From 180° stripe domains to more exotic patterns of polarization in ferroelectric nanostructures. A first principles view

Pablo Aguado-Puente
Javier Junquera
Ferroelectricity: Basic definitions

Existence of **two or more states with a non-zero polarization** in the **absence** of an electric field

Can be **shifted** from one to another of these states by the application of an electric field

**Hysteresis loop**

**Double well energy**

**Soft-mode**
Technological applications: ABO$_3$ perovskites oxides as multifunctional materials

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

NV-FRAM

perovskite oxide
(PZT,BST)

metal
(SrTiO$_3$-Nb, SrRuO$_3$,Pt)

28 Gbit/cm$^2$
Line width < 20nm

100 nm

... is there a fundamental limit?
Ferroelectricity is a collective effect with delicate balance between short and long range interactions.

Both interactions strongly affected in small particles and thin films.

Finite size effect: a subtle problem.
Fundamental motivation: what’s the most stable phase for epitaxial ferroelectric ultrathin films?

- Long time question.
- Hot field.

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

Experimental measurements, global result
Experimentally: small changes in boundary conditions, great changes in ground state

D. D. Fong et al. (2004)
S. K. Streiffer et al. (2002)

C. Lichtensteiger et al. (2005)
A. T. J. van Helvoort et al. (2005)

D. D. Fong et al. (2005)

V. Nagarajan et al. (2006)
First-principles calculations allow to isolate their respective influence.
Strain imposed by the substrate affects the properties of ferroelectric materials

\[ u_m = \frac{a - a_o}{a_o} \]

Typical picture:

Compressive strain ⇒ tetragonal c
Tensile strain ⇒ orthorrombic aa

Mechanisms for screening of the polarization charge

Vacuum
no screening

\[ E_d = -4\pi P \]

Screening by free charges
(electrodes or adsorbates)

Formation of domains
(no net charge at surface)
Imperfect screening by real metallic electrodes produces a depolarizing field

Vacuum
no screening

Real electrodes
imperfect screening

Ideal electrodes
perfect screening

Depolarizing field \( \mathcal{E}_d \):

\[
\mathcal{E}_d = -4 \pi \frac{\Delta V}{d}
\]

\( \Delta V = 4 \pi \sigma_{pol} \lambda_{eff} \)

\( \sigma_{pol} = P \cdot n \)

\[
\mathcal{E}_d = -4 \pi \left[ 2 \cdot \frac{\lambda_{eff}}{d} \right] \cdot P
\]

\( \alpha \)

depends on:

- the metal and interface chemistry: screening length \( \lambda_{eff} \)
- the ferroelectric: the spontaneous polarization \( P \)
- the film thickness \( d \)
Simulations of ferroelectric nanocapacitors from first-principles


Thickness:

$m$ number of BTO cells

Polarization control:

$\xi$ percentage bulk soft mode

$\xi=0$  $\xi=1$
Existence of a critical thickness in monodomain films
DFT versus model results

\[ E = U - \varepsilon_d \cdot P \]

Behavior can be explained by *electrostatic* effects.
The *chemistry* of the interface buried in \( \lambda_{\text{eff}} \)

Minima below bulk (\( \xi = 1 \))

\( P_s \) deduced from \( \xi_{\text{min}} \)
**Twofold effect of the depolarizing field in monodomain films**

\[ \mathcal{E}_d = -4\pi\alpha P \]

\[ E = U - \mathcal{E}_d \cdot P \]

**Below the critical thickness:** suppression of the ferroelectricity

**Above the critical thickness:** reduction of spontaneous polarization


Many DFT first-principles computations on size effects in ferroelectric ultrathin films

Ferroelectricity in ultrathin perovskite films

Na Sai, Alexie M. Kolpak, and Andrew M. Rappe

Ionic Polarizability of Conductive Metal Oxides and Critical Thickness for Ferroelectricity in BaTiO$_3$

G. Gerra,$^{1,9}$ A. K. Tagantsev,$^1$ N. Setter,$^1$ and K. Parlinski$^2$

Ab initio study of the critical thickness for ferroelectricity in ultrathin Pt/PbTiO$_3$/Pt films

Yoshitaka Umeno,$^{1,2}$ Bernd Meyer,$^3$ Christian Elsässer,$^{4,1}$ and Peter Gumbsch$^{1,4}$

Interface Effect on Ferroelectricity at the Nanoscale

Chun-Gang Duan,$^{1,4,5}$ Renat F. Sabirianov,$^{1,5}$ Wai-Ning Mei,$^{1,5}$ Sitaram S. Jaswal,$^{1,5}$ and Evgeny Y. Tsybail$^{1,5}$

Stabilization of Monodomain Polarization in Ultrathin PbTiO$_3$ Films

D. D. Fong,$^{1}$ A. M. Kolpak,$^2$ J. A. Eastman,$^1$ S. K. Streiffer,$^1$ P. H. Fuoss,$^1$ G. B. Stephenson,$^1$ Carol Thompson,$^5$ D. M. Kim,$^4$ K. J. Choi,$^4$ C. B. Eom,$^4$ I. Grinberg,$^2$ and A. M. Rappe$^2$
Many DFT first-principles computations on size effects in ferroelectric ultrathin films

<table>
<thead>
<tr>
<th>Reference</th>
<th>Heterostructure</th>
<th>Method</th>
<th>Functional</th>
<th>Interface</th>
<th>$a_{\parallel}$</th>
<th>$t_c$</th>
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<tr>
<td>Junquera et al. [56]</td>
<td>SrRuO$_3$/BaTiO$_3$/SrRuO$_3$</td>
<td>NAO</td>
<td>LDA (CA)</td>
<td>SrO-TiO$_2$</td>
<td>3.874 Å ($a_{\text{SrTiO}_3}^{\text{th}}$)</td>
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<td></td>
<td>SrRuO$_3$/PbTiO$_3$/SrRuO$_3$</td>
<td>NAO</td>
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<td>Gerra et al. [63]</td>
<td>SrRuO$_3$/BaTiO$_3$/SrRuO$_3$</td>
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<td>GGA (PW91)</td>
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<td>Umeno et al. [89]</td>
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<td>Pt/PbO</td>
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<td>Duan et al. [86]</td>
<td>SrRuO$_3$/KNbO$_3$/SrRuO$_3$</td>
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<td>Na Sai et al. [64,90]</td>
<td>SrRuO$_3$/BaTiO$_3$/SrRuO$_3$</td>
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<td>RuO$_2$-BaO</td>
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<td>D. D. Fong et al. [47]</td>
<td>SrRuO$_3$/PbTiO$_3$/vacuum</td>
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<td>SrRuO$_3$/PbTiO$_3$/OH, O or H</td>
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<tr>
<td></td>
<td>SrRuO$_3$/PbTiO$_3$/H$_2$O</td>
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<td></td>
<td></td>
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<td>&gt; 3</td>
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</table>
Be careful with the functional used…
GGA overestimates tetragonality and double-well depth in bulk PbTiO₃

<table>
<thead>
<tr>
<th></th>
<th>Cubic phase</th>
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<th>Tetragonal phase</th>
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<tr>
<td></td>
<td>a</td>
<td>E₁</td>
<td>a</td>
<td>c/a</td>
<td>uₓ(Ti)</td>
<td>uₓ(O₁)</td>
<td>uₓ(O₃)</td>
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<td>LDA, MBPP</td>
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<td>LDA⁺</td>
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<td>PW91, MBPP</td>
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<tr>
<td>PBE⁺</td>
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<tr>
<td>Expt. (298 K)ᵇ</td>
<td>3.969</td>
<td>3.905</td>
<td>1.064</td>
<td>0.539</td>
<td>0.114</td>
<td>0.617</td>
<td>3.5</td>
<td></td>
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</tr>
</tbody>
</table>

...responsible for the absence of critical thickness in PbTiO₃ nanocapacitors?

Until today, monodomain studies, goal of this work: \textit{ab initio} multidomain simulations

- Uniform reduction of the polarization
- Break down into domains

Present work

- Full first-principles simulation using \textit{siesta}
- Explicitly included electrodes.
Building the cell: the paraelectric unit cell

- Building the reference cell following the scheme of Junquera and Ghosez (2003).

\[ N_{at} = 40 \text{ atoms} \]
Building the cell: replicating the paraelectric structure

- $N_x$ repetitions in [100] direction.
- The energies of these cells as references.

$$a = N_x \cdot a_{\text{SrTiO}_3}$$

$$N_{at} = N_x \cdot 40 \text{ atoms}$$
Building the cell: inducing a polarization by hand

- Chosing a domain wall.
- Inducing a polarization by hand in the FE layer displacing the atoms a percentage of the bulk soft mode.

Twinning on both BaO (Ba-centered) TiO2 (Ti-centered)

\[ N_{at} = N_x \cdot 40 \text{ atoms} \]
Relaxing all the atomic coordinates, both in the ferroelectric layer and the electrodes

Forces smaller than 0.01 eV/Å

No constraints imposed on the atomic positions
Polydomain phases more stable than paraelectric structure for $2 < N_x < 8$

2-unit-cells thick $\text{BaTiO}_3$ layer

Polar domains stabilized below critical thickness for the monodomain configuration
Polydomain phases more stable than paraelectric structure for $2 < N_x < 8$

2-unit-cells thick BaTiO$_3$ layer

Polar domains stabilized below critical thickness for the monodomain configuration

As $180^\circ$ domains in bulk,

Ba centered domain wall preferred
Polydomain phases more stable than paraelectric structure for $2 < N_x < 8$

2-unit-cells thick BaTiO$_3$ layer

Polar domains stabilized below critical thickness for the monodomain configuration

As $180^\circ$ domains in bulk, Ba centered domain wall preferred

No energy difference between $N_x = 4$ and $N_x = 6$

Both of them might be equally present in an sample

(α and β phases in PbTiO$_3$/SrTiO$_3$ interfaces?)

Polydomain phases adopt the form of a “domain of closure”, common in ferromagnets. 

\[ N_x = 4 \]

BaO domain walls

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Ferromagnetic domains}
\end{figure}

\[ N_x = 4 \]

BaO domain walls

C. Kittel (1971)
Polydomain phases adopt the form of a “domain of closure”, common in ferromagnets.

$N_x=4$
BaO wall

$N_x=6$
BaO wall

2-unit-cells thick BaTiO$_3$ layer

Energy/N$_x$ (meV) vs $N_x$

$m=2$

Ba-wall

Ti-wall

$N_x=6$
BaO wall

TiO$_2$ wall

TiO$_2$ wall
SrO layer at the interface behaves more like SrTiO$_3$ than SrRuO$_3$ ⇒ highly polarizable

Projected Density of States in the reference paraelectric structure
Resulting phases show in-plane displacements and small polarization

\[ N_x = 4 \]

BaO domain walls

Small polarization inside the domains

About 1/10 of bulk soft-mode polarization
In-plane displacements are essential to stabilize the domains

When in-plane coordinates are fixed, structure goes back to the paraelectric phase.
Relevant energy differences very small in the ultrathin $m = 2$ capacitors

$N_x = 4$
Relevant energy differences increase with thickness

Monodomain

Ti-centered domains

Ba-centered domains

$N_x = 4$
Transition from vortices to standard $180^\circ$ domains. 4-unit-cell thick layer, great increase in polarization
In-plane displacements, essential to stabilize domains

\[ N_x = 4 \]

- Monodomain
- In-plane constraint
- Ti-centered domains
- Ba-centered domains

Energy/$N_x$ (meV) vs. $N_x$
Changing the electrode, the ground state of PbTiO$_3$ changes from monodomain to polydomain.

**Monodomain to polydomain transition in ferroelectric PbTiO$_3$ thin films with La$_{0.67}$Sr$_{0.33}$MnO$_3$ electrodes**

Lichtensteiger, et al.

**Ferroelectricity and Tetragonality in Ultrathin PbTiO$_3$ Films**

Lichtensteiger, Triscone, Junquera, Ghosez.
Analysis of the electrostatic potential: large field in \( x \) at the interface, residual depolarizing field in \( z \).

Two unit cells thick of \( \text{BaTiO}_3 \).
Conclusions

- **Polydomain phases** in ultrathin FE films are stabilized below critical thickness in monodomain configurations.

- The chemical interaction through the interface is an essential factor since it affects the **in-plane mobility** of the atoms.

- **Closure domains** in FE capacitors are predicted (recently detected expt. in FE ultrathin films by Scott).

Slides available at: [http://personales.unican.es/junqueraj]

Contact: pablo.aguado@unican.es

javier.junquera@unican.es
Method: Computational details

First-principles calculations within Kohn-Sham Density Functional Theory (DFT)

**siesta**: Numerical Atomic Orbital DFT code.

http://www.uam.es/siesta


*Exchange-correlation functional*: LDA, fit to Ceperley-Alder data

*Norm conserving pseudopotentials*: Ti, Sr, Ba, Ru: semicore in valence

*Basis set*:

  *NAO*: valence: Double-\(\zeta\) + Polarization ; semicore: Single-\(\zeta\)

*Real-space grid cutoff*: 400 Ry

*\(k\)-point grid*: equivalent to 12x12x12 for simple cubic perovskite

*Supercell geometry*
Ferroelectric layer: fundamental parameters of the simulations

FE layer: $N_x$ repetitions in [100] direction and $m$ cells in [001] direction

- $N_x$ from 2 to 8 cells
- $m$ from 2 to 4 cells
- FE layer made of BaTiO$_3$
- Domain wall in BaO and TiO$_2$
Very small energy differences, very accurate simulations needed

\[ m=2, \ N_x = 4 \]

BaO domain walls

<table>
<thead>
<tr>
<th>Structure</th>
<th>Total Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraelectric</td>
<td>-138326.083054</td>
</tr>
<tr>
<td>Multidomain</td>
<td>-138326.084463</td>
</tr>
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</table>

\[ (E-E_{para})/N_x = -0.00035 \text{ eV} \]
Analysis of the electrostatic potential:
huge field in $x$ at the interface, residual depolarizing field in $z$

Four unit cells thick of BaTiO$_3$