First-principles modeling of screening in ferroelectric ultrathin capacitors

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CITIMAC

Many thanks to the collaboration with

Massimiliano Stengel

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UCSB

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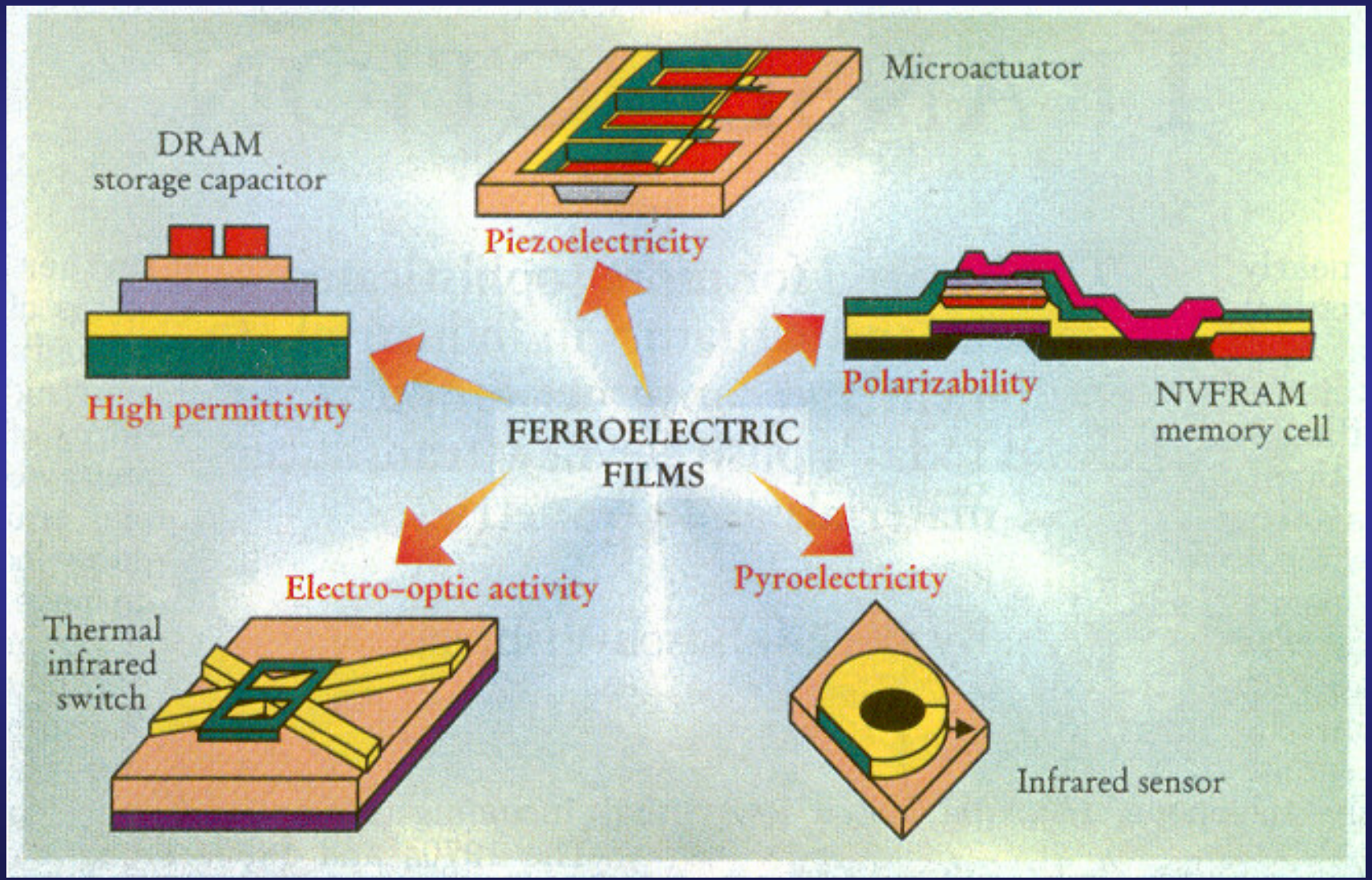
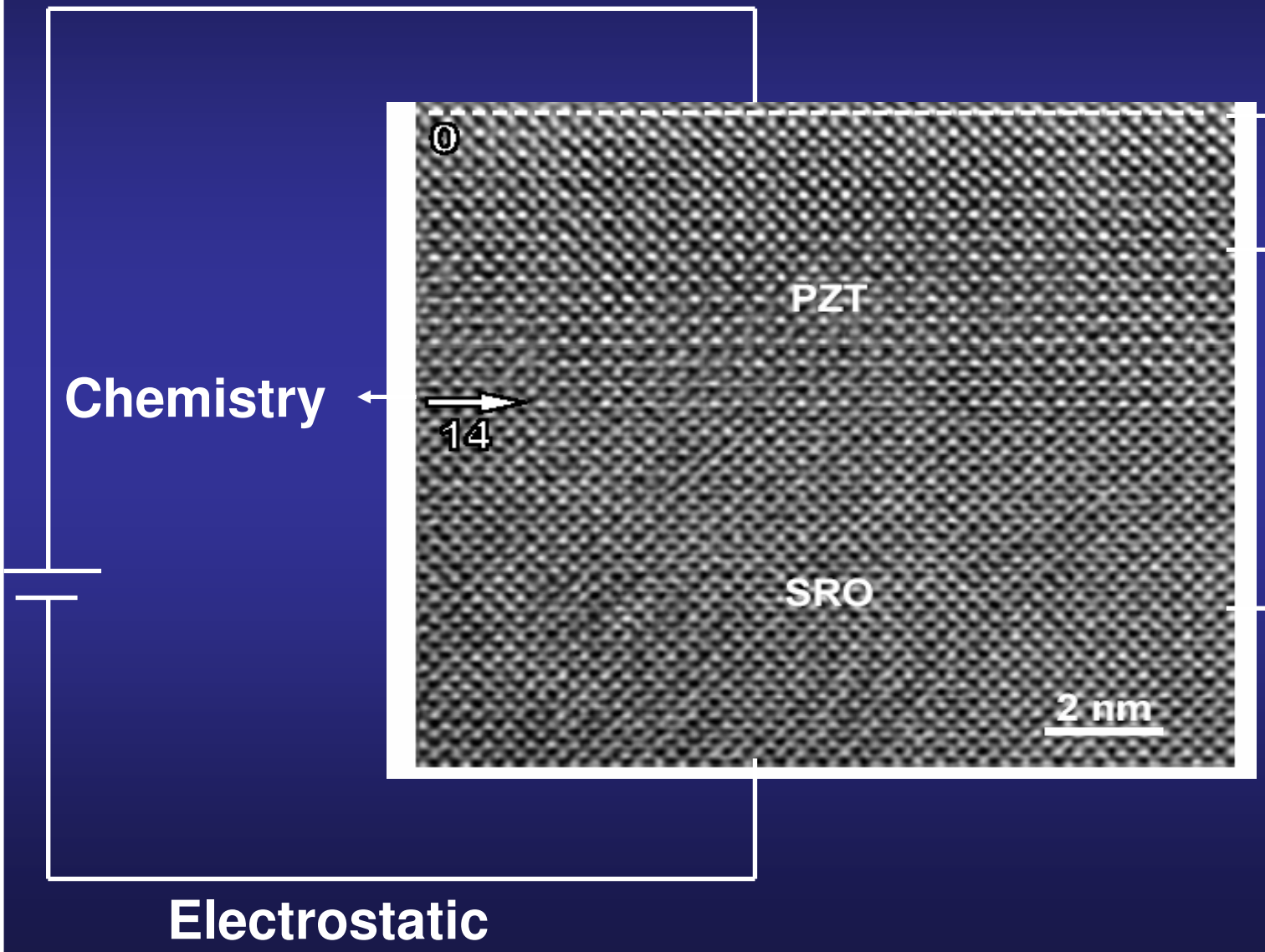
Technological applications of ferroelectric thin films: ABO_3 perovskites oxides as multifunctional materials



O. Auciello *et al.*, Physics Today July 1998, 22-27

Many effects might alter the delicate balance between long and short range forces



Surface

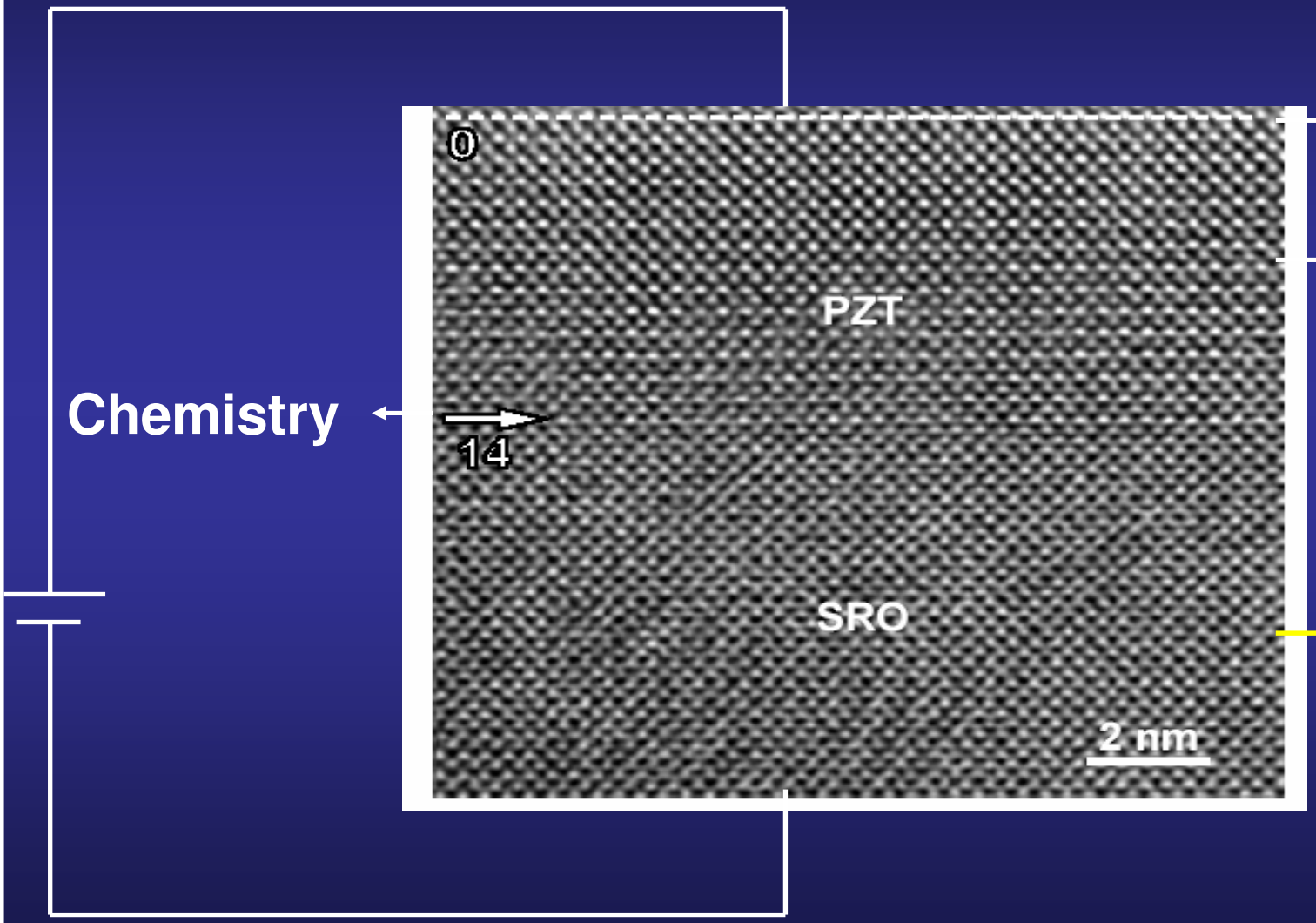
Defects

(vacancies, misfit dislocations…)

Finite conductivity

Mechanical

Many effects might alter the delicate balance between long and short range forces



Surface

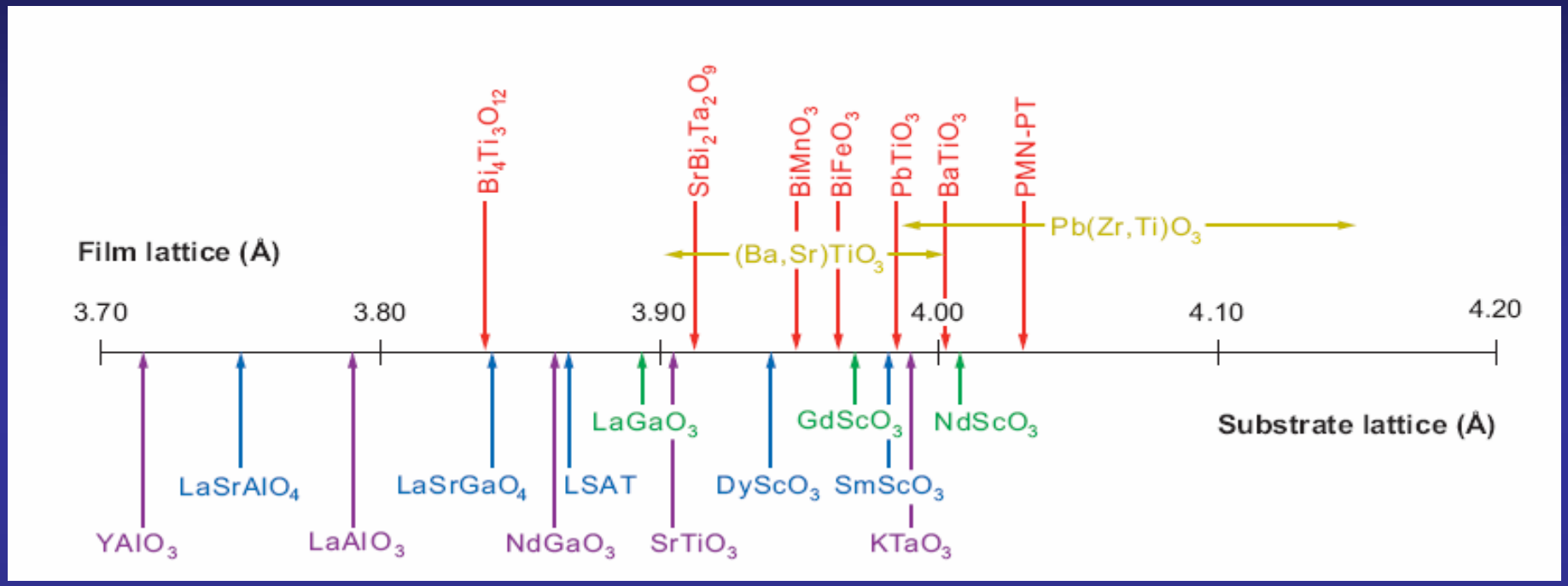
Defects

(vacancies, misfit dislocations…)

Finite conductivity

Mechanical

Many oxides have similar lattice constants allowing for a good match at the interfaces



D. G. Schlom *et al.*, Annu. Rev. Mater. Res. 37, 589 (2007)

What would happen if we could mix materials with different properties?

Potential for novel behaviour

Recent reviews on strain effects in epitaxial ferroelectric oxides

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ScienceDirect

Current Opinion in Solid State and Materials Science 9 (2005) 122–127

Current Opinion in **Solid State & Materials Science**

Theoretical investigations of epitaxial strain effects in ferroelectric oxide thin films and superlattices

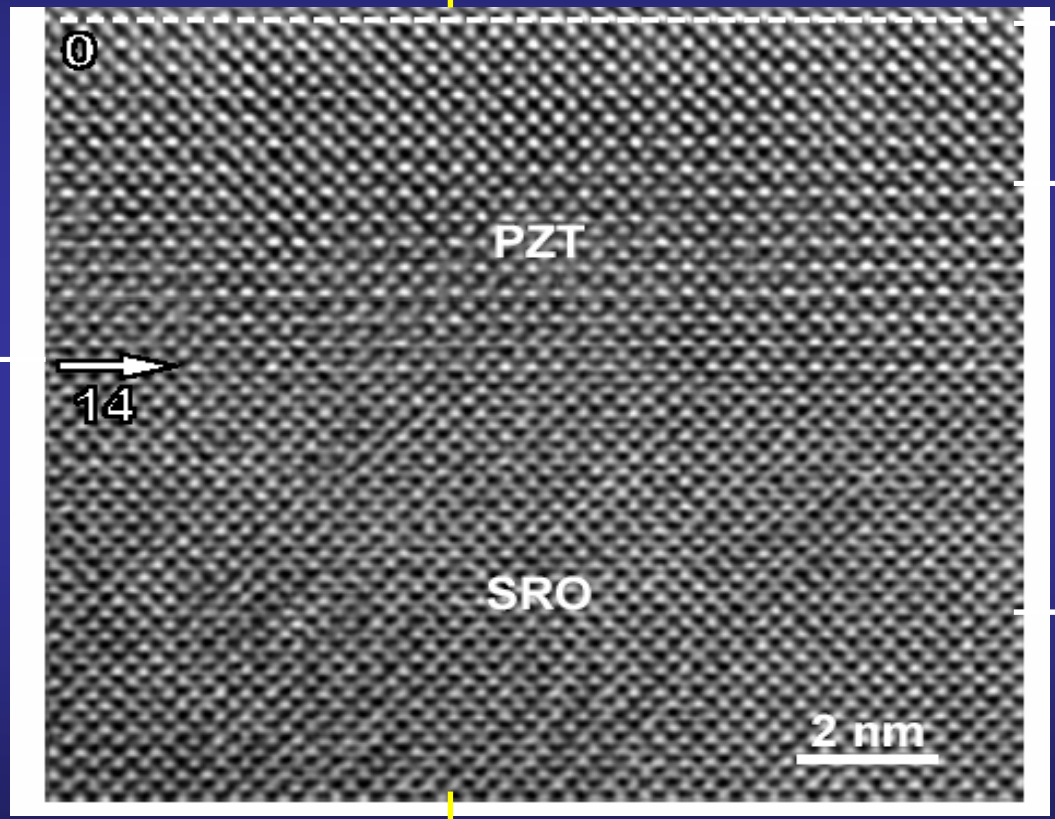
Karin M. Rabe *

Strain Tuning of Ferroelectric Thin Films*

Darrell G. Schlom,[1,†] Long-Qing Chen,[2] Chang-Beom Eom,[3] Karin M. Rabe,[4] Stephen K. Streiffer,[5] and Jean-Marc Triscone[6]

Annu. Rev. Mater. Res. 2007. 37:589–626

Many effects might alter the delicate balance between long and short range forces



Surface

Defects

(vacancies, misfit dislocations…)

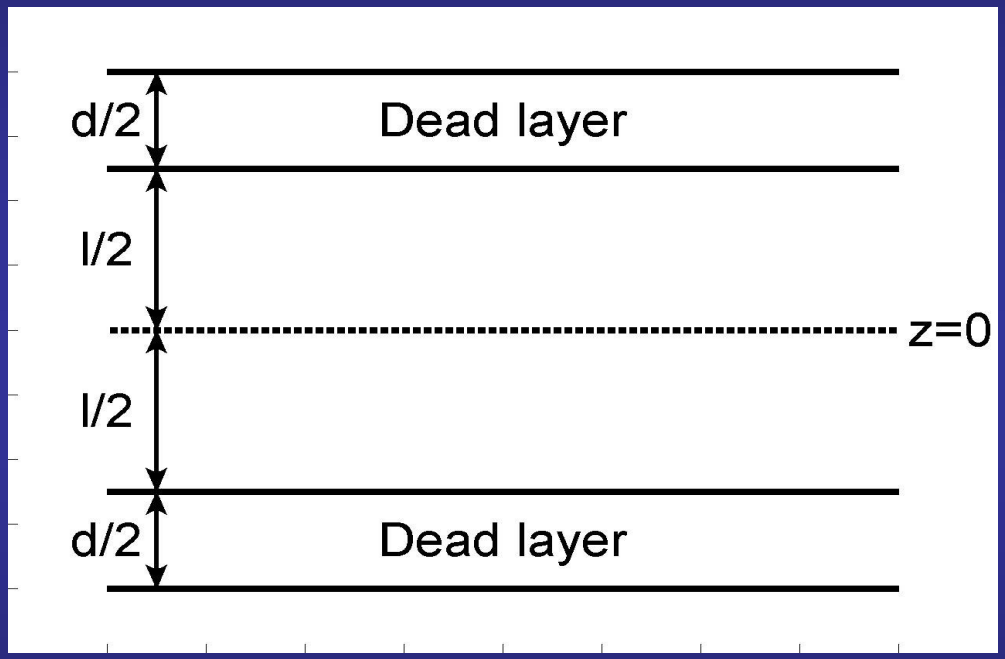
Finite conductivity

Mechanical

Chemistry

Electrostatic

Interface electrostatics within Landau-Ginzburg theories. The “dead layer”



The “dead layer”

A layer of a standard dielectric in between an ideal electrode and the ferroelectric film

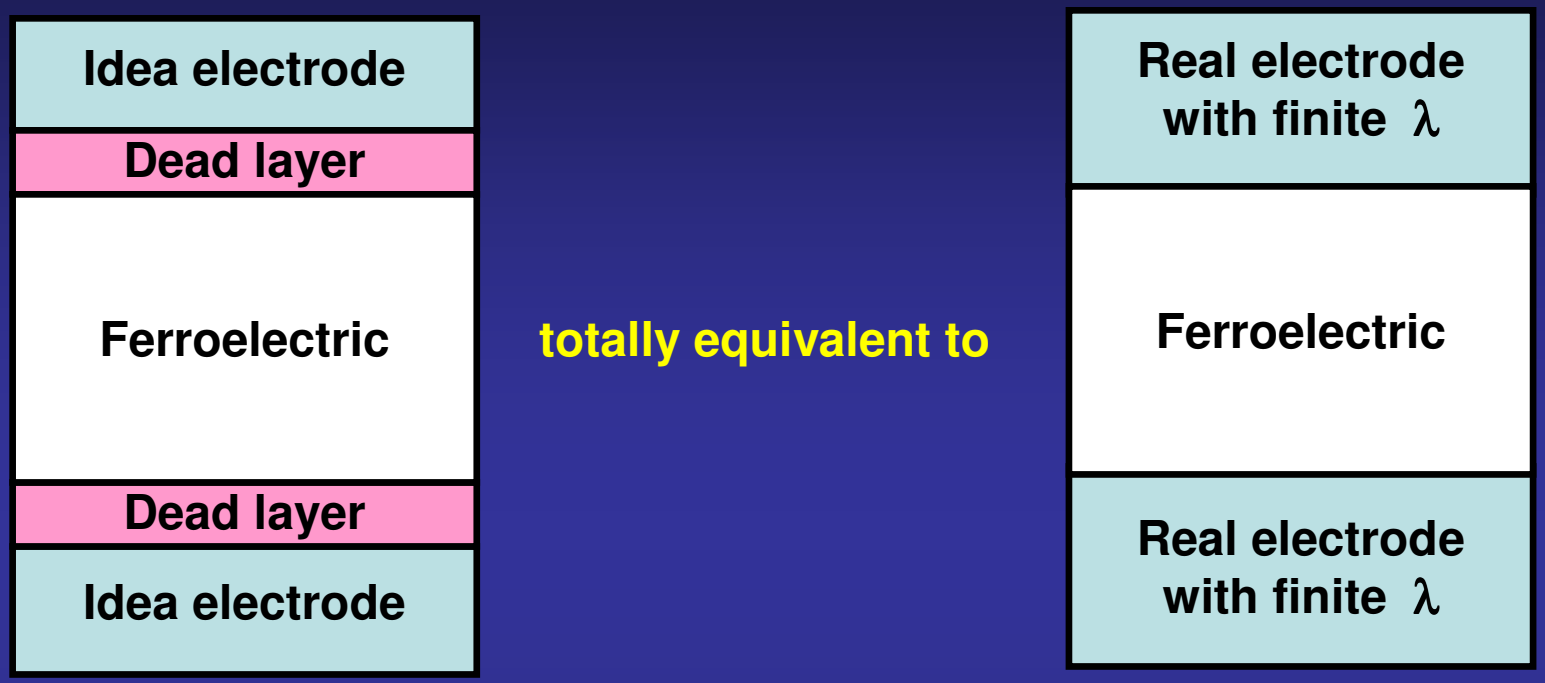
Responsible of a depolarizing field, that tends to suppress the polarization

Continuous theory of ferroelectric states in ultrathin films with real electrodes

A.M. Bratkovsky[1] and A.P. Levanyuk[1,2]

J. Comp. Theor. Nanosci. 6, 465 (2009)

The "dead layer" model is totally equivalent to consider an electrode with a finite screening length



Continuous theory of ferroelectric states in ultrathin films with real electrodes

A.M. Bratkovsky[1] and A.P. Levanyuk[1,2]

separating the electrodes and the film. In the FE capacitors with metallic electrodes, the role of the "dead layers" is played by the metallic electrode interfacial regions over the Thomas-Fermi screening length. Within the continuous medium theory the mathematical analogy between the two cases is practically exact (see below).

J. Comp. Theor. Nanosci. 6, 465 (2009)

Difficulties of the applicability of continuum theories to model electrode/ferroelectric interfaces at the nanoscale

Some assumptions might not be justified in some cases

Applicability of continuum theories to systems where variations of the relevant physical quantities occur over length scales comparable to the interatomic distances

Assumptions in the choice of the parameters:

the capacitance (or the effective screening length) is a constant as a function of the ferroelectric displacement

For a quantitative model of the electrode/ferroelectric interface there is a clear need for a theory that provides a microscopic reliable description of the local chemistry and electrostatics.

DFT has many virtues…

Wealth of information at the atomic level (atomic resolution)

Free of adjustable parameters

… but also limitations.

If overlooked might lead to erroneous physical conclusions

Be careful with the choice of the DFT-functional: description in the atomic structure

$PbTiO_3$ bulk	Cubic phase		Tetragonal phase						
	a	E_{gap}	a	c/a	$u_z(Ti)$	$u_z(O_1)$	$u_z(O_3)$	E_{gap}	ΔE
LDA, MBPP	3.880	1.55	3.853	1.050	0.5312	0.0923	0.6012	1.62	−0.053
LDA, PAW	3.894	1.48	3.867	1.043	0.5334	0.0883	0.6018		−0.056
LDA[a]	3.894		3.858	1.051					
PW91, MBPP	3.957	1.69	3.827	1.247	0.5571	0.1938	0.6670	2.04	−0.196
PW91, PAW	3.969	1.61	3.841	1.233	0.5559	0.1859	0.6660		−0.192
PBE, MBPP	3.962	1.69	3.836	1.244	0.5579	0.1949	0.6675	2.05	−0.208
PBE[a]	3.971		3.857	1.230					
Expt. (298 K)[b]	3.969		3.905	1.064	0.539	0.114	0.617	3.5	

Some of the widely flavours of the GGA functional strongly overstimates ferroelectric character at the bulk level, even yielding to erroneous supertetragonal structures

DFT has many virtues…

Wealth of information at the atomic level (atomic resolution)

Free of adjustable parameters

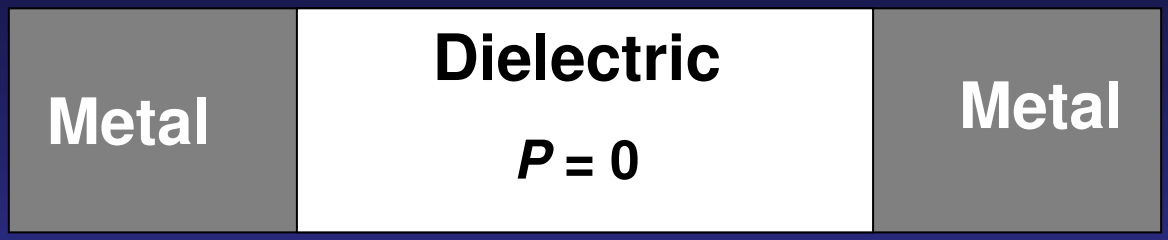
… but also limitations.

If overlooked might lead to erroneous physical conclusions

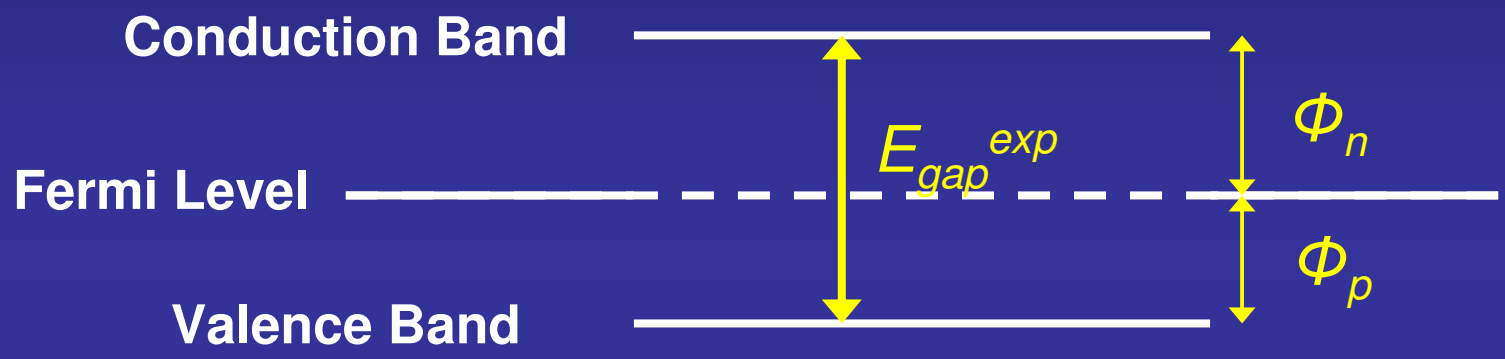
Be careful with the choice of the DFT-functional: description in the atomic structure

Be careful with the electronic structure at the interface: the “band alignment issue”

DFT band alignment problem in an unpolarized capacitor

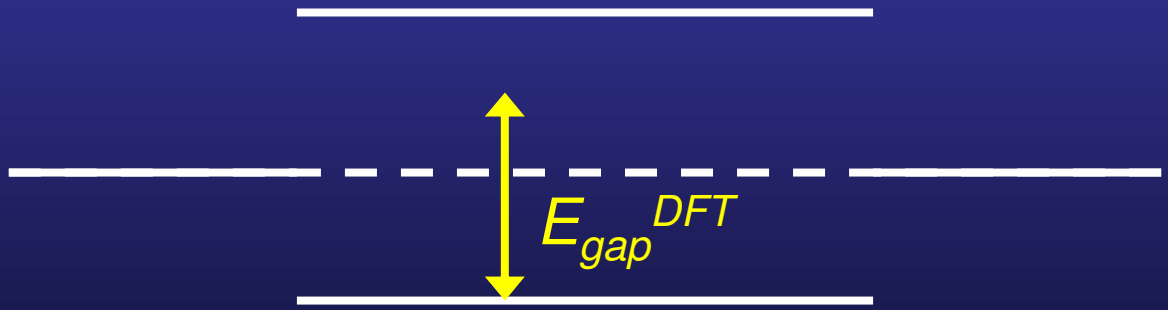


REAL WORLD

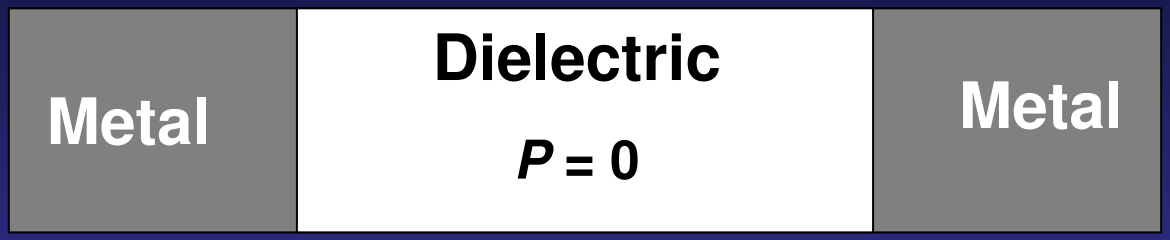


DFT

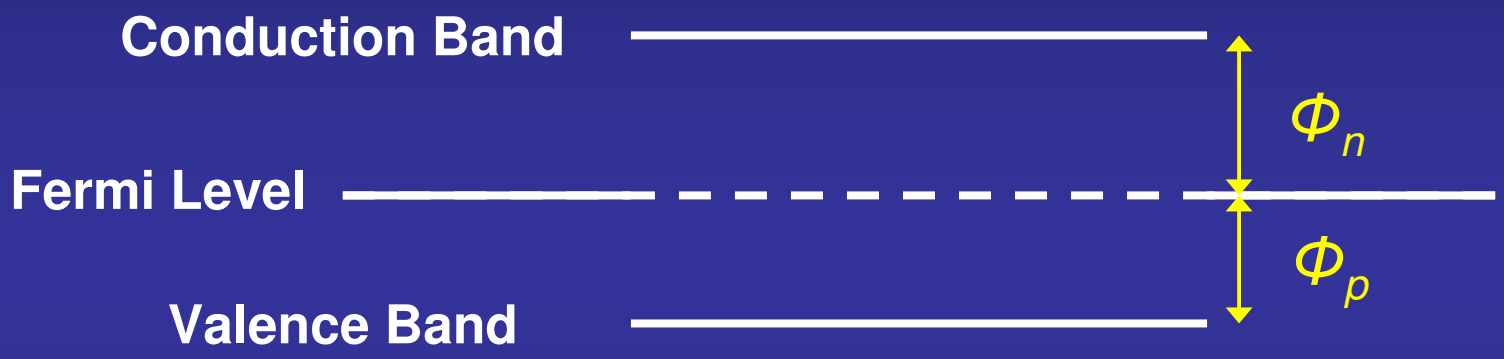
- "Normal" case



DFT band alignment problem in an unpolarized capacitor



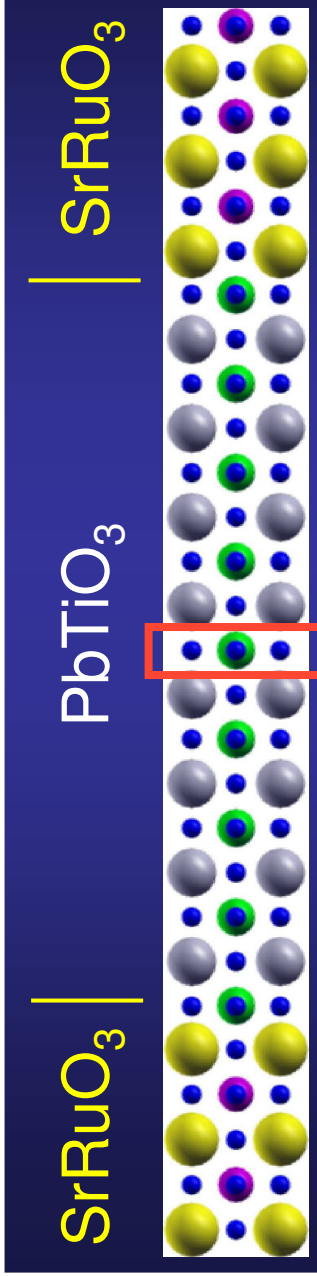
REAL WORLD



DFT

- Pathological case
- Transfer of charge in the non-polarized case

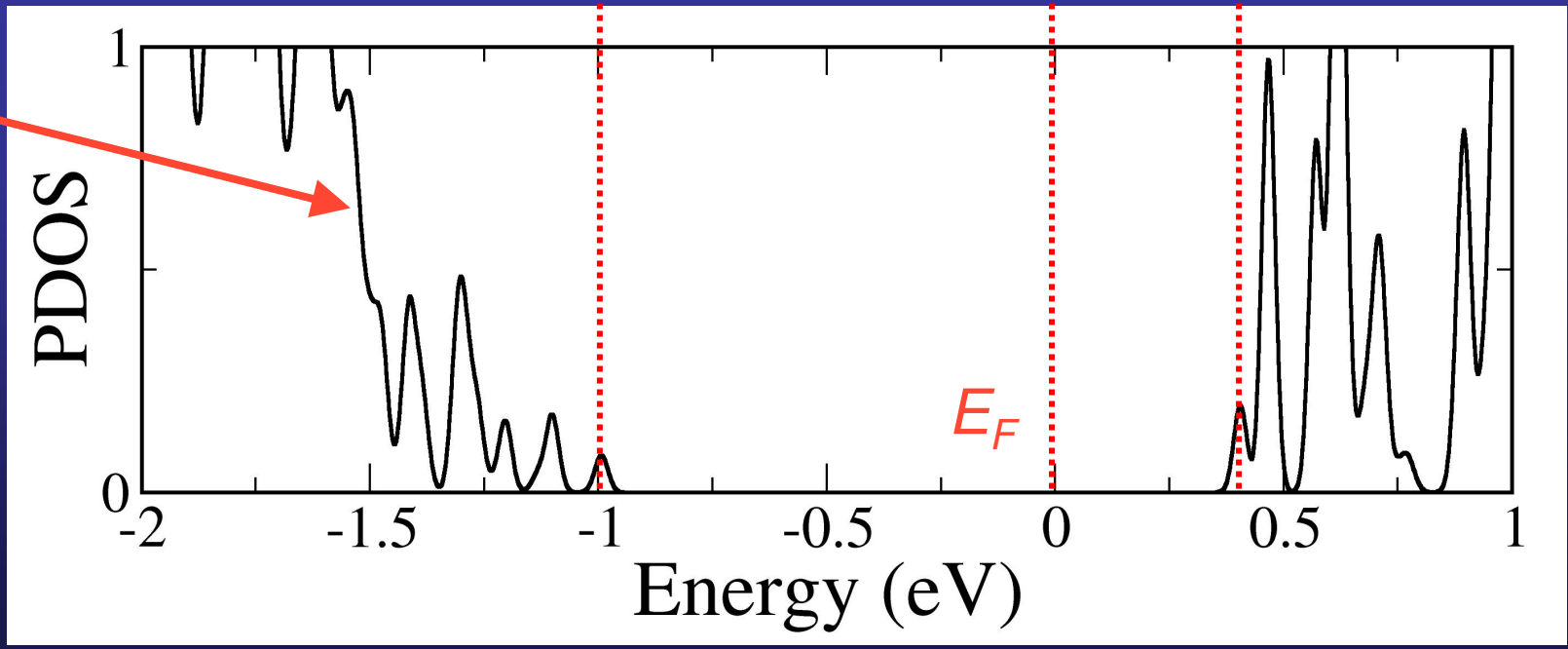
Calculating the Schottky barriers using the PDOS



Unpolarized phase

LDA gap ≈ 1.40 eV

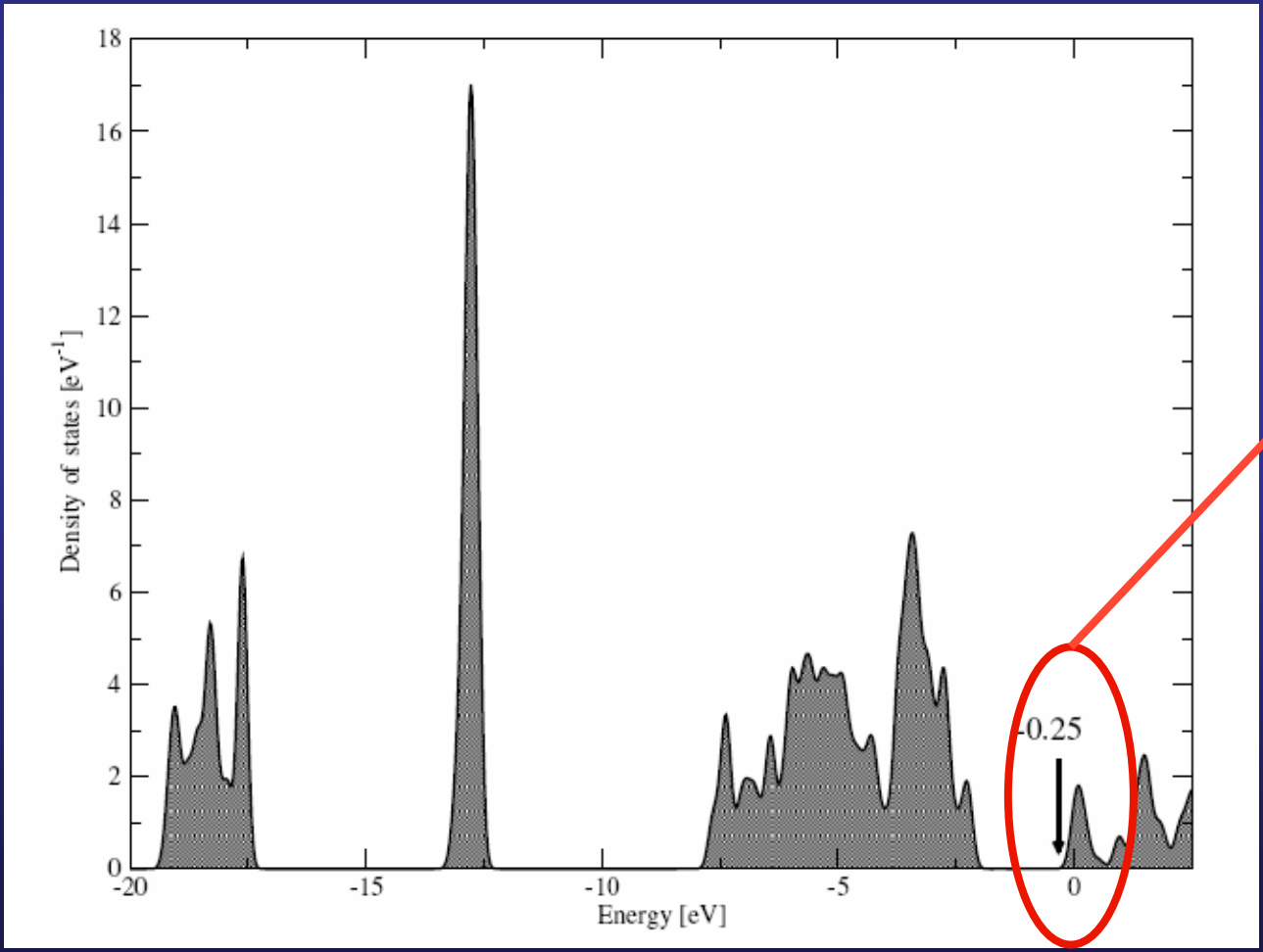
Expt. gap ≈ 3.2 eV



Transfer of charge in $KNbO_3/SrRuO_3$ nanocapacitors

Work by M. Stengel & N. Spaldin

$[KNbO_3]_{m=6.5}$ / $[SrRuO_3]_{n=7.5}$ **nanocapacitor**



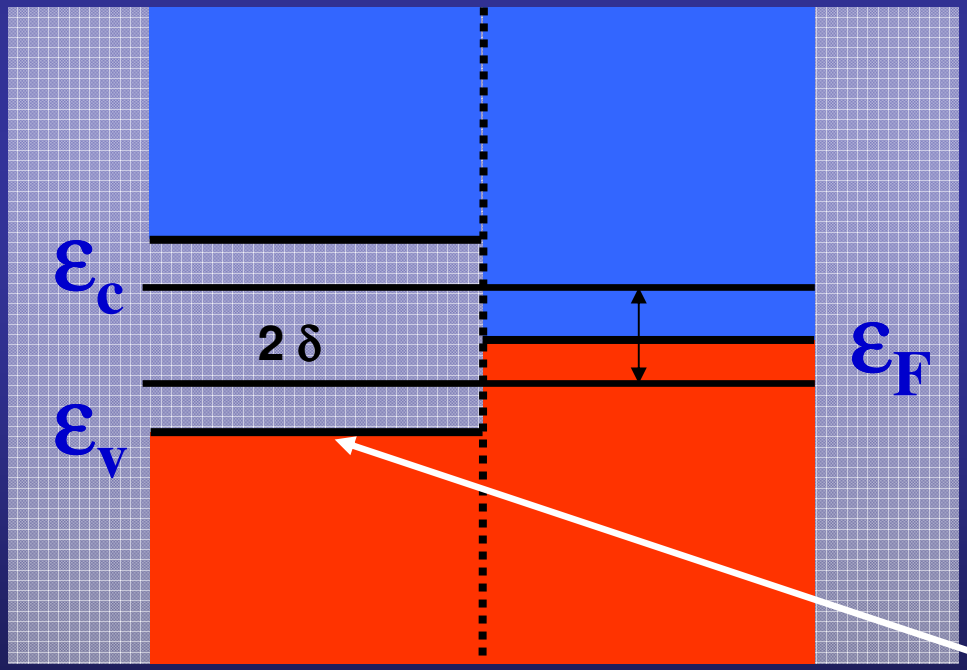
DOS proyected over the central $KNbO_3$ layer

CB of $KNbO_3$ crosses the Fermi level

Transfer of charge in $KNbO_3/SrRuO_3$ nanocapacitors

Work by M. Stengel & N. Spaldin

$$\rho_{COND}(\vec{r}) = \int_{E_F-\delta}^{E_F+\delta} \rho(\vec{r},E)dE = \sum_n \sum_{\vec{k}} |\psi_{n,\vec{k}}(\vec{r})|^2 \quad / \quad \varepsilon_{n,\vec{k}} \in (E_F-\delta, E_F+\delta)$$



In a well behaved heterostructure, we would expect no charge in layers of the dielectric far enough from the interface, since there are no states within the energy window with significant weight there.

Transfer of charge in $KNbO_3/SrRuO_3$ nanocapacitors

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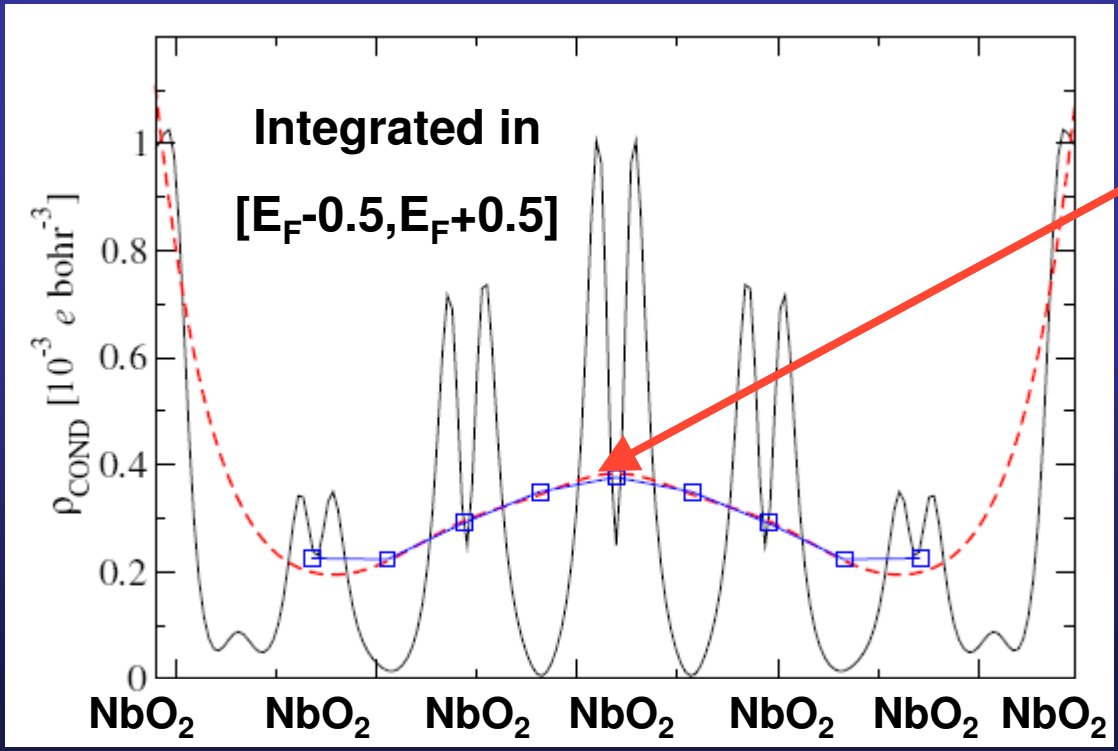
$[KNbO_3]_{m=6.5}$ / $[SrRuO_3]_{n=7.5}$ **nanocapacitor**



Spurious transfer of charge to the KNO layer

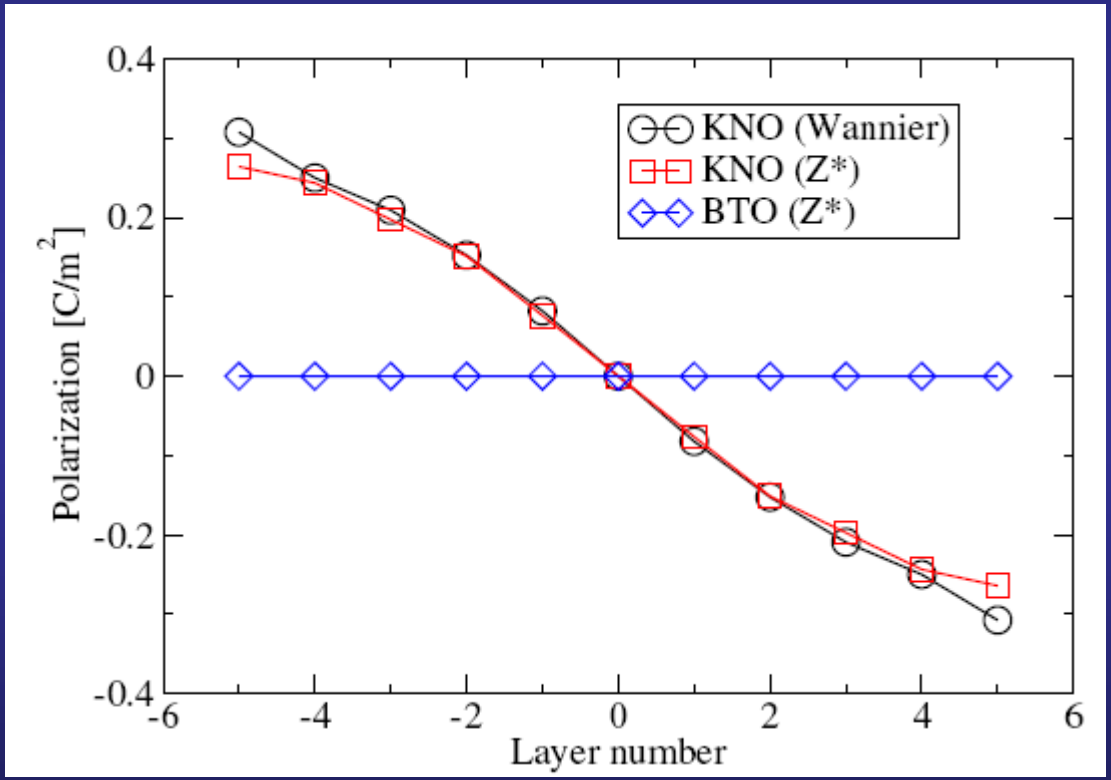
The system is not locally charge neutral

⇓

Non uniform electric fields arise in the insulating film that act on the ionic lattice

The highly polarizable ferroelectric material will then displace in an attempt to screen the perturbation

Local polarization profile



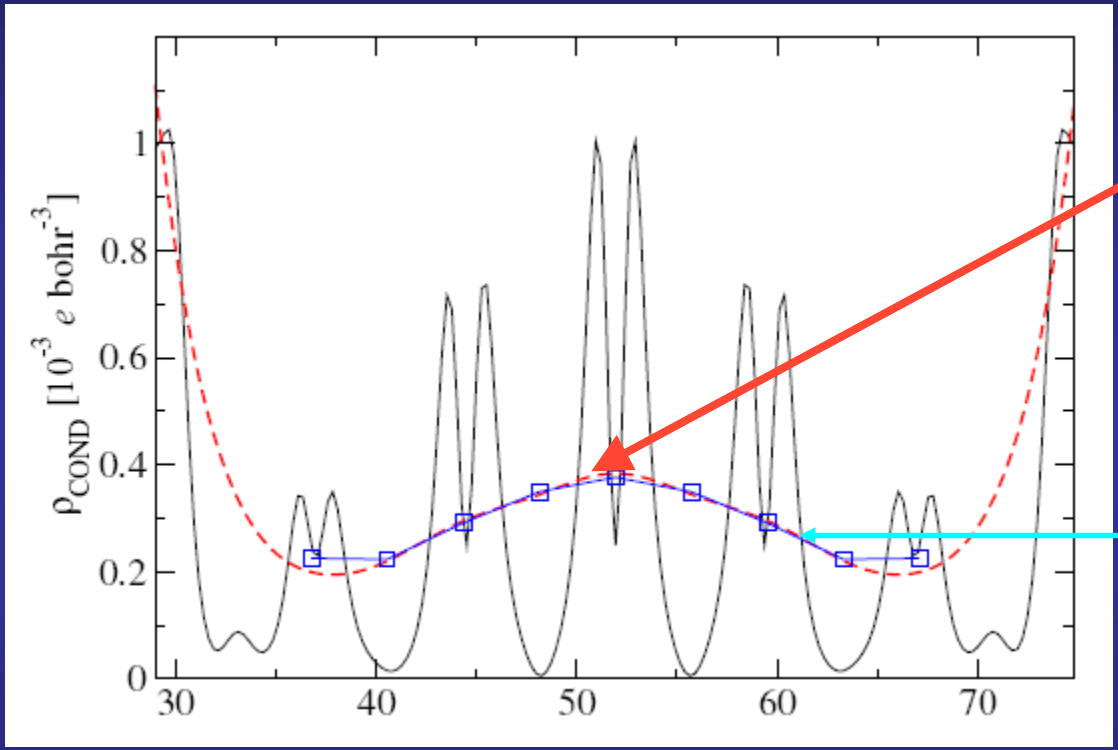
A gradient of polarization generates polarization charges

$$\frac{dP}{dx} = -\rho_B$$

If, uncompensated, has a high electrostatic energy cost

Work by M. Stengel & N. Spaldin

The excess of charge in the conduction band and the bound charge almost perfectly cancel each other



ρ_{cond}

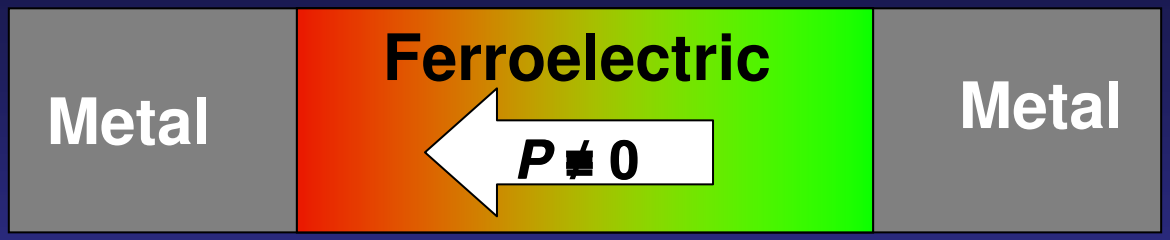
ρ_B

Taken as a finite difference of the polarization profile

The polarization profile is a consequence of $KNbO_3$ responding to the spurious population of the conduction band.

Work by M. Stengel & N. Spaldin

DFT band alignment problem



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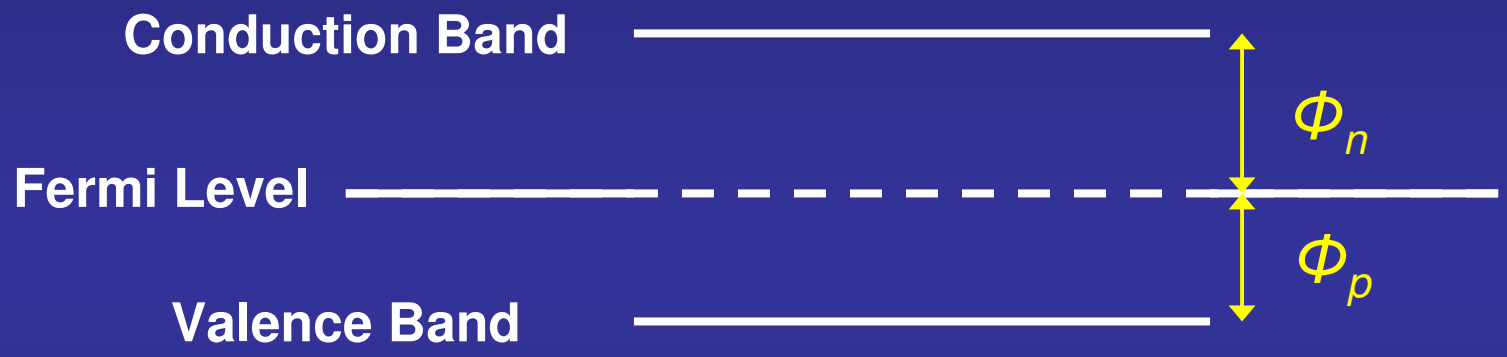
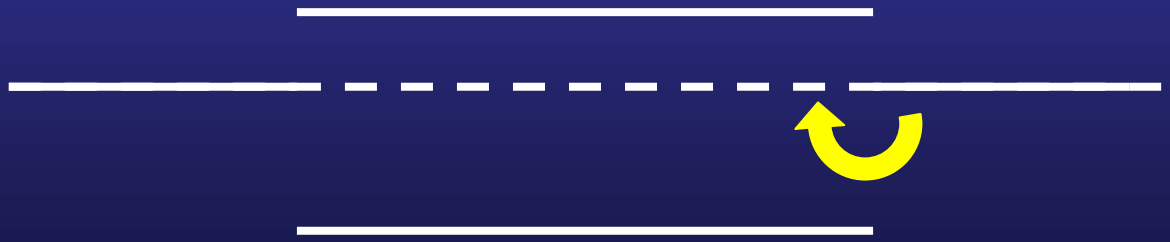


DFT (LDA)

- Pathological case

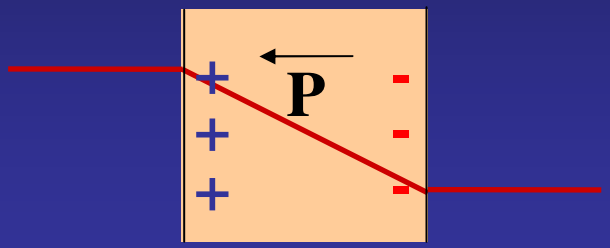
- Transfer of charge at $P \neq 0$



Many applications depend on the stability of films with a switchable polarization along the film normal

Vacuum

no screening



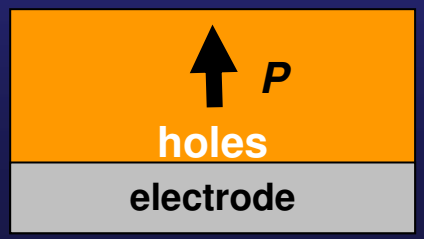
$$\mathcal{E}_d = -4\pi P$$

Screening of polarization charge is essential

Screening by

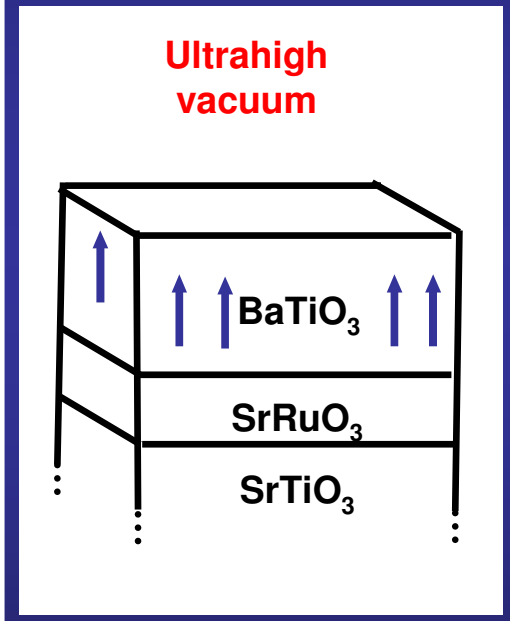
Surface relaxations and/or surface carrier layer

electrons



Inward dipole due to surface relaxations can compensate surface charge and associated depolarizing fields

Low-energy electron diffraction intensitity versus voltage (LEED I-V)



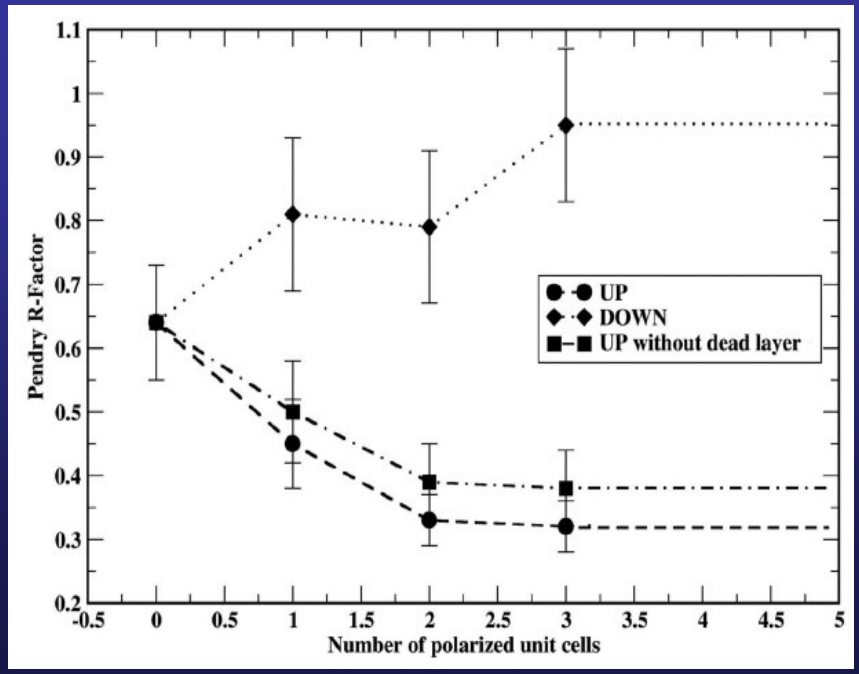
Monodomain upward polarization

Quantitative theory-experiment comparison

Reliability Pendry factor

0 — Perfect correlation

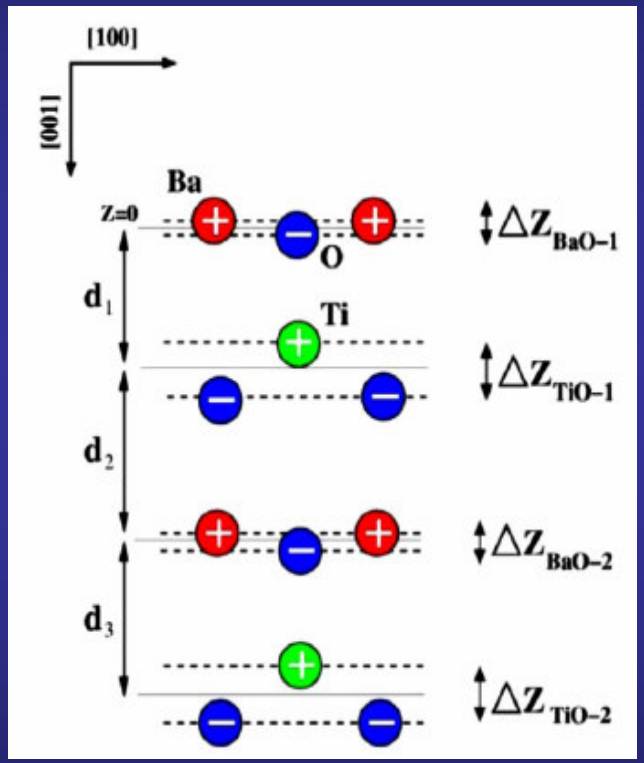
1 — Uncorrelated



J. Shin *et al.*, Phys. Rev. B 77, 245437 (2008)

Inward dipole due to surface relaxations can compensate surface charge and associated depolarizing fields

Best-fit surface structure



Monodomain upward polarization

No polarization charges

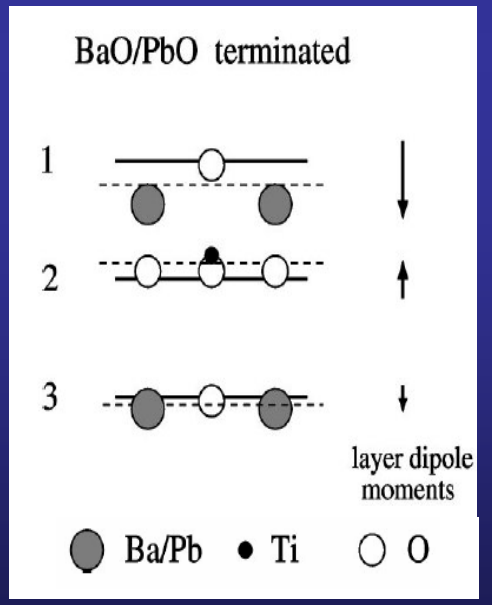
⇑

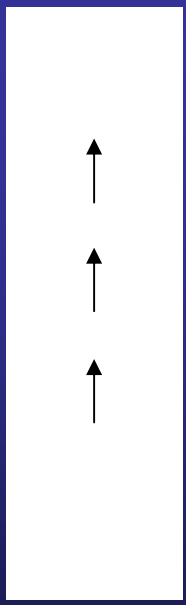
Lack of polarization at the top BaO layer

Atomic displacements associated with upward polarization

=

surface relaxation + FE soft mode



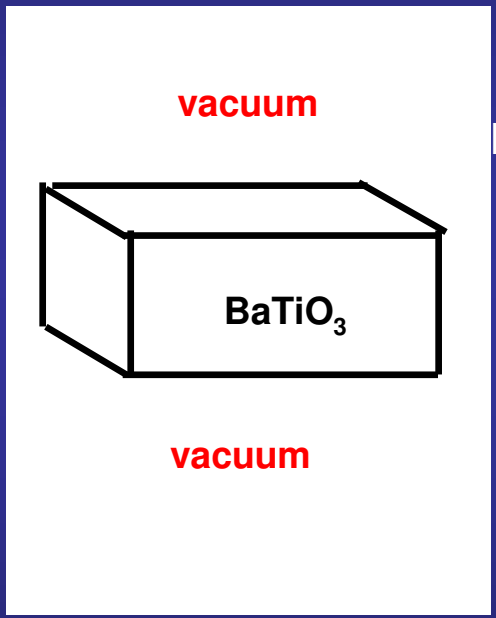


J. Shin *et al.*, Phys. Rev. B 77, 245437 (2008)

Meyer *et al.*, Phys. Rev. B 63, 205426 (2001)

Polarization surface charges might be screened by a surface carrier layer

First-principles calculations on an isolated free-standing slab



Bottom of the conduction band

Ti 3d, uncharged

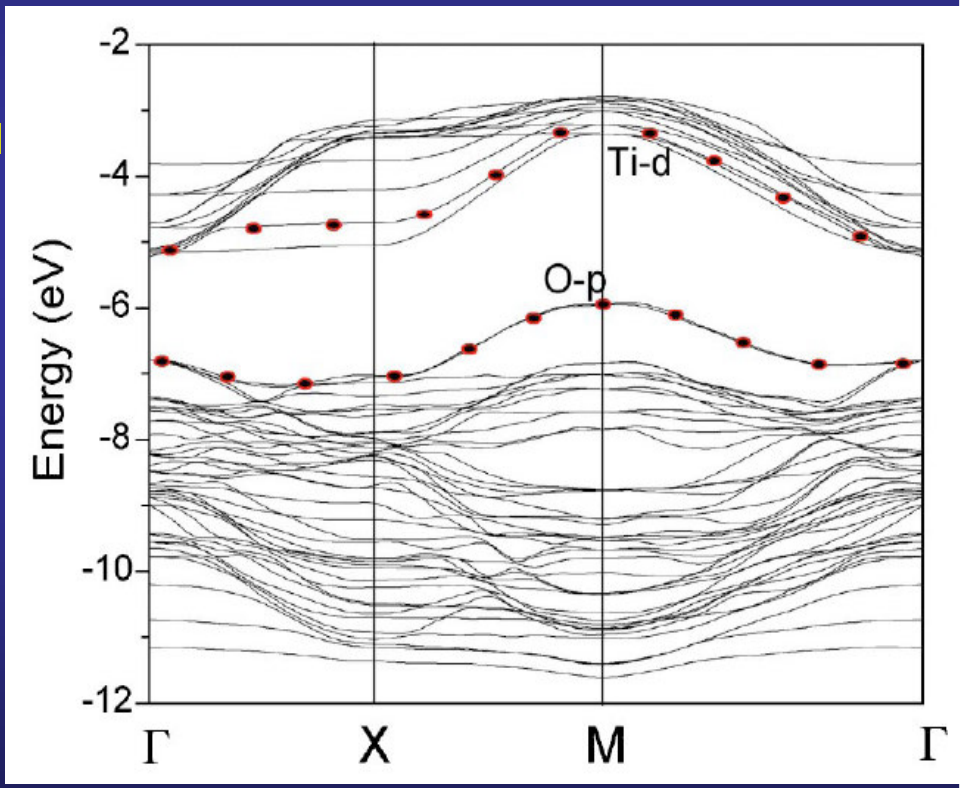
Top of the valence band

O 2p, uncharged

TiO_2 termination

Convergence criterion
0.06 eV/Å

Band structure of the unpolarized slab



M. Krcmar and C. L. Fu, Phys. Rev. B 68, 115404 (2003)

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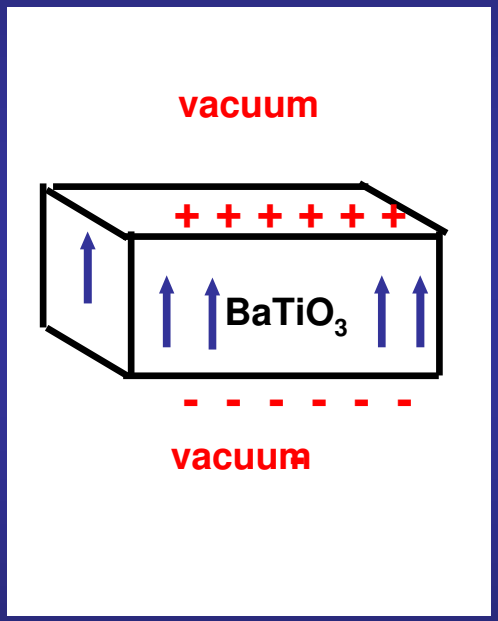


$\mathcal{E}_d$

Electrons at the top

- - - - - - - - -

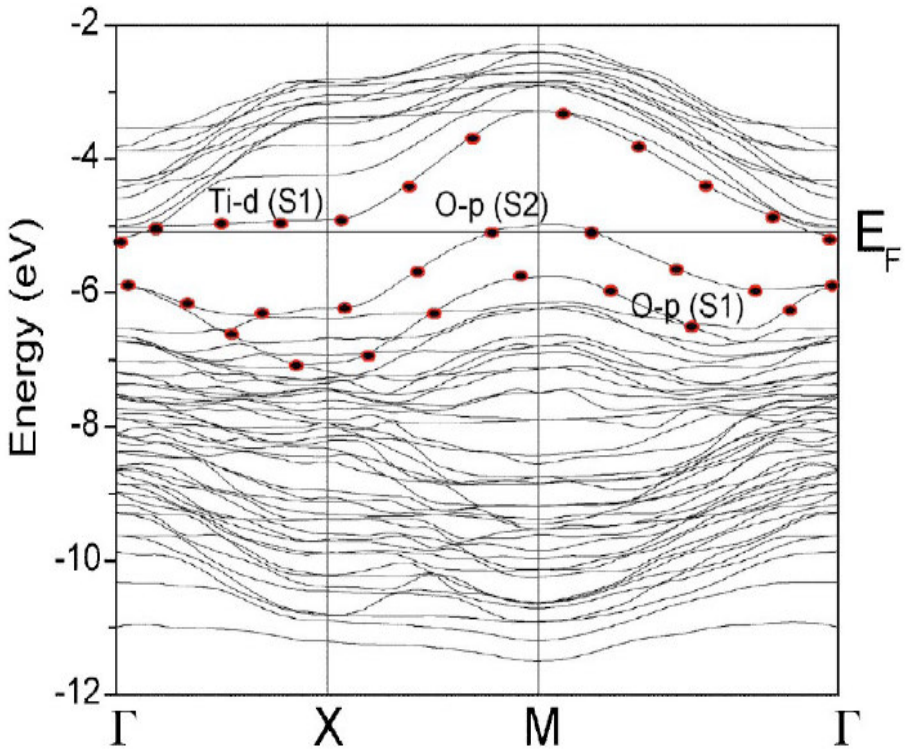
+ + + + + + + + +

Holes at the bottom

TiO_2 termination

Convergence criterion 0.06 eV/Å

Band structure of the polarized slab



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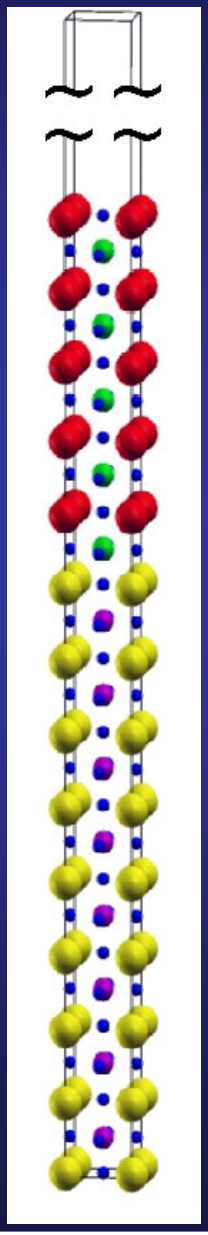
First-principles LDA simulations: surface relaxations as in non-polar free-standing slabs



≈ 600 bohrs of vacuum

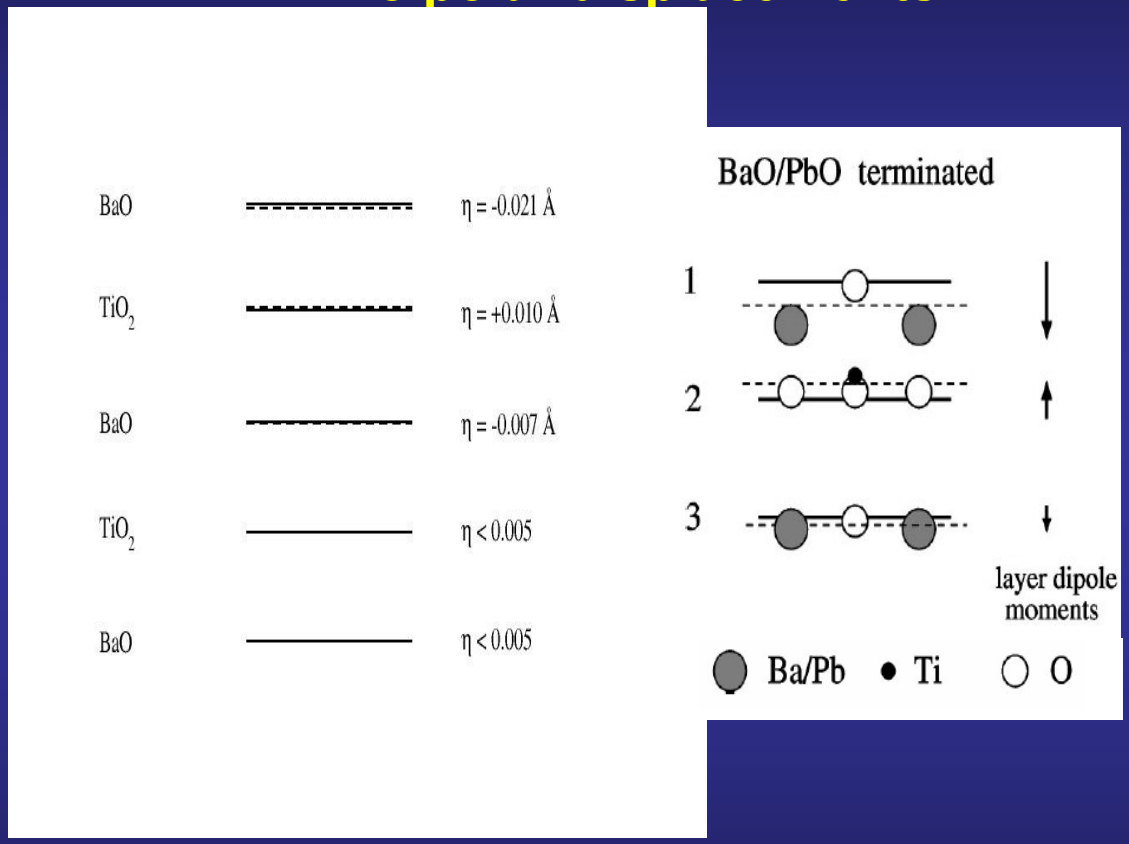
BaO termination

4.5 unit cells of $BaTiO_3$

SrO/TiO_2 interface

9.5 unit cells of $SrRuO_3$

No polar displacements



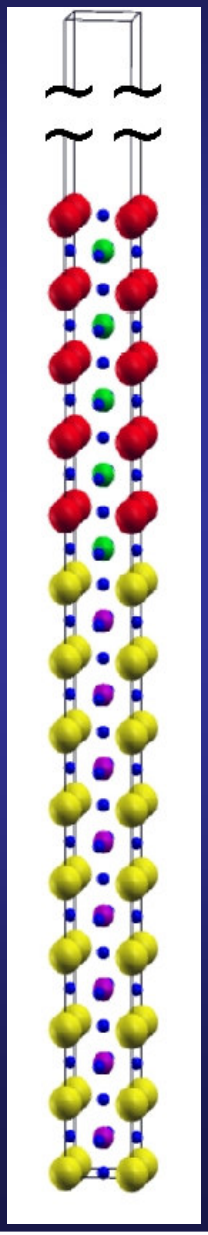
Rumpling as in unpolarized free-standing slab:

O above Ba in the topmost layer

Oscillatory pattern

Rapid decay in the interior

First-principles simulations: no band crossing at the surface



≈ 600 bohrs of vacuum

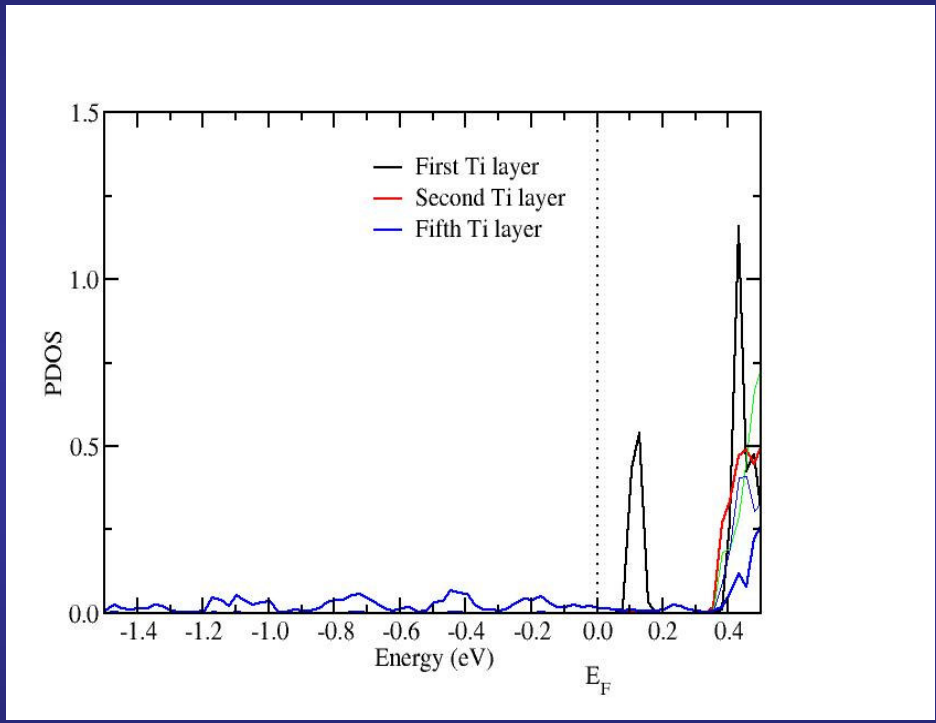
BaO termination

4.5 unit cells of $BaTiO_3$

SrO/TiO_2 interface

9.5 unit cells of $SrRuO_3$

No surface carrier layer

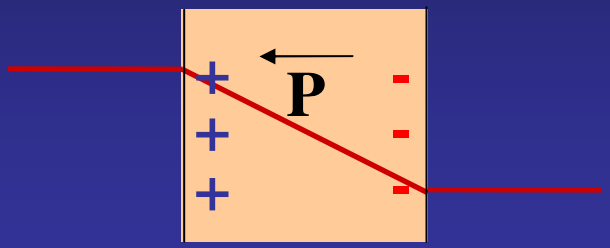


Bottom of conduction band (Ti 3d states) does not cross the Fermi level

Many applications depend on the stability of films with a switchable polarization along the film normal

Vacuum

no screening

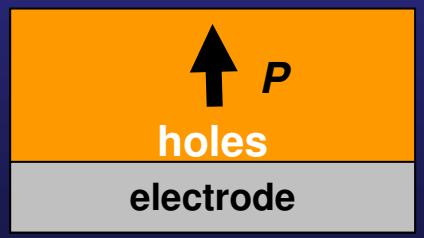


$$\mathcal{E}_d = -4\pi P$$

Screening by

Surface relaxations and/or surface carrier layer

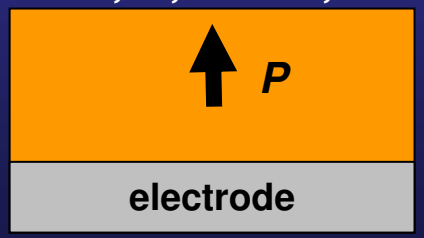
electrons



Screening by

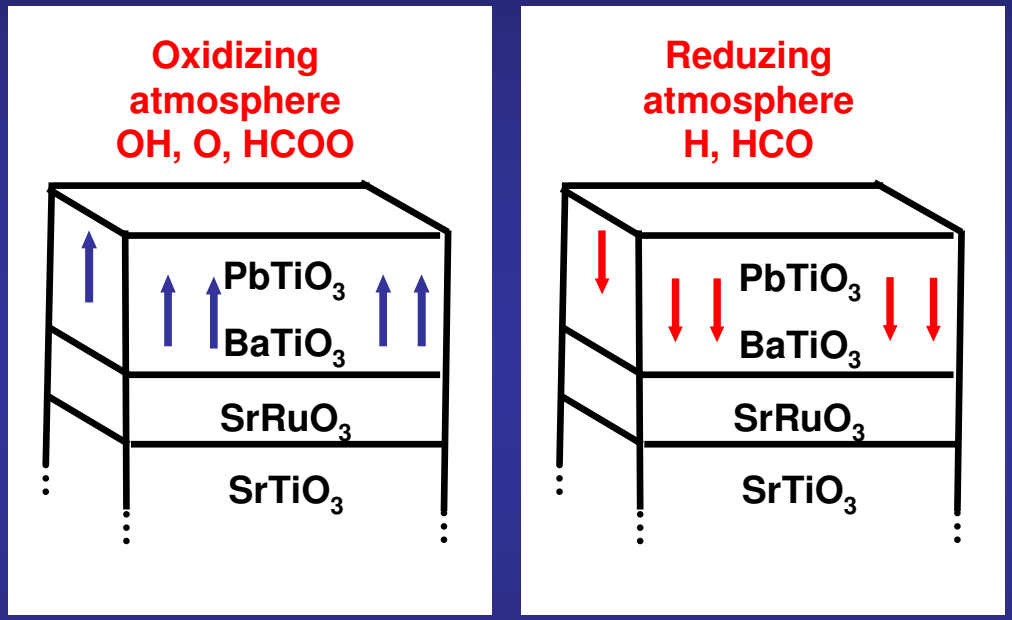
adsorbates

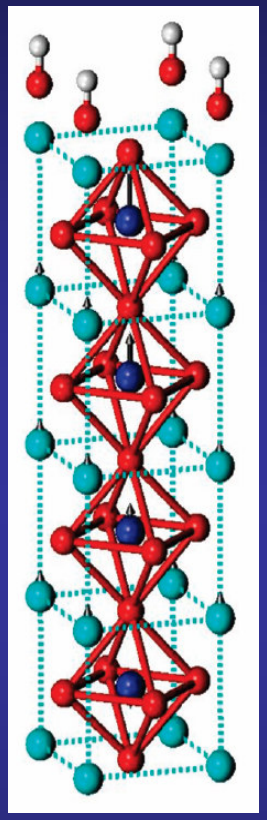
OH, O, HCOO,...



Adsorbed ions can stabilize the polar monodomain state in ultrathin films

DFT simulations + Gibbs free energy estimations

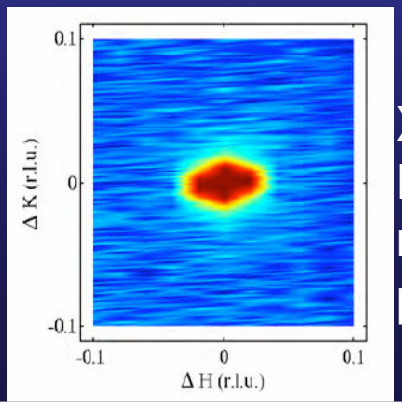




Full coverage of OH

4 unit cells (1.6 nm) $BaTiO_3$

Atomic or molecular adsorption screens a significant amount of polarization charge on the surface



X-ray scattering + PFM: Direct transition to a monodomain state, polarized "up"

D. D. Fong *et al.*, Phys. Rev. Lett. 96, 127601 (2006)

J. E. Spanier *et al.*, Nano Lett. 6, 735 (2006)

Adsorbed ions can stabilize the polar monodomain state in ultrathin films

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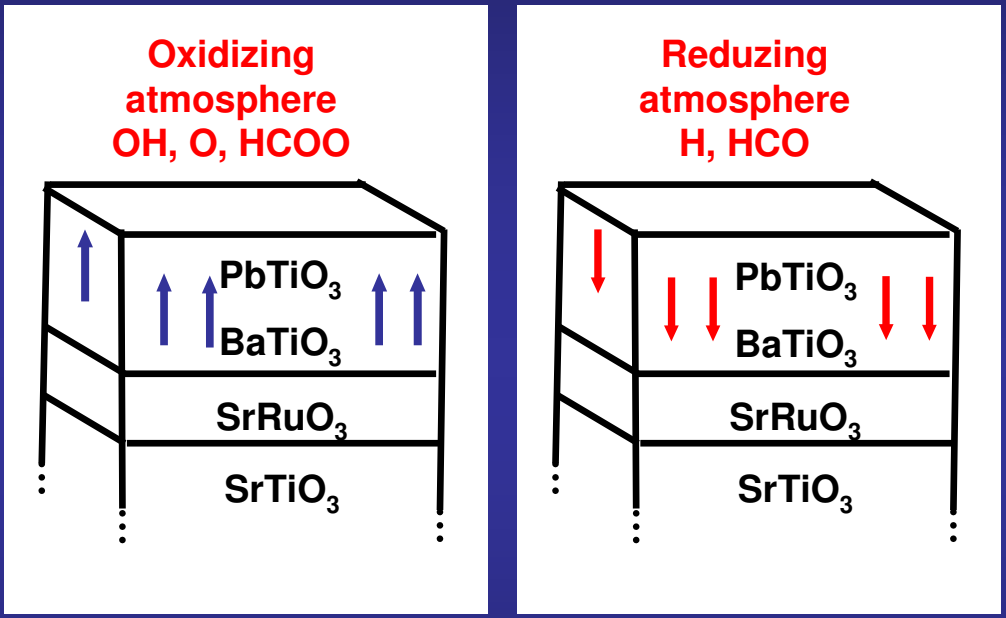
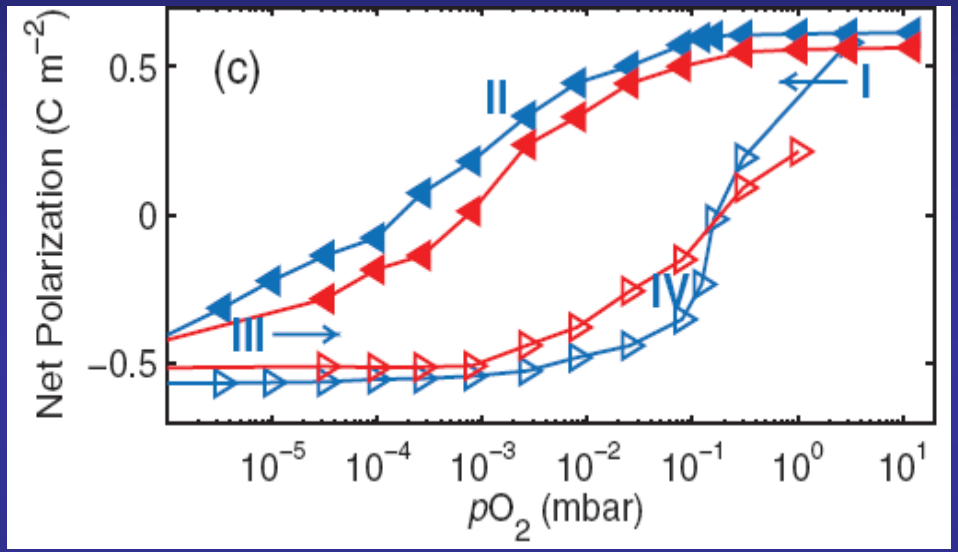


Chemical switching of a ferroelectric



Atomic or molecular adsorption screens a significant amount of polarization charge on the surface

Thin film can be reversibly and reproducibly switched by varying the partial O pressure above its surface

D. D. Fong *et al.*, Phys. Rev. Lett. 96, 127601 (2006)

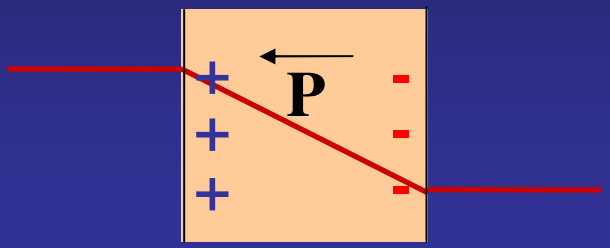
J. E. Spanier *et al.*, Nano Lett. 6, 735 (2006)

R. V. Wang *et al.*, Phys. Rev. Lett. 102, 047601 (2009)

Many applications depend on the stability of films with a switchable polarization along the film normal

Vacuum

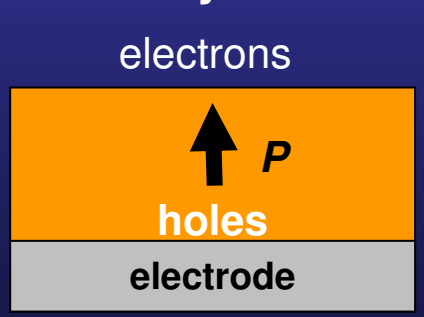
no screening



$$\mathcal{E}_d = -4\pi P$$

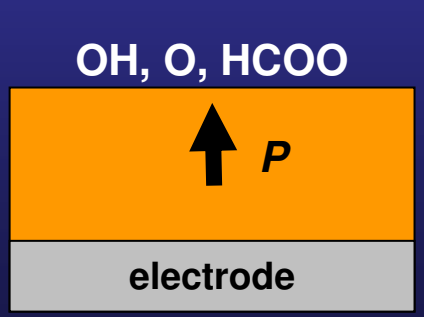
Screening by

Surface relaxations and/or surface carrier layer



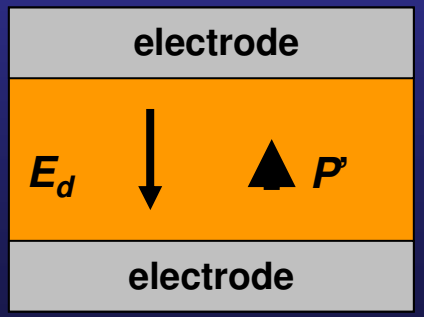
Screening by

adsorbates

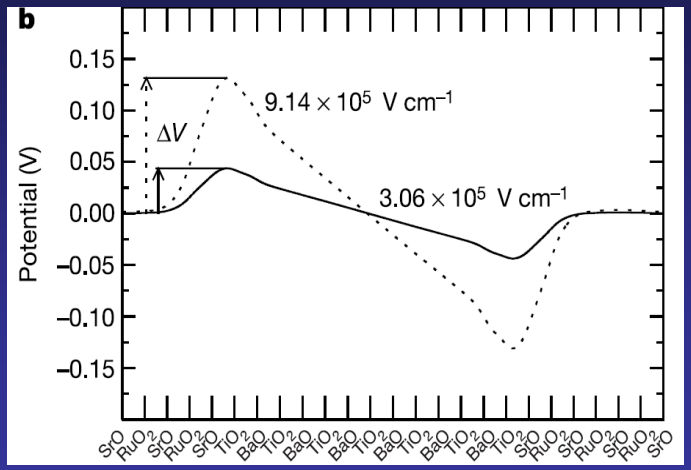


Screening by

metallic electrodes

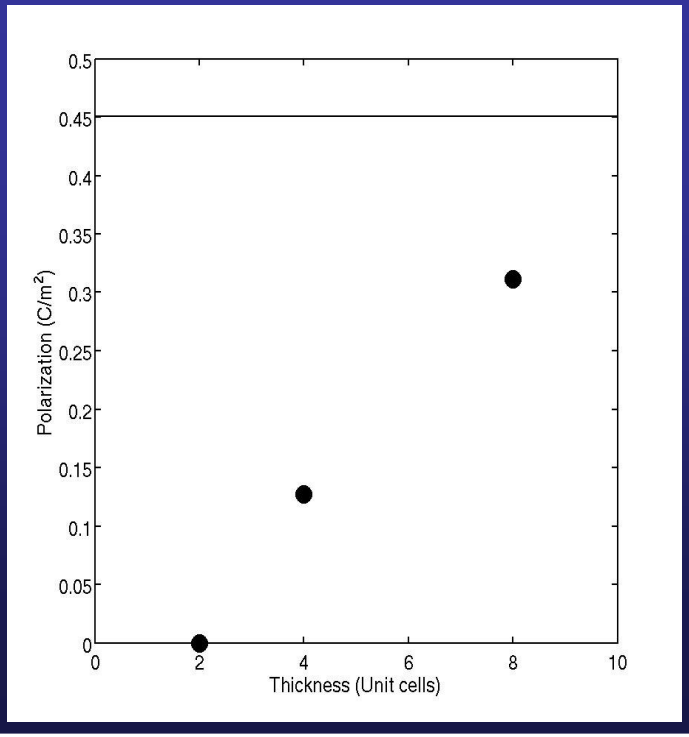


Standard case: depolarizing field due to imperfect screening of polarization charges reduces the spontaneous polarization



J. Junquera and Ph. Ghosez, Nature 422, 506 (2003)

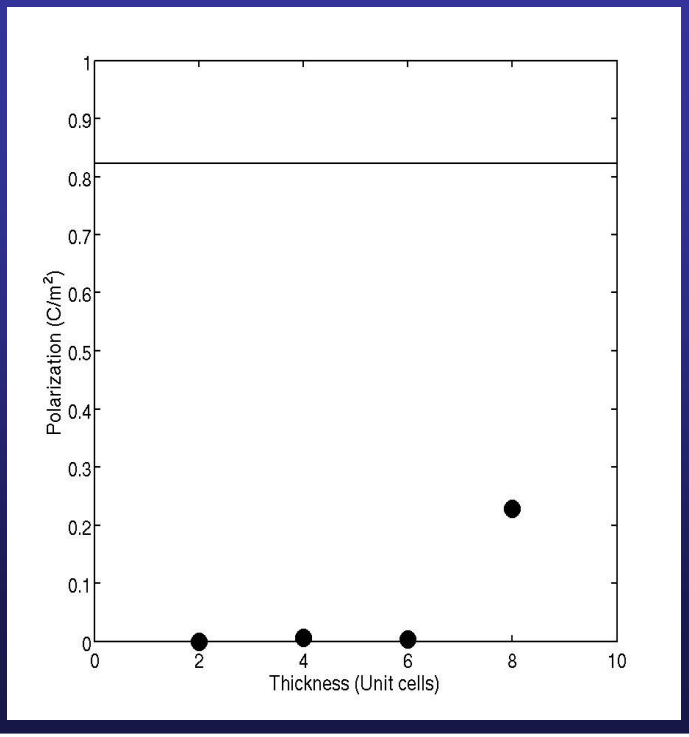
$SrRuO_3/BaTiO_3/SrRuO_3$



Bulk strained polarization

All atomic positions and c-lattice vector relaxed

$SrRuO_3/PbTiO_3/SrRuO_3$

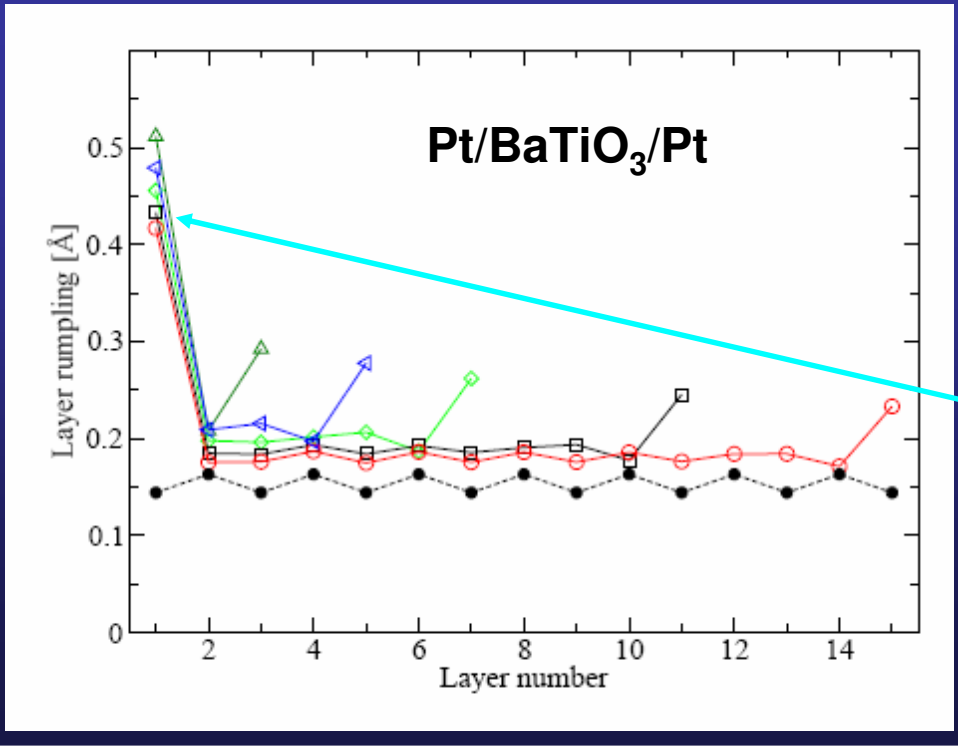


Particular combinations of AO-term. perovskites and simple metals: enhancement of ferroelectricity

ARTICLES
PUBLISHED ONLINE: 19 APRIL 2009 | DOI: 10.1038/NMAT2429
nature materials

Enhancement of ferroelectricity at metal–oxide interfaces

Massimiliano Stengel[1], David Vanderbilt[2] and Nicola A. Spaldin[1]*



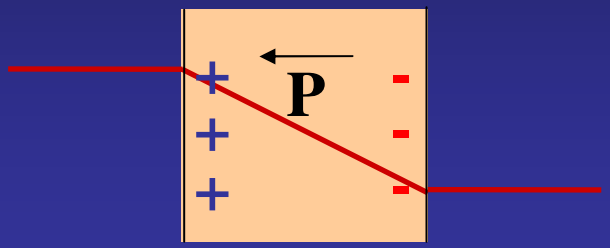
The mechanism leading to such a an enhancement is related to an interfacial chemical bonding effect

Huge enhancement of the rumpling parameter at the AO layer directly in contact with the Pt surface

Many applications depend on the stability of films with a switchable polarization along the film normal

Vacuum

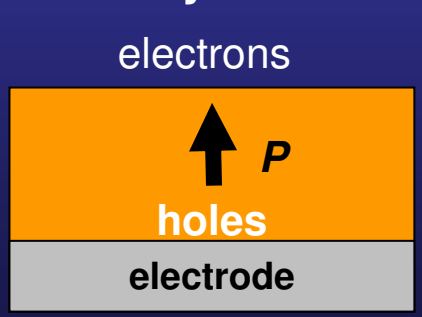
no screening



$$\mathcal{E}_d = -4\pi P$$

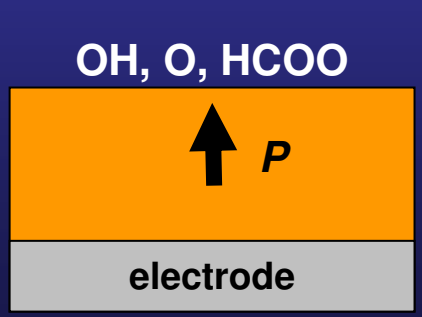
Screening by

Surface relaxations and surface carrier layer



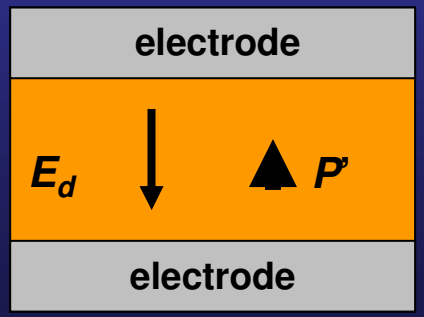
Screening by

adsorbates



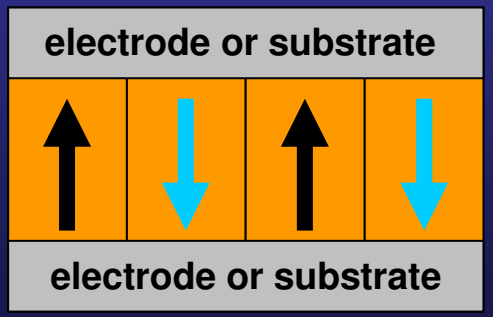
Screening by

metallic electrodes



Screening by

formation of domains



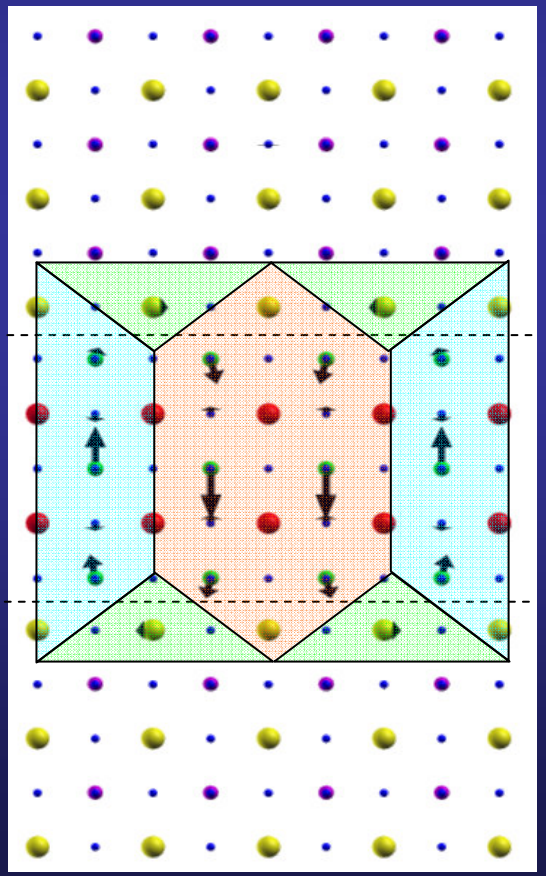
Polydomain phases stable, even below t_c in monodomain. Adopt the "domain of closure", common in ferromagnets

P. Aguado-Puente and J. Junquera
Phys. Rev. Lett. 100, 177601 (2008)

$SrRuO_3/BaTiO_3/SrRuO_3$

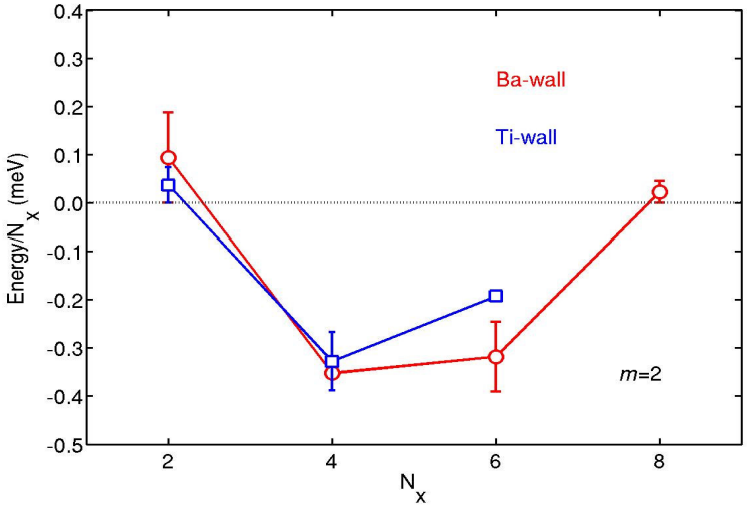
$N_x = 4$

BaO domain walls

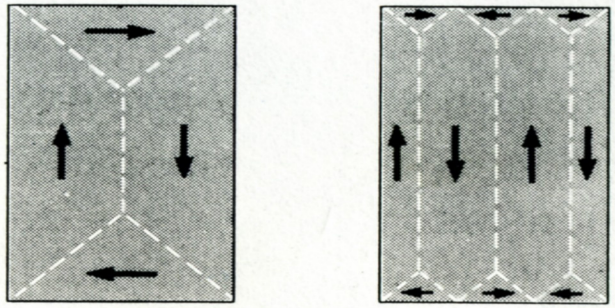


2 unit cell thick

Below critical thickness for monodomain polarization



Ferromagnetic domains



C. Kittel (1946)

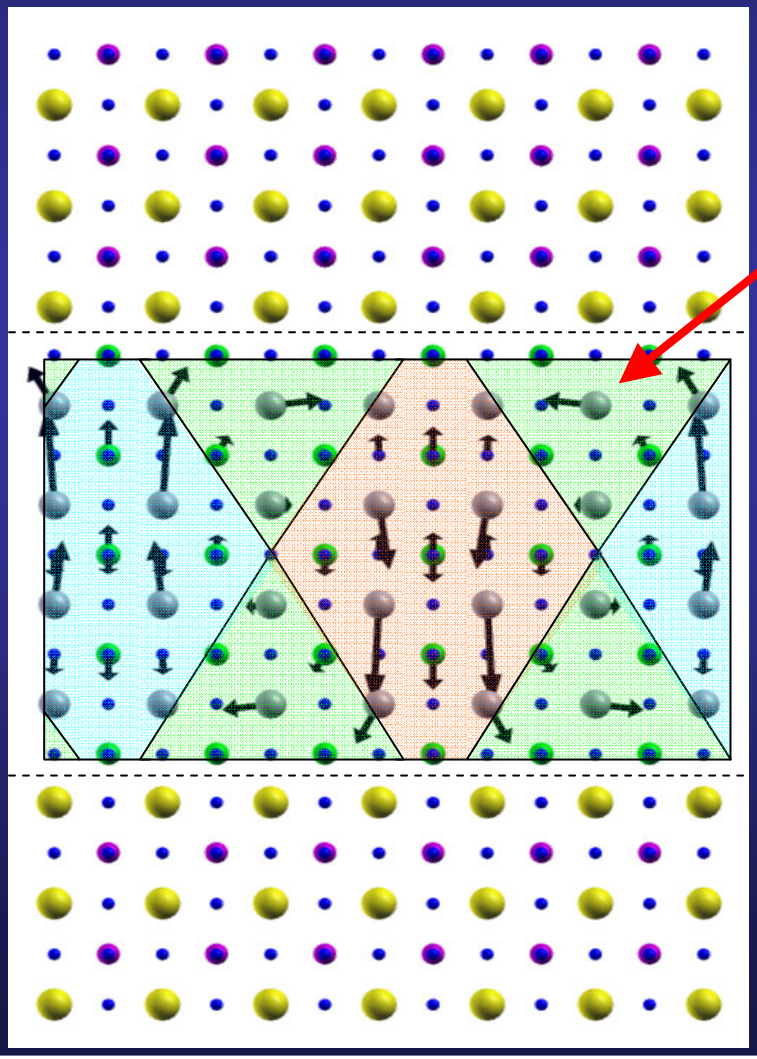
Domains of closure in $PbTiO_3/SrRuO_3$ capacitor

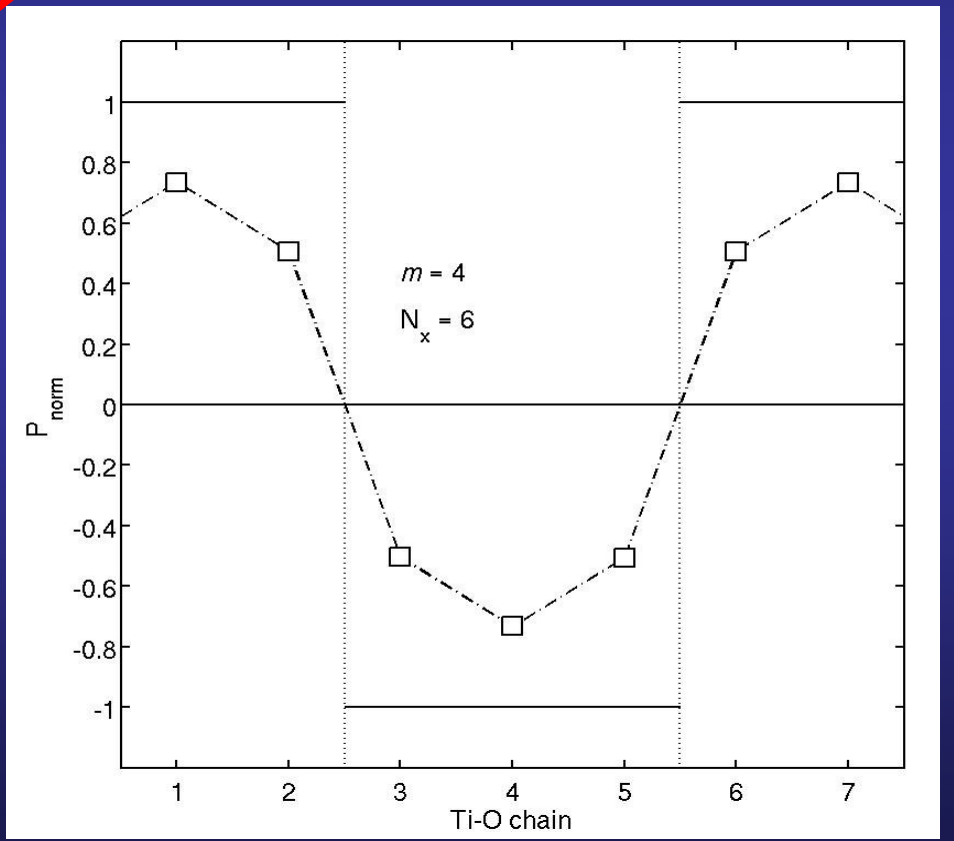
$m = 4, N_x = 6$

PbO domain walls

$E_{domains} - E_{para} = -50$ meV

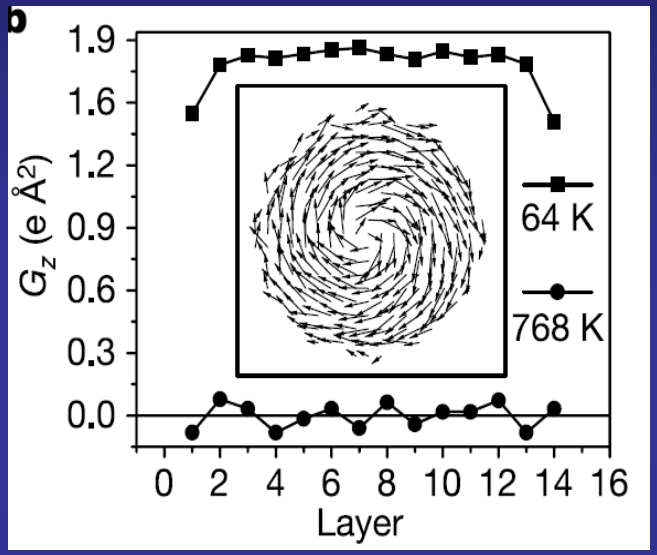
Domains close inside the FE





Vortices in ferroelectric nanostructures: theoretical and experimental results

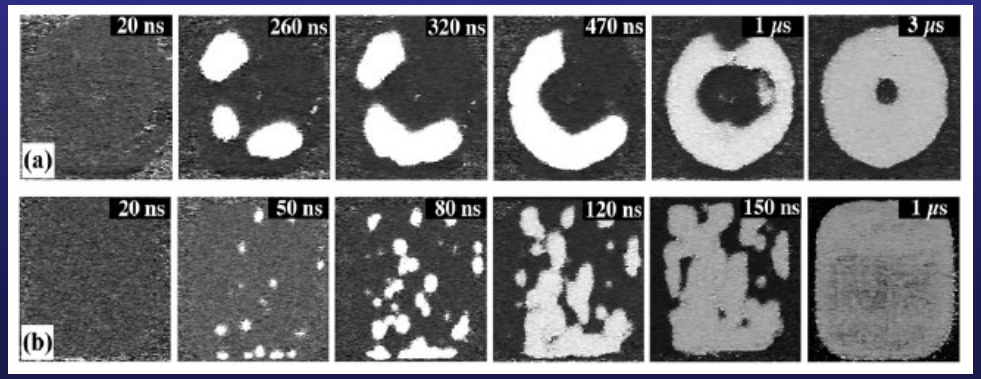
Model hamiltonian



$PbTiO_3$

I. Naumov *et al.*, Nature 432, 737 (2004)

Time Resolved Atomic Force Microscopy



$Pb(Zr_{0.2}Ti_{0.8})O_3$

A. Gruverman *et al.*,
J. Phys.: Condens. Matter 20, 342201 (2008)

Conclusions

Getting simultaneously an accurate determination of the structural and electronic properties of interfaces and superlattices from first-principles

A challenging problem

Be careful also with the band alignment at the interface

(both in the unpolarized and polarized cases)

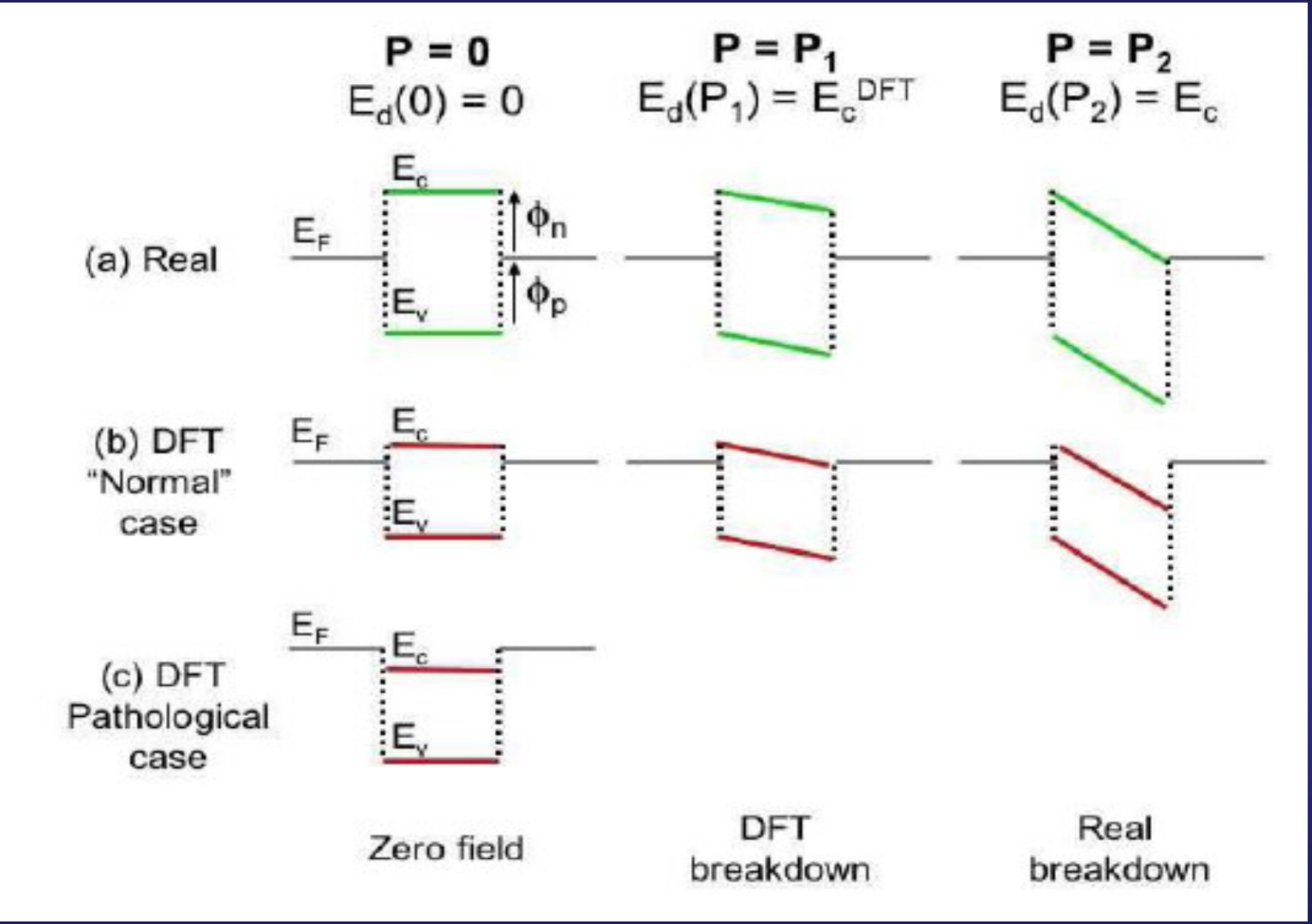
Screening by free charges, adsorbates and formation of domains seems to be efficient to minimize electrostatic energy.

Surface dipoles, and surface metallization seems not be so efficient.

Calculations done on

Arquitetura y Tecnología de Ordenadores de la Universidad de Cantabria

Due to the DFT band gap problem critical breakdown field in DFT is smaller than real breakdown field



J. Junquera and Ph. Ghosez,

Journal of Computational and Theoretical Nanoscience 5, 2071-2088 (2008)