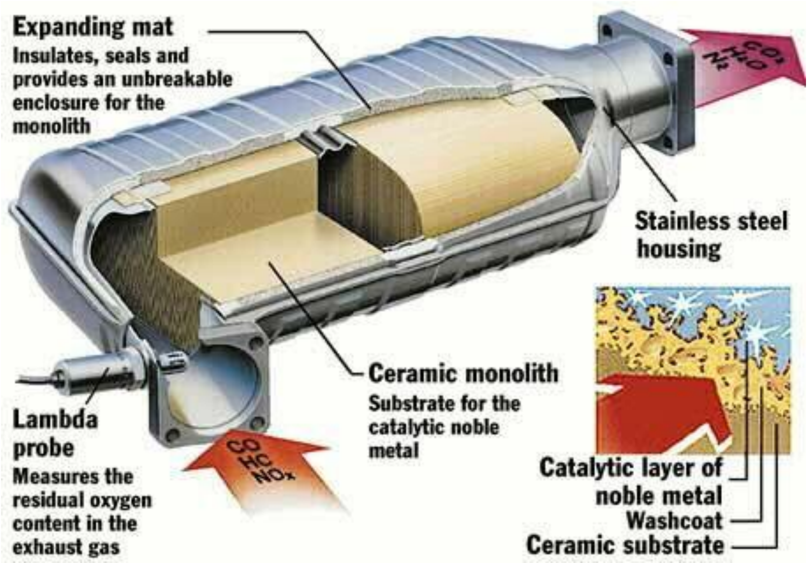
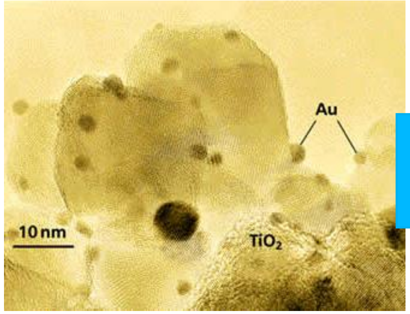
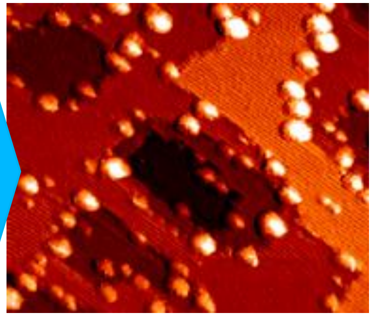
Catalysis by Supported Metal Nanoclusters



Role of oxide support ?

Heterogeneous catalysis → Surface science

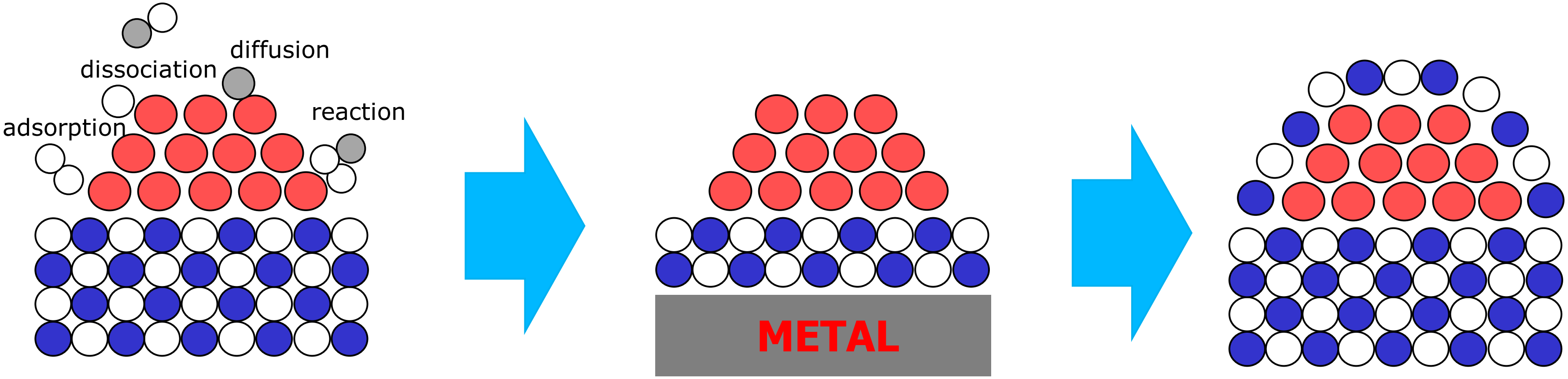




Real system: Au / TiO_2

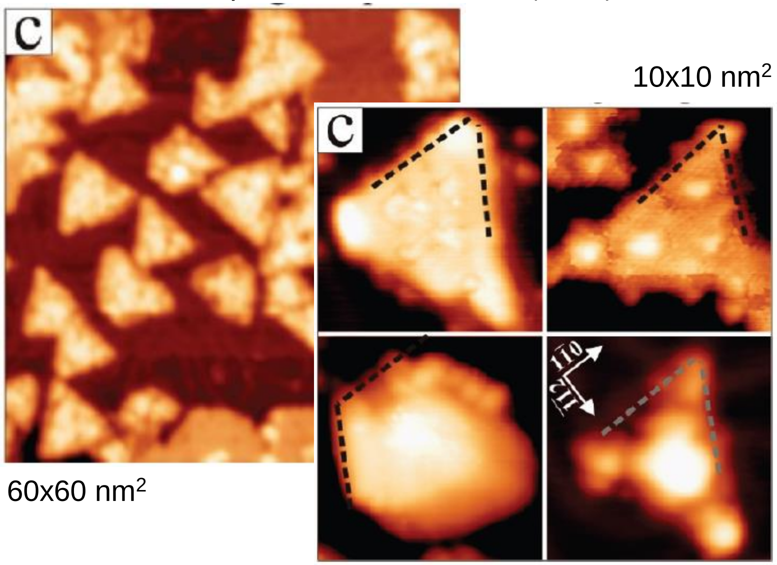
Model system: Au / TiO_2 (110)

Bulk oxide surfaces → ultra-thin oxide films → complex oxide/metal systems



Metal-supported oxides nano-objects: MgO/Au(111)

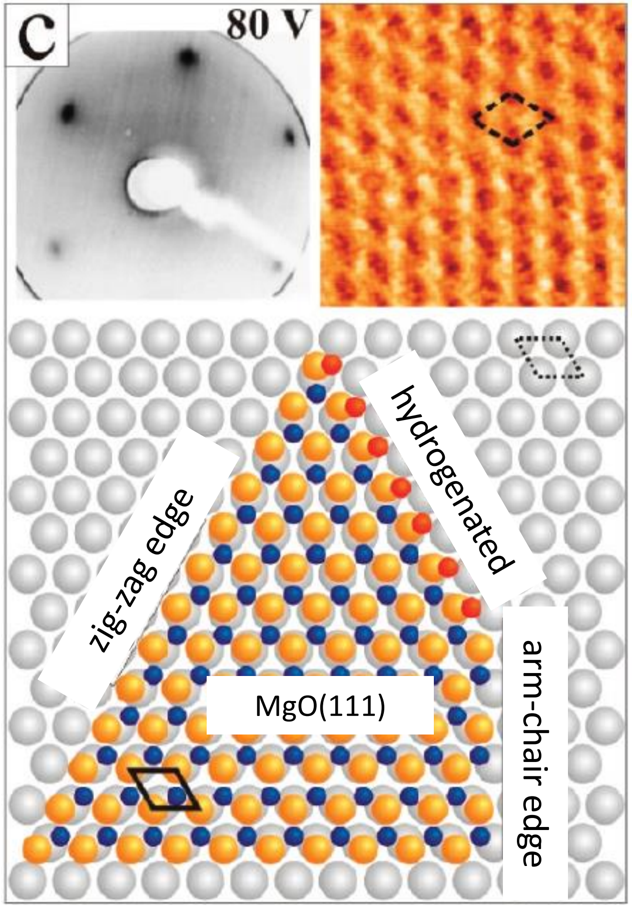
Y. Pan et al., J. Phys. Chem. C 116 11126 (2012).



- Triangular MgO(111) 1 ML islands, ~ 100 Å large.
- MgO lattice parameter larger than in MgO bulk.
- MgO zig-zag edges parallel to the Au[110] rows.

Hexagonal phase:

Mg@300K
p_{O2} = 5x10^{-7} mbar
p_{H2O} > 1x10^{-9} mbar

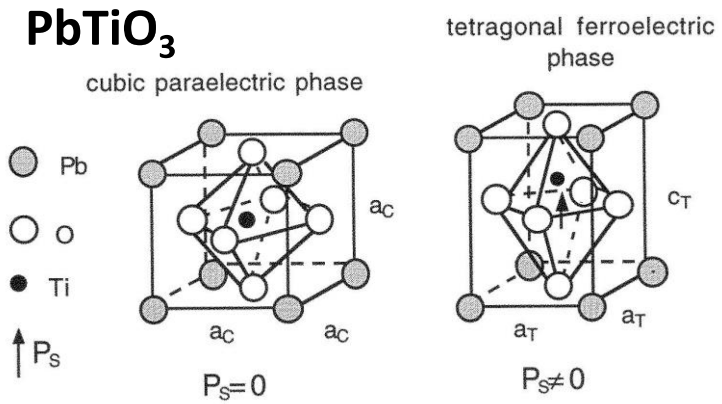


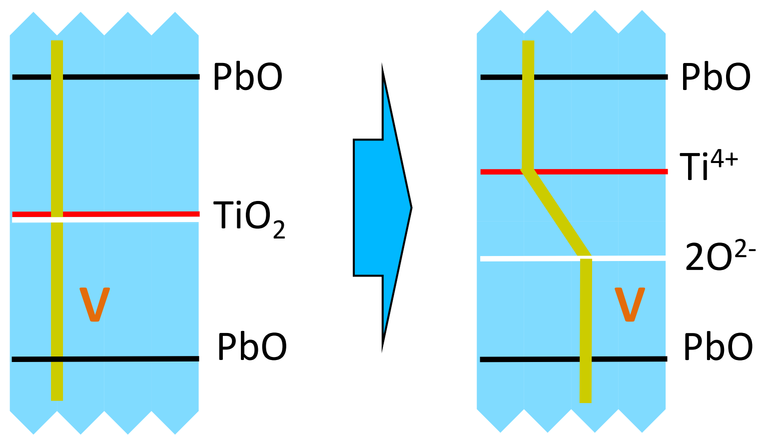
Outline

- **Effect of film thickness**
- **Metal-supported oxide monolayers**
- **Polarity in low dimensional and finite-size objects**
- **Compensation of edge polarity**

Polar materials *versus* polar surfaces

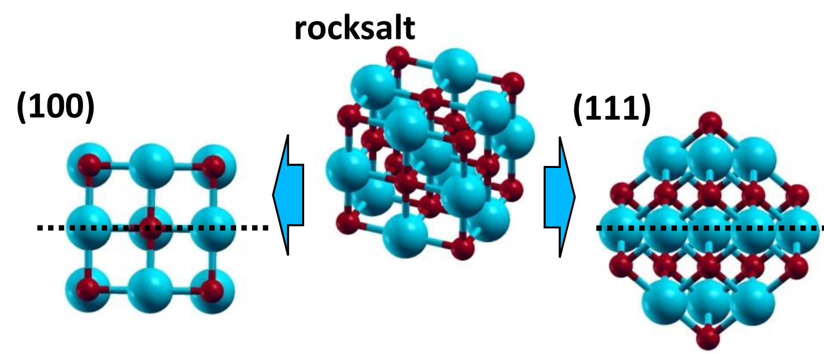
Bulk ferroelectrics

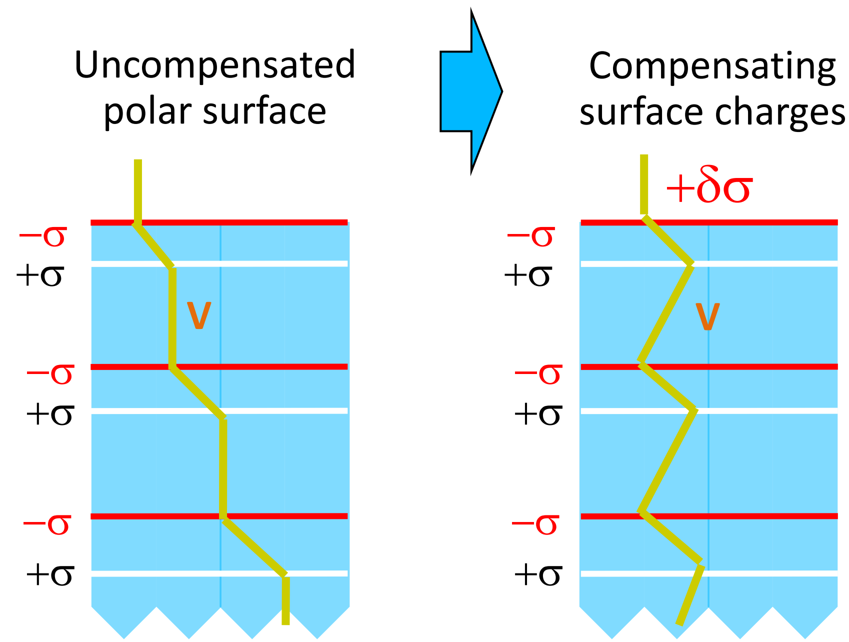




Jump of the electrostatic potential ΔV due to the charge separation

Polar orientations in non-polar crystals

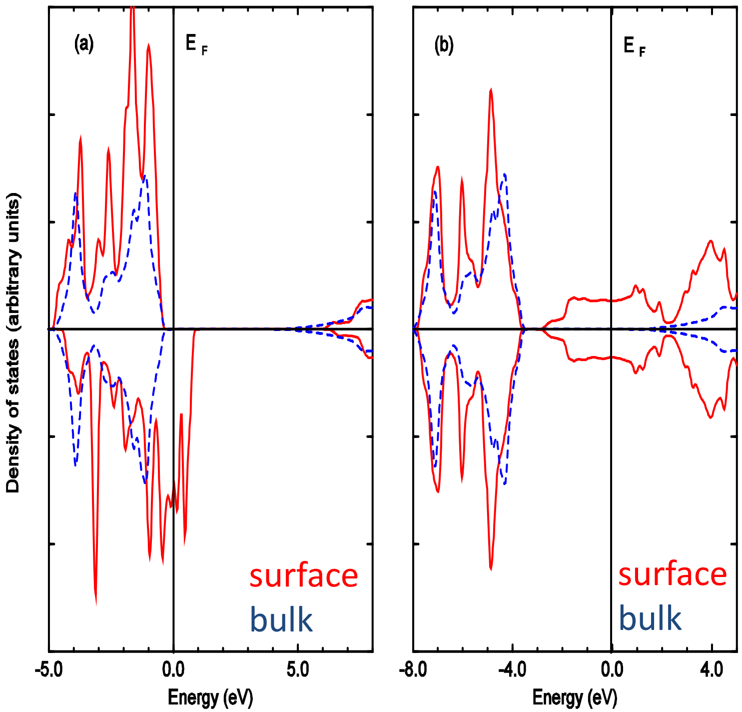




Polar (111) surface of bulk MgO

(1x1) surface: 2D electron gas

O-termination **Mg-termination**

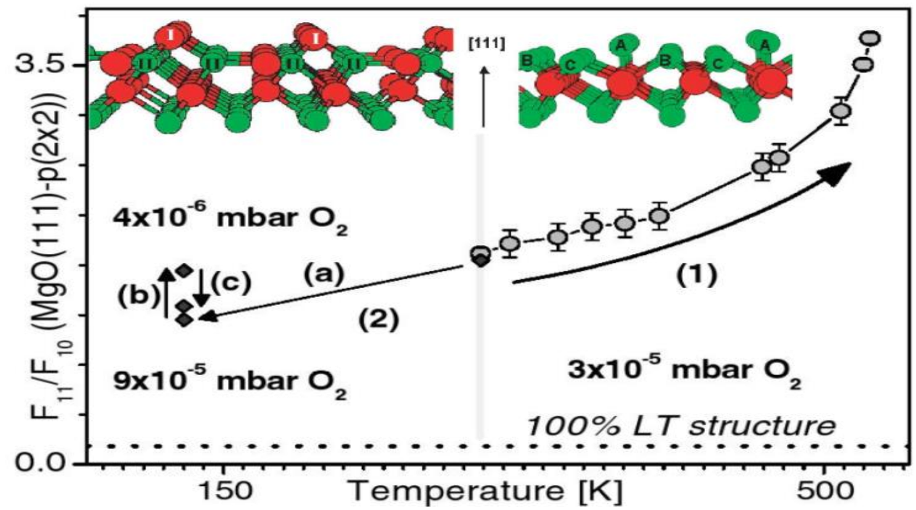


E_{surf} ~ 5 J/m^2

A. Pojani, et al., Surf. Sci. 387, 354 (1997).
J. Goniakowski, C. Noguera, PRB 60, 16120 (1999).

(2x2) surface: Non-stoechiometric reconstructions

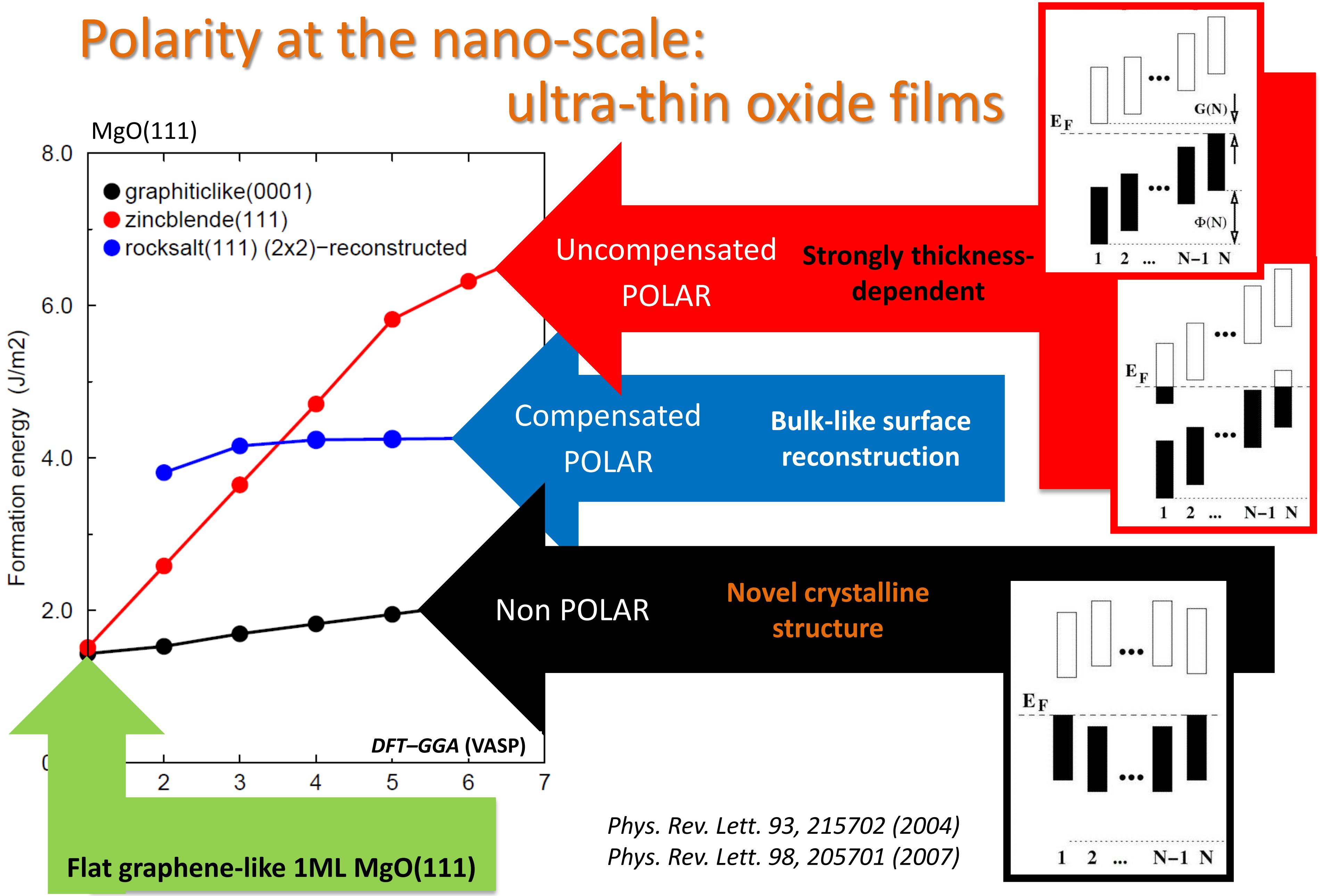
(2x2) octopolar **(2x2) α-hex**



E_{surf} ~ 2 J/m^2

F. Finocchi et al., PRL 92, 136101 (2004).

Polarity at the nano-scale: ultra-thin oxide films

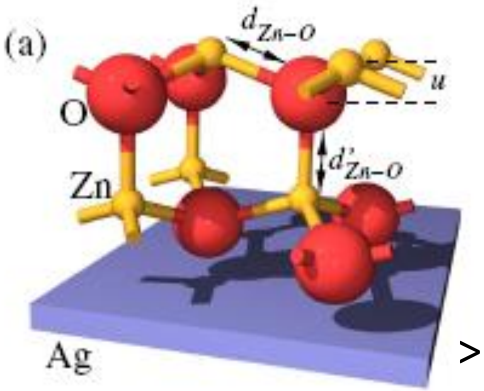


Phys. Rev. Lett. 93, 215702 (2004)
Phys. Rev. Lett. 98, 205701 (2007)

Polarity at the nano-scale: experimental evidence

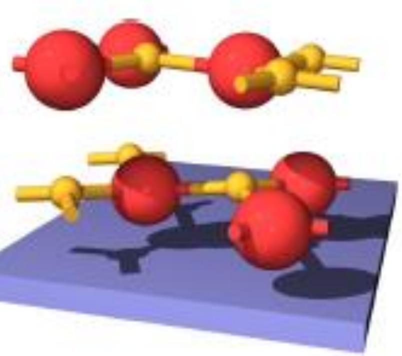
Wurtzite → graphitic transition: ZnO(0001)/Ag

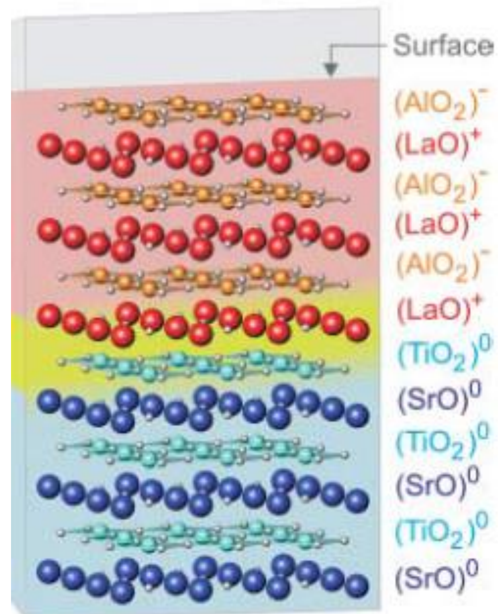
C. Tusche et al.
PRL (2007)



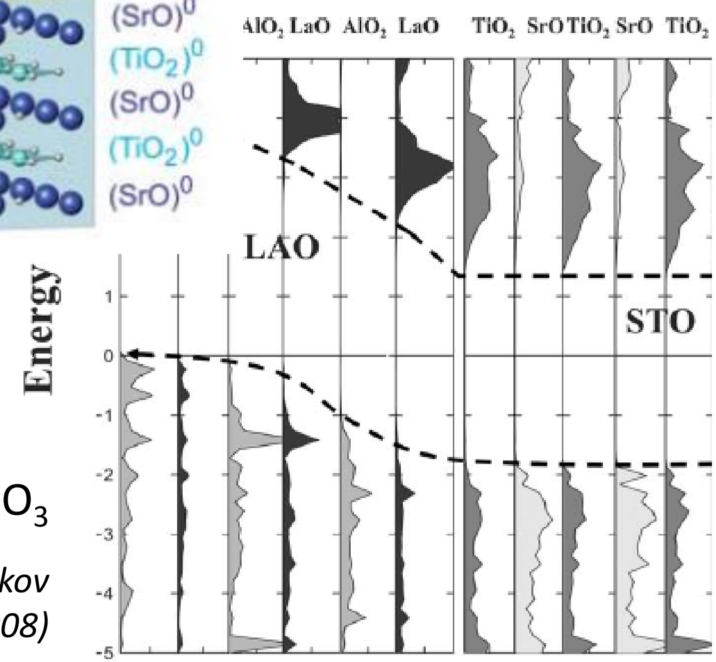
> 2ML ZnO(0001)

2ML ZnO(0001)





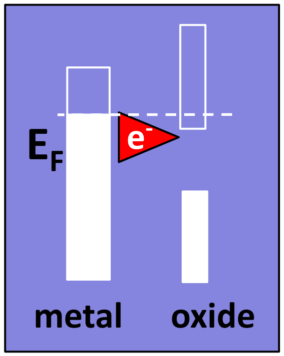
Uncompensated polarity and polar catastrophe: $LaAlO_3/SrTiO_3$

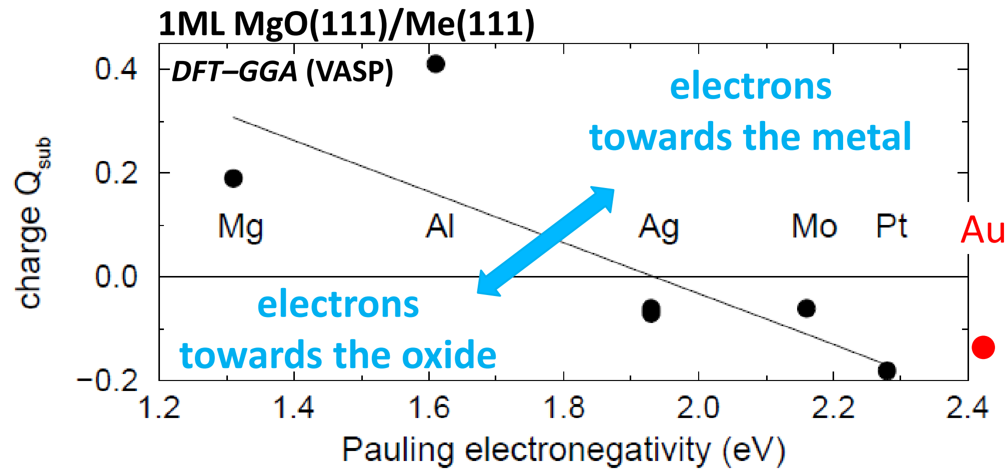


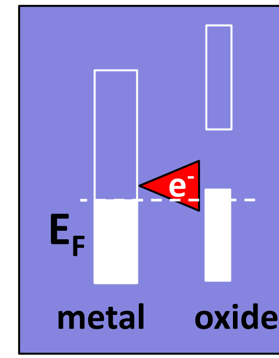
3ML $LaAlO_3$

Lee and Demkov
PRB (2008)

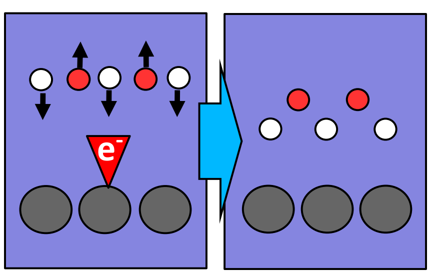
Metal-supported ultra-thin films → Induced polarity

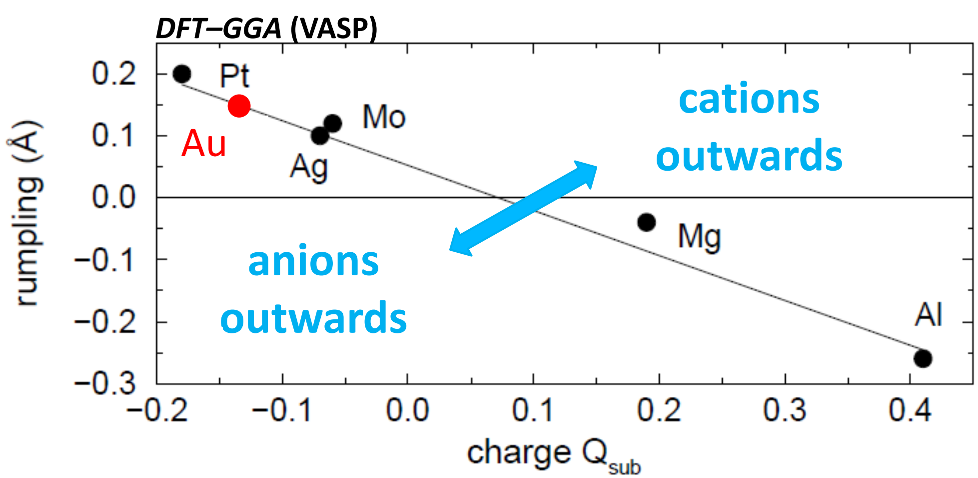


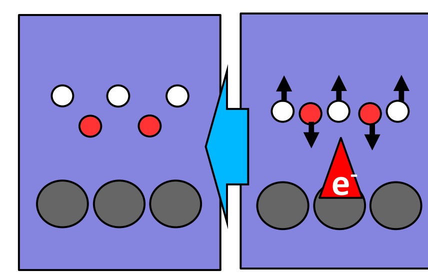




Electrostatic coupling between charge & structure → induced film polarization



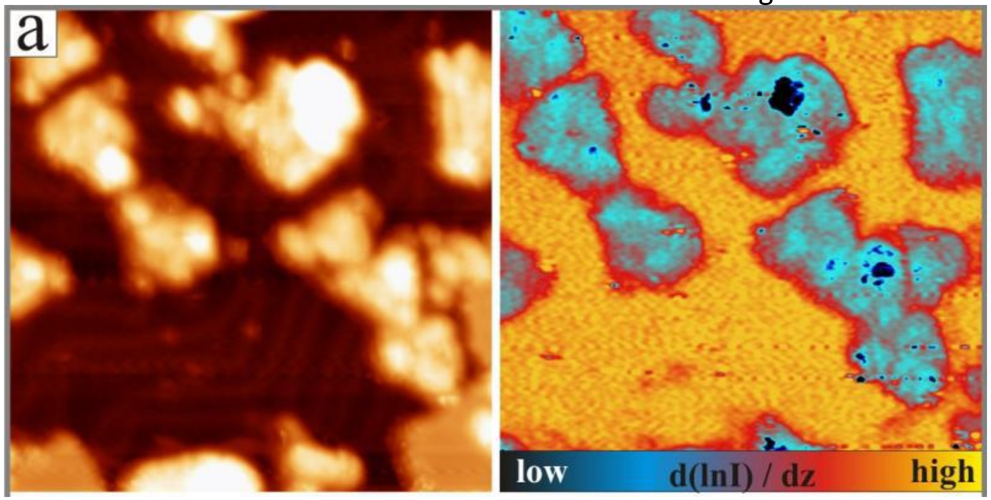




J. Goniakowski, C. Noguera, Phys. Rev. B 79, 155433 (2009)

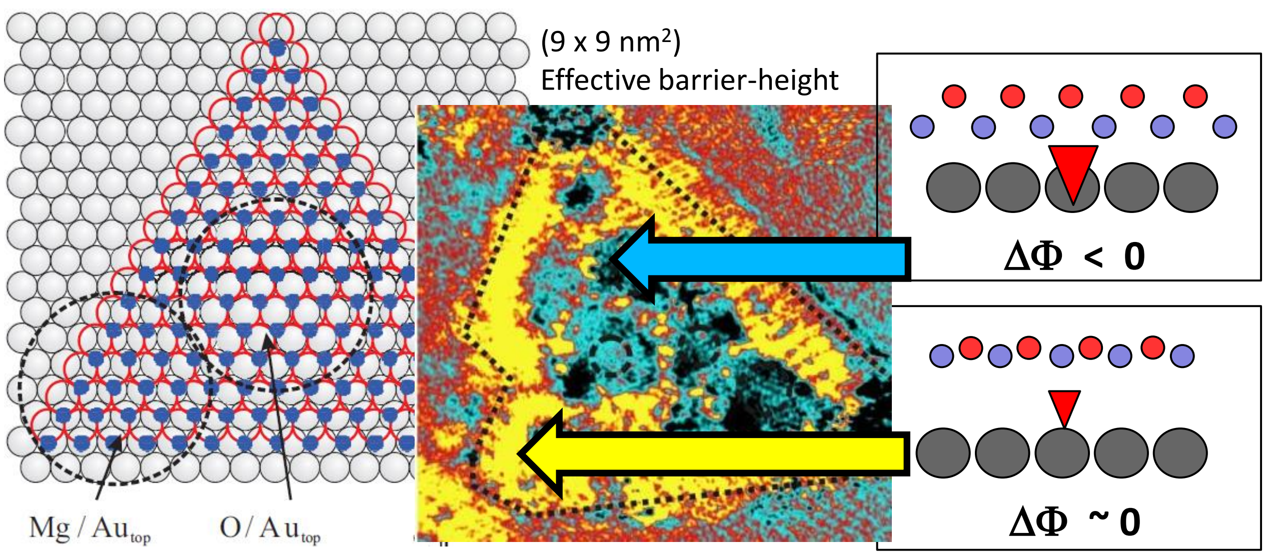
Induced polarity + lattice mismatch → patterning

Topographic (50 x 50 nm^2)   Effective barrier-height Φ



- systematic reduction of the barrier height $\Delta\Phi <$ 0 due to electron density compression at the interface,
- charge transfer and film rumpling dipole moments cancel each other.

(9 x 9 nm^2)
Effective barrier-height

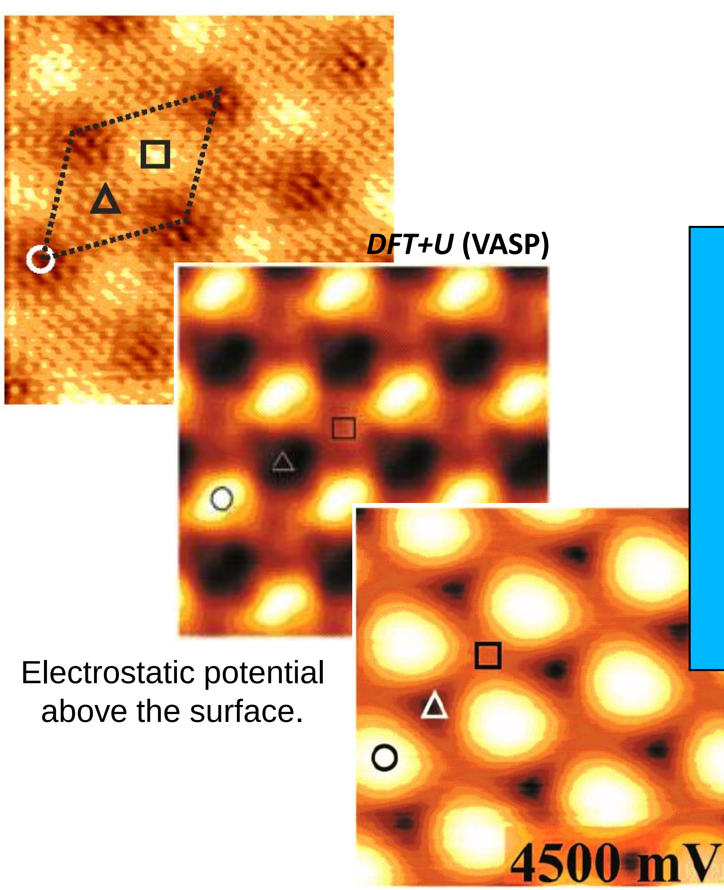


- self-limited island growth,
- surface potential driven by the local interface register → barrier enhancement at island edges.

N. Nilius et al., Phys. Rev. B 86 205410 (2012).

Induced polarity + lattice mismatch → modulation of surface potential

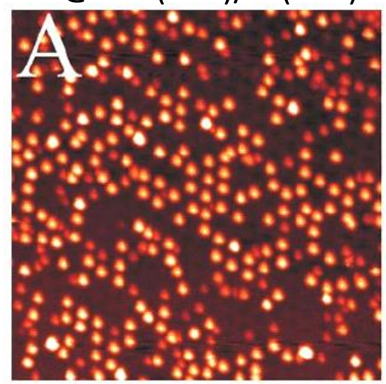
1ML FeO(111)/Pt(111)



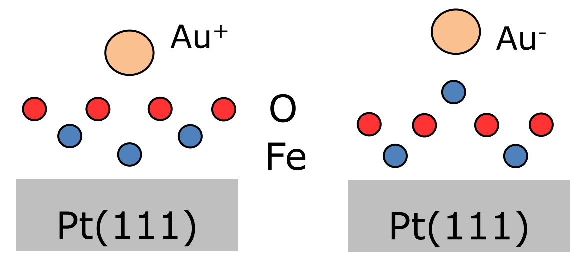
Electrostatic potential above the surface.

STM topographic image
4500 mV, 0.1 nA

Au@FeO(111)/Pt(111)

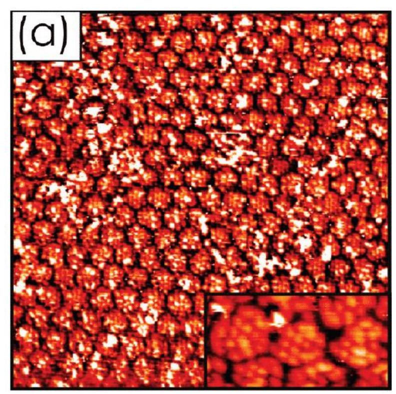


2D Lattice of charged Au monomers

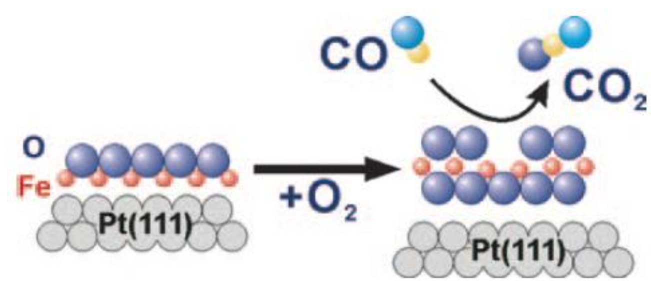


Phys. Rev. Lett. 101, 026102 (2008)
Phys. Rev. B 80, 125403 (2009)

O@FeO(111)/Pt(111)

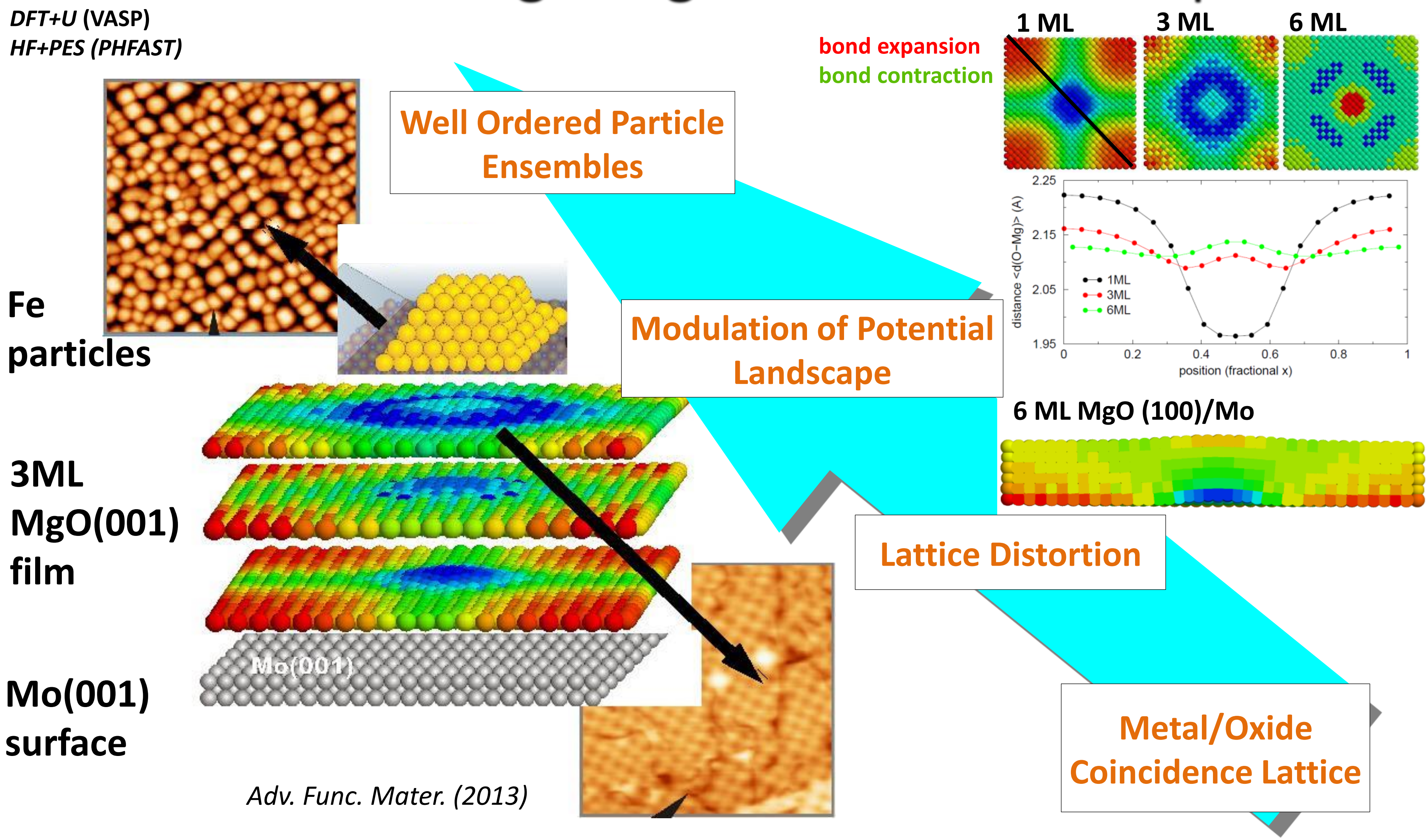


Embedded islands of FeO_2 nano-oxide



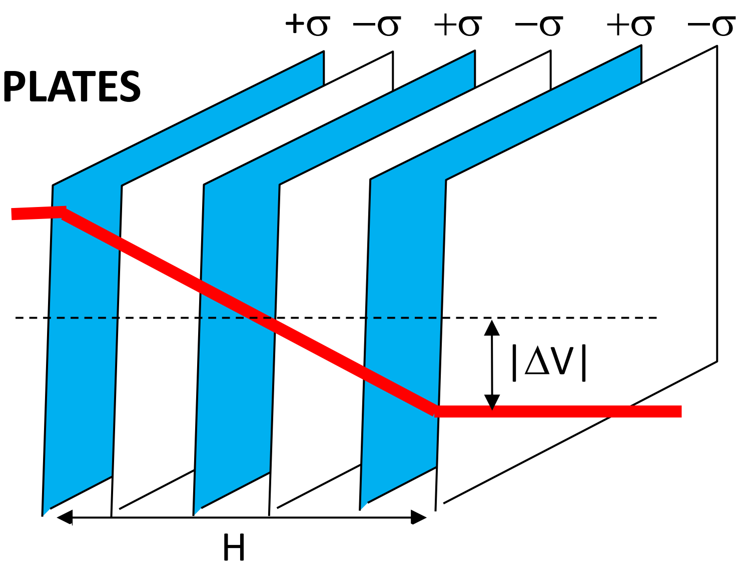
J. Phys. Chem. C 114, 21504 (2010)
Angew. Chem. Int. Ed. 49, 4418 (2010)

Lattice mismatch → oxide film distortion→ steering the growth of metal ad-particles

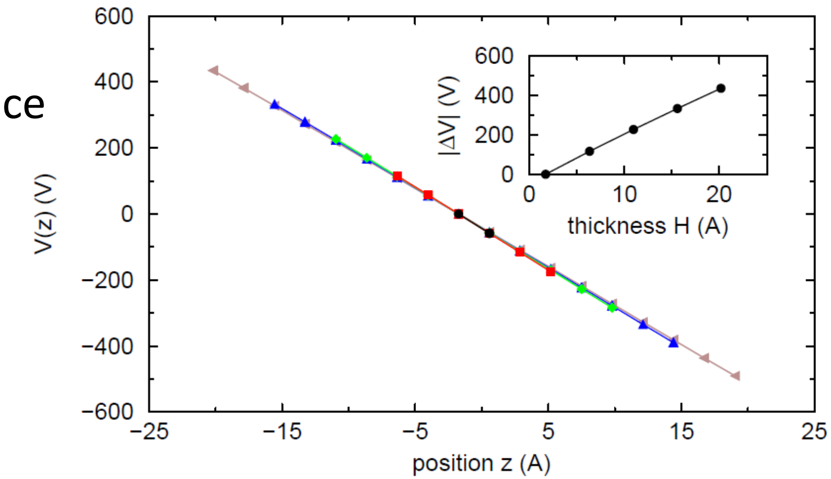


Edge polarity: low dimensionality

PLATES

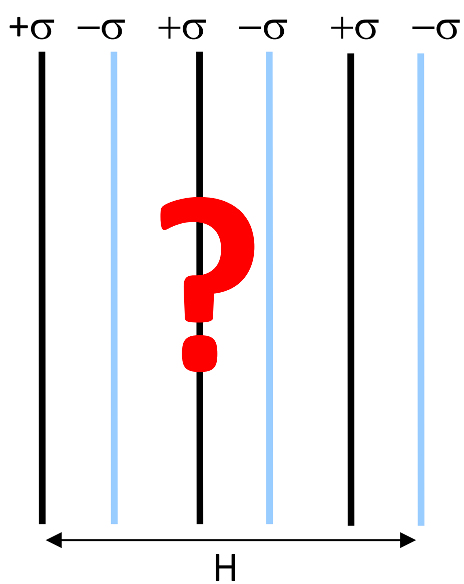


$\mathbf{V}_{\mathrm{PLATE}}(d) \sim d$
Linear divergence

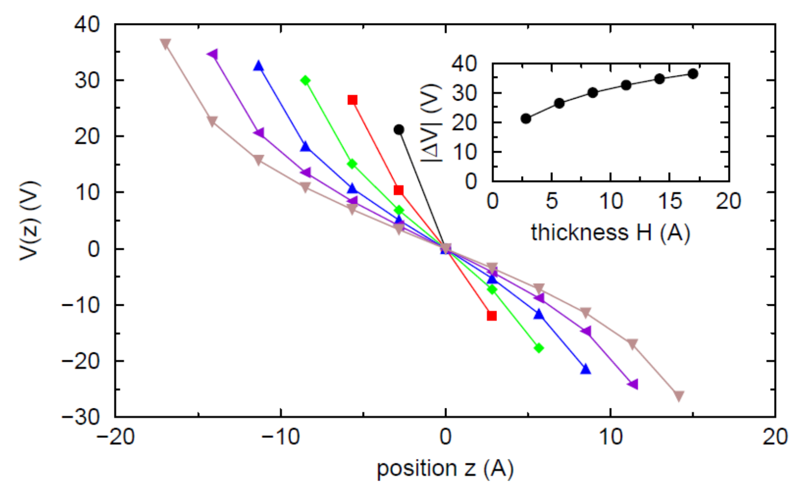


Rock-salt lattice a= 4 Å, point charges q = ± 2
Electrostatic potential on anions.

WIRES



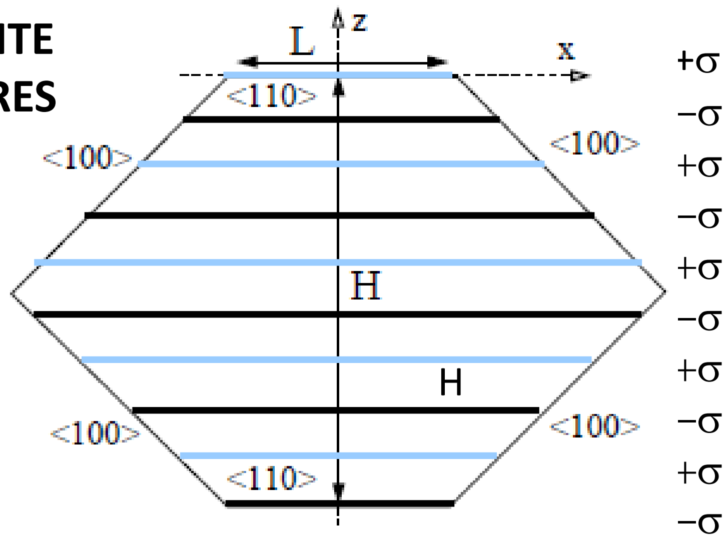
$\mathbf{V}_{\mathrm{WIRE}}(d) \sim \ln d$
Log divergence

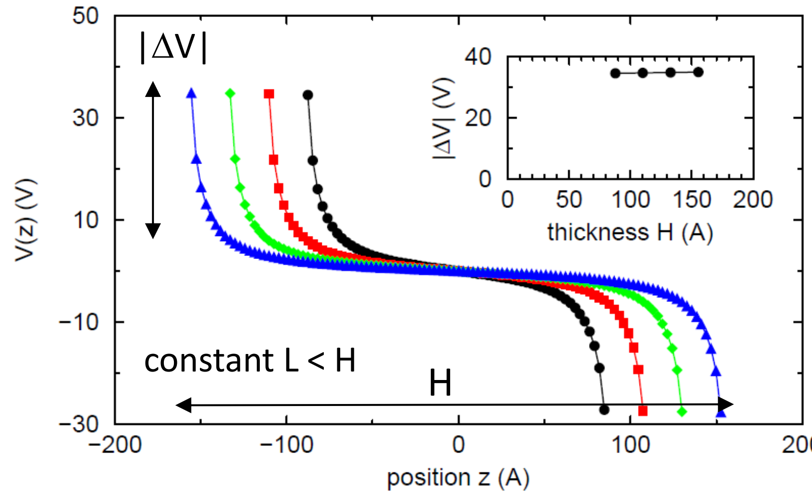


J. Goniakowski, C. Noguera, Phys. Rev. B 83 115413 (2011).

Edge polarity: finite size

FINITE WIRES



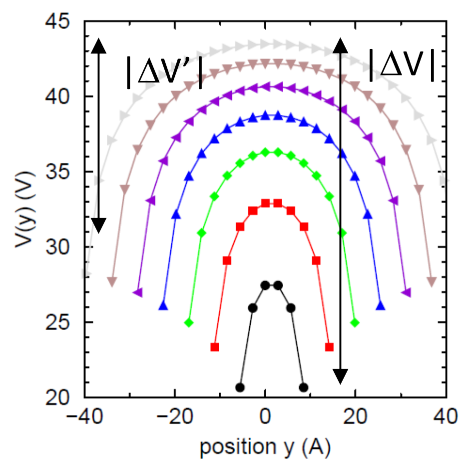


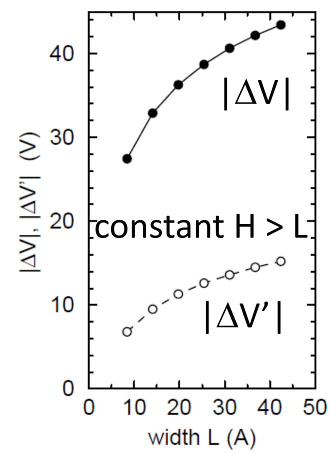
Rock-salt lattice a= 4 Å, point charges q = ± 2
Electrostatic potential on anions.

H >> L:

$\mathbf{V}_{WIRE}(d) \sim \ln 1/d$ & $|\Delta V|, |\Delta V'| \sim \ln L$

- no divergence as function of object size H
- log divergence as function of size of the polar edge L

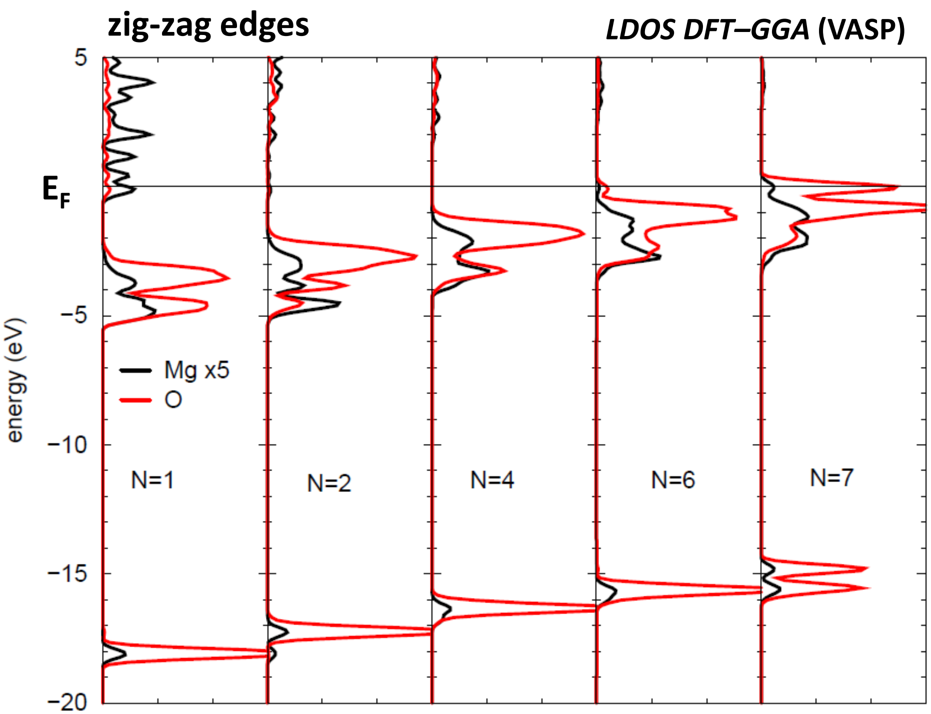


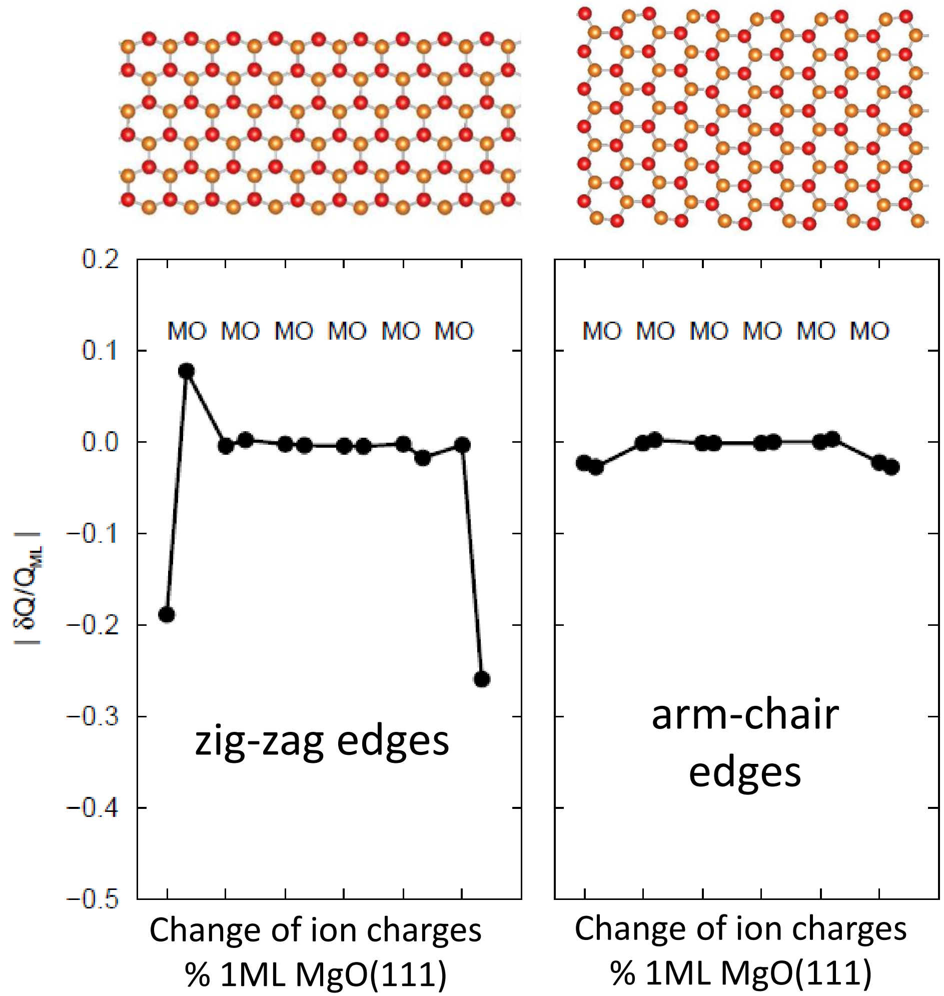


J. Goniakowski, C. Noguera, Phys. Rev. B 83 115413 (2011).

Compensation of edge polarity: metallization

Unsupported 1 ML MgO(111) nano-ribbons





Overlap of edge valence and conduction bands:

* edge metallization;
* $\delta\sigma = \sigma R_1/(R_1+R_2)$ =
  1/3 σ for zig-zag edges.

J. Goniakowski, L. Giordano, C. Noguera, Phys. Rev. B 87 035405 (2013).

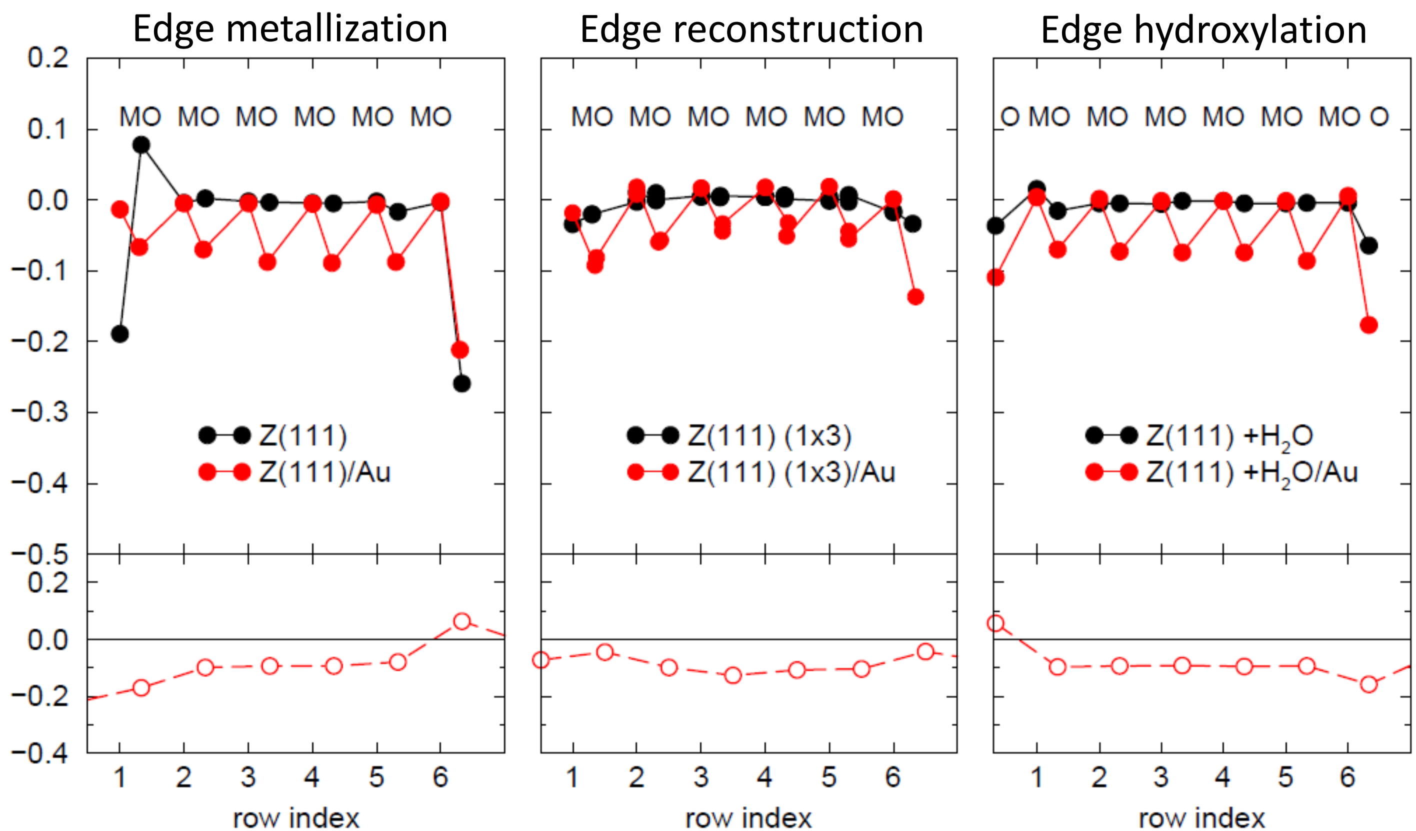
Edge polarity: compensation mechanisms

1 ML MgO(111) nano-ribbons with zig-zag edges: **free** **Au(111)-supported**

***DFT–GGA* (VASP) + Bader**

Change of ion charge wrt 1ML MgO(111)

Change of Au charges wrt clean Au(111)



Au(111) substrate efficiently screens the non-neutrality of dry unreconstructed and of fully hydroxylated zig-zag edges.

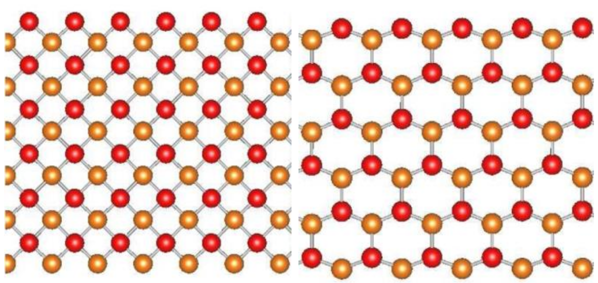
J. Goniakowski, L. Giordano, C. Noguera, Phys. Rev. B 87 035405 (2013).

Edge polarity: relative edge/island stability

Au(111)-supported
1ML MgO nano-ribbons:

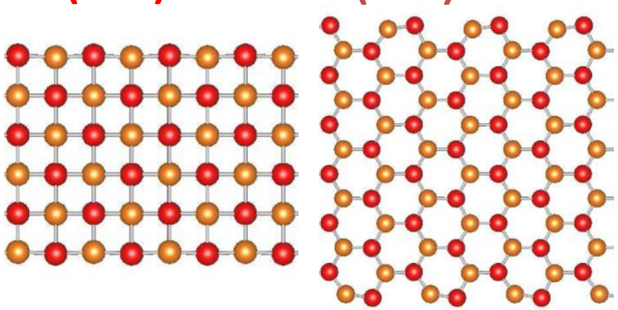
Polar:

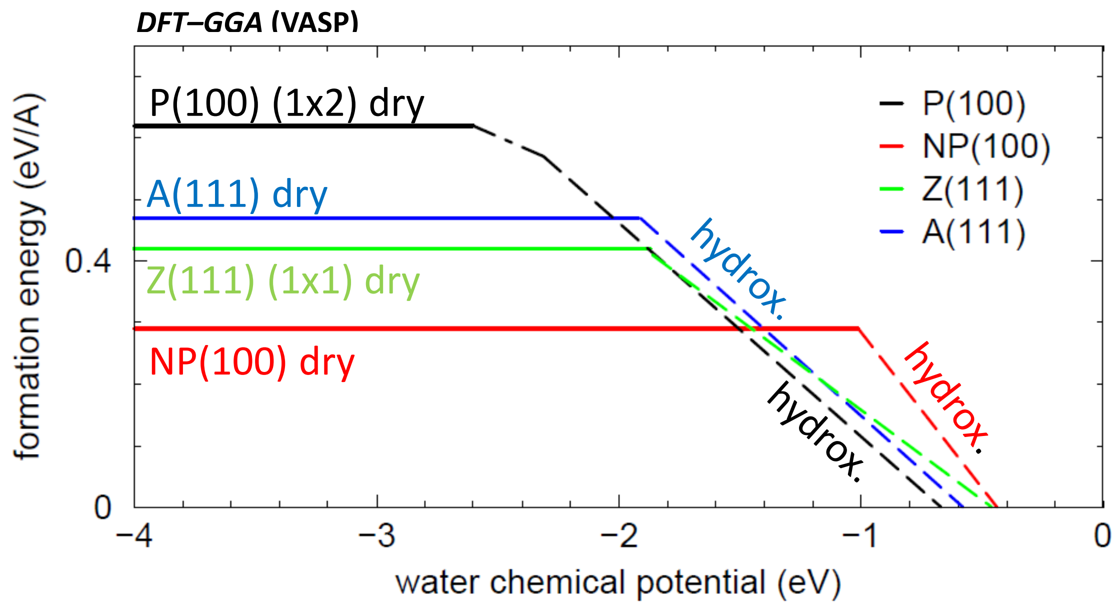
P(100) **Z(111)**



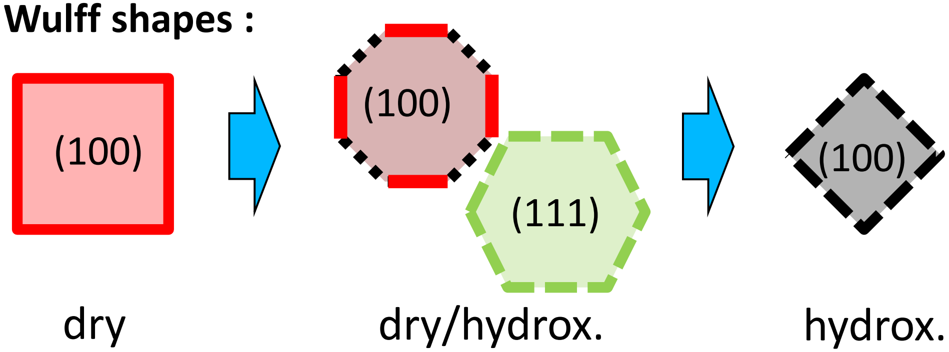
Non-polar:

NP(100) **A(111)**





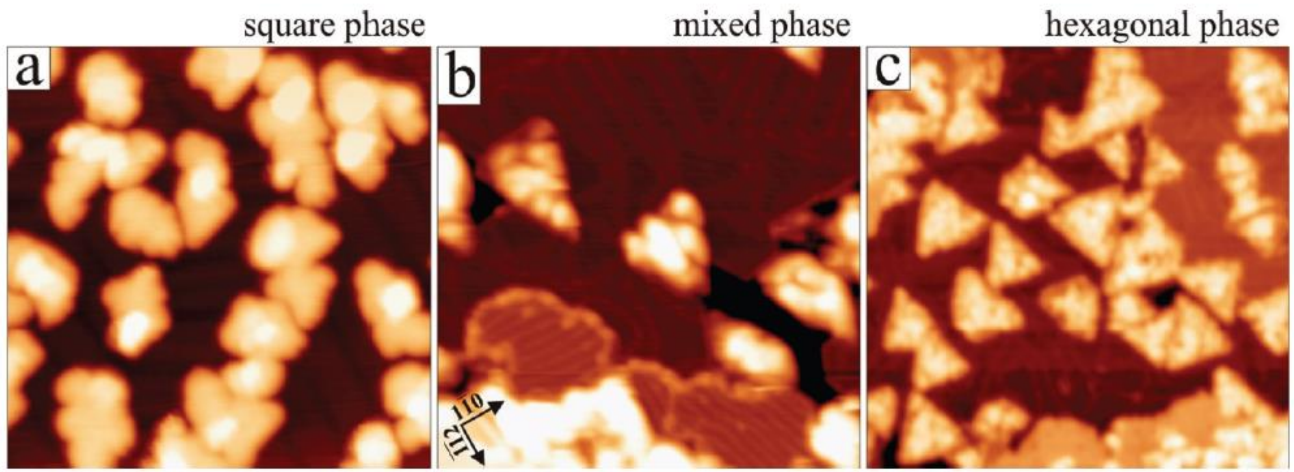
→ **2D Wulff shapes :**



J. Goniakowski, L. Giordano, C. Noguera, Phys. Rev. B 87 035405 (2013).

Au(111)-supported MgO nano-islands:

Y. Pan et al., J. Phys. Chem. C 116 11126 (2012).



Mg@550K
p_{O2} = 5x10^{-6} mbar
p_{H2O} < 2x10^{-10} mbar

Mg@450K
p_{O2} = 1x10^{-6} mbar

Mg@300K
p_{O2} = 5x10^{-7} mbar
p_{H2O} > 1x10^{-9} mbar

Summary

- **Effect of film thickness**
  uncompensated polarity and polarity-drivien structural transformations
- **Lattice mismatch + Induced polarity in metal-supported oxide monolayers**
  nano-patterning of structural and electronic characteristics
- **Different polar behaviour in low dimensional and finite-size objects**
  linear/logarithmic divergence in 3D/2D, no divergence in 1D (chains)
  divergence as function of the smaller structural parameter L or H
- **Compensation of edge polarity**
  screening by the metal substrate / hydroxylation / reconstruction: stability reversal

C. Noguera, J. Goniakowski, Chem. Rev. 113, 4073 (2013)

Acknowledgments

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Reducible oxide chemistry, structure and functions
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