First-principles modeling of screening in ferroelectric ultrathin capacitors

Javier Junquera
Pablo Aguado-Puente

Many thanks to the collaboration with

Massimiliano Stengel
Nicola Spaldin

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

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

- Surface
- Defects (vacancies, misfit dislocations, ...)
- Finite conductivity
- Mechanical

Chemistry

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


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

Potential for novel behaviour
Recent reviews on strain effects in epitaxial ferroelectric oxides

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 Triscone⁶

Many effects might alter the delicate balance between long and short range forces.
Interface electrostatics within Landau-Ginzburg theories. 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\textsuperscript{1} and A.P. Levanyuk\textsuperscript{1,2}

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\textsuperscript{1} and A.P. Levanyuk\textsuperscript{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).

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

<table>
<thead>
<tr>
<th>PbTiO₃ bulk</th>
<th>Cubic phase</th>
<th>Tetragonal phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$</td>
<td>$E_{\text{gap}}$</td>
</tr>
<tr>
<td>LDA, MBPP</td>
<td>3.880</td>
<td>1.55</td>
</tr>
<tr>
<td>LDA, PAW</td>
<td>3.894</td>
<td>1.48</td>
</tr>
<tr>
<td>LDA$^a$</td>
<td>3.894</td>
<td>3.858</td>
</tr>
<tr>
<td>PW91, MBPP</td>
<td>3.957</td>
<td>1.69</td>
</tr>
<tr>
<td>PW91, PAW</td>
<td>3.969</td>
<td>1.61</td>
</tr>
<tr>
<td>PBE, MBPP</td>
<td>3.962</td>
<td>1.69</td>
</tr>
<tr>
<td>PBE$^a$</td>
<td>3.971</td>
<td>3.857</td>
</tr>
<tr>
<td>Expt. (298 K)$^b$</td>
<td>3.969</td>
<td>3.905</td>
</tr>
</tbody>
</table>

Some of the widely flavours of the GGA functional strongly overestimates 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

Conduction Band

Fermi Level

Valence Band

DFT

- “Normal” case

Metal

Dielectric

Metal

$P = 0$

$\Phi_n$

$\Phi_p$

$E_{gap}^{exp}$

$E_{gap}^{DFT}$
DFT band alignment problem in an unpolarized capacitor

REAL WORLD

<table>
<thead>
<tr>
<th>Metal</th>
<th>Dielectric</th>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P = 0$</td>
<td></td>
</tr>
</tbody>
</table>

Conduction Band

Fermi Level

Valence Band

$\Phi_n$

$\Phi_p$

DFT

- Pathological case

- Transfer of charge in the non-polarized case
Calculating the Schottky barriers using the PDOS

Unpolarized phase

$\Phi_p = -1.00 \text{ eV}$

$\Phi_n = 0.40 \text{ eV}$

LDA gap $\approx 1.40 \text{ eV}$

Expt. gap $\approx 3.2 \text{ eV}$
Transfer of charge in K\(\text{NbO}_3\)/Sr\(\text{RuO}_3\) nanocapacitors

Work by M. Stengel & N. Spaldin

\[ [\text{K} \text{NbO}_3]_{m=6.5} / [\text{SrRuO}_3]_{n=7.5} \text{ nanocapacitor} \]

DOS projected over the central K\(\text{NbO}_3\) layer

CB of K\(\text{NbO}_3\) crosses the Fermi level
Transfer of charge in K\(\text{NbO}_3\)/SrRuO\(_3\) nanocapacitors

Work by M. Stengel & N. Spaldin

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

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 KNO$_3$/SrRuO$_3$ nanocapacitors

Work by M. Stengel & N. Spaldin

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

$[\text{KNO}_3]_{m=6.5} / [\text{SrRuO}_3]_{n=7.5}$ nanocapacitor

Spurious transfer of charge to the KNO layer

The system is not locally charge neutral

$\downarrow$

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.

A gradient of polarization generates polarization charges. 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.

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

REAL WORLD

Conduction Band
Fermi Level
Valence Band

\[ \Phi_n \]
\[ \Phi_p \]

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

\[ \varepsilon_d = -4\pi P \]

Screening of polarization charge is essential

Screening by
Surface relaxations
and/or surface carrier layer
electrons

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

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

4 and 10 unit cells

Monodomain upward polarization

Quantitative theory-experiment comparison

Reliability Pendry factor

Perfect correlation Uncorrelated

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

Best-fit surface structure

Monodomain upward polarization

Lack of polarization at the top BaO layer

No polarization charges

Atomic displacements associated with upward polarization

= surface relaxation + FE soft mode


Polarization surface charges might be screened by a surface carrier layer.

First-principles calculations on an isolated free-standing slab.

Band structure of the unpolarized slab:

- Top of the valence band: O 2p, uncharged
- Bottom of the conduction band: Ti 3d, uncharged

TiO$_2$ termination

Convergence criterion: 0.06 eV/Å

Polarization surface charges might be screened by a surface carrier layer

First-principles calculations on an isolated free-standing slab

Band structure of the polarized slab

TiO$_2$ termination

Convergence criterion 0.06 eV/Å

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$_3$

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

\[ \approx 600 \text{ bohrs of vacuum} \]

BaO termination

4.5 unit cells of BaTiO$_3$

SrO/TiO$_2$ interface

9.5 unit cells of SrRuO$_3$

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.

\[ \varepsilon_d = -4\pi P \]

**Vacuum**

no screening

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

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

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

Full coverage of OH

4 unit cells (1.6 nm) BaTiO₃

X-ray scattering + PFM: Direct transition to a monodomain state, polarized “up”
Adsorbed ions can stabilize the polar monodomain state in ultrathin films

DFT simulations + Gibbs free energy estimations

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


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

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

\[ \varepsilon_d = -4 \pi P \]

**Vacuum**
- No screening

**Screening by**
- Surface relaxations and/or surface carrier layer
  - Electrons
  - Holes

**Screening by**
- Adsorbates
  - OH, O, HCOO

**Screening by**
- Metallic electrodes
  - Electrode
Standard case: depolarizing field due to imperfect screening of polarization charges reduces the spontaneous polarization

\[ \text{SrRuO}_3/\text{BaTiO}_3/\text{SrRuO}_3 \]

\[ \text{SrRuO}_3/\text{PbTiO}_3/\text{SrRuO}_3 \]

Bulk strained polarization

All atomic positions and c-lattice vector relaxed

\[ \text{J. Junquera and Ph. Ghosez, Nature 422, 506 (2003)} \]
Particular combinations of AO-term. perovskites and simple metals: enhancement of ferroelectricity

Enhancement of ferroelectricity at metal-oxide interfaces

Massimiliano Stengel¹, David Vanderbilt² and Nicola A. Spaldin¹*

The mechanism leading to such 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.

\[ \varepsilon_d = -4 \pi P \]

Vacuum
no screening

Screening by
Surface relaxations and surface carrier layer
- electrons
- holes

Screening by
adsorbates
- OH, O, HCOO

Screening by
metallic electrodes
- electrode
- electrode

Screening by
formation of domains
- electrode or substrate

[Diagram with arrows and labels for each screening method]
Polydomain phases stable, even below \( t_c \) in monodomain. Adopt the “domain of closure”, common in ferromagnets.

P. Aguado-Puente and J. Junquera

\[ N_x = 4 \]

**SrRuO\(_3\)/BaTiO\(_3\)/SrRuO\(_3\)**

**BaO domain walls**

2 unit cell thick

Below critical thickness for monodomain polarization

**Ferromagnetic domains**

C. Kittel (1946)
Domains of closure in PbTiO₃/SrRuO₃ capacitor

$m = 4, N_x = 6$

PbO domain walls

Domains close inside the FE

$E_{\text{domains}} - E_{\text{para}} = -50$ meV
Vortices in ferroelectric nanostructures: theoretical and experimental results

Model Hamiltonian

\[ G_z (e \text{Å}^2) \]

Layer

PbTiO\(_3\)


Time Resolved Atomic Force Microscopy

Pb(Zr\(_{0.2}\)Ti\(_{0.8}\))\(_3\)

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,