Full first-principles simulations on 180° stripe domains in realistic ferroelectric capacitors

Pablo Aguado-Puente
Javier Junquera
Technological applications: $\text{ABO}_3$ perovskites oxides, promising candidates for NV-FRAM

The use as a NV-FRAM depends on the existence of a polar ground state …

… is there a fundamental limit?
Fundamental motivation: what’s the most stable phase for epitaxial ferroelectric ultrathin films?

- Long time question.
- Hot field.

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)
Many effects might alter the delicate balance between long and short range forces.
First-principles calculations allow to isolate their respective influence.
Until today, monodomain studies, goal of this work: *ab initio* multidomain simulations

- Uniform reduction of the polarization
  - Umeno et al. (2006)
- Break down into domains
  Present work

- Full first-principles simulation using *siesta*
- Explicitly included electrodes.
Ferroelectric layer: fundamental parameters of the simulations

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

$m = \text{layer thickness}$

$N_x = \text{domain period}$

- $N_x$ from 2 to 8 cells
- $m$ from 2 to 4 cells
- FE layer made of $\text{BaTiO}_3$.
- Domain wall in $\text{BaO}$ and $\text{TiO}_2$
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.

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

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

\( N_{at} = N_x \cdot 40 \text{ atoms} \)
Relaxing all the atomic coordinates coordinates, both in the FE layer and the electrodes

Forces smaller than 0.01 eV/Å

No constraints impossed on the atomic positions
Results: multidomain phases more stable than paraelectric structure for $N_x > 4$

2-unit-cells thick BaTiO$_3$ layer
Results: multidomain phases more stable than paraelectric structure for $N_x > 4$

$N_x = 4$

BaO domain walls

C. Kittel (1971)
Results: multidomain phases more stable than paraelectric structure for $N_x > 4$
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 get polarization domains.

When in-plane coordinates are fixed, structure goes back to the paraelectric phase.
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.
Transition from vortices to standard 180° domains. 4-unit-cell thick layer, great increase in polarization.

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

TiO\textsubscript{2} domain walls

\[ \Delta_{\text{bulk}} \]

\[ \Delta_{\text{capacitor}} \]

\[ (E-E_{\text{para}})/N_x < -16.6 \text{ meV} \]

Displacements 10 times bigger than in the 2-cells thick layer.
Conclusions

- There are stable multidomain phases in ultrathin FE films.

- 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.

Slides available at: http://personales.unican.es/junqueraj
Contact: pablo.aguado@unican.es, javier.junquera@unican.es
More information ...
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**
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>
</tbody>
</table>

$(E-E_{para})/N_x = -0.00035$ eV