First-principles modeling of ferroelectric oxide nanostructures

Javier Junquera
First-principles modeling of ferroelectric oxide nanostructures
Transition metal oxide compounds
Simple structures with different phase transitions

Insulating
Semi-conducting

OXIDES

Metallic
Superconducting
Transition metal oxide compounds
Simple structures with different fundamental properties

- Ferroelectricity
- High $T_c$ superconductivity
- Ferromagnetism
- Colossal magnetoresistance
- Multiferroics
First-principles modeling of ferroelectric oxide nanostructures
Atomically precise methods for preparing thin films and multilayer structures

**Methods**

- Pulsed Laser Deposition (PLD)
- Molecular Beam Epitaxy (MBE)
- Off-axis rf magnetron sputtering

Control at the atomic level
Crystalline and surface quality ≈ semiconductor heterostructures

Both AFM tip and Au top electrode

**AFM**

PbTiO₃

Nb-SrTiO₃

C. Lichtensteiger *et al*.,

**HRTEM**

Pb(Zr₀.₂Ti₀.₈)O₃

SrRuO₃

SrTiO₃

V. Nagarajan, J. Junquera *et al*.,
### Accurate characterization methods

<table>
<thead>
<tr>
<th>Methods</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray scattering</td>
<td>High (atomic) resolution</td>
</tr>
<tr>
<td>analysis of satellites</td>
<td>Local proofs of:</td>
</tr>
<tr>
<td>COBRA</td>
<td>atomic structure</td>
</tr>
<tr>
<td>High resolution Transmission Electron Microscopy (HRTEM)</td>
<td>piezoelectric properties</td>
</tr>
<tr>
<td>Reflection High-energy Electron Diffraction (RHEED)</td>
<td>ferroelectric properties</td>
</tr>
<tr>
<td>Atomic Force Microscopy (AFM)</td>
<td></td>
</tr>
<tr>
<td>Piezoelectric Force Microscopy (PFM)</td>
<td></td>
</tr>
<tr>
<td>Photoemission based photoelectron diffraction (XPD)</td>
<td></td>
</tr>
<tr>
<td>PUND Hysteresis loops</td>
<td></td>
</tr>
</tbody>
</table>

...
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
Some surprises at the interfaces between two oxides

New type of ferroelectricity in PbTiO$_3$/SrTiO$_3$ superlattices

E. Bousquet et al., Nature (in press)

The interface between two good insulators (LaAlO$_3$ and SrTiO$_3$) is metallic

Recent discoveries on transition metal oxides: one of the “top tens” scientific breakthroughs of 2007

**Breakthrough of the Year**

5 **BEYOND SILICON?** Sixty years ago, semiconductors were a scientific curiosity. Then researchers tried putting one type of semiconductor up against another, and suddenly we had diodes, transistors, microprocessors, and the whole electronic age. Startling results this year may herald a similar burst of discoveries at the interfaces of a different class of materials: transition metal oxides.

Transition metal oxides first made headlines in 1986 with the Nobel Prize–winning discovery of high-temperature superconductors. Since then, solid-state physicists keep finding unexpected properties in these materials—including colossal magnetoresistance, in which small changes in applied magnetic fields cause huge changes in electrical resistance. But the fun should really start when one oxide rubs shoulders with another.

If different oxide crystals are grown in layers with sharp interfaces, the effect of one crystal structure on another can shift the positions of atoms at the interface, alter the population of electrons, and even change how

**Tunable sandwich.** In lanthanum aluminate sandwiched between layers of strontium titanate, a thick middle layer (right) produces conduction at the lower interface; a thin one does not.

*Science, 318, 1846 (2007)*
The field is still in an incipient stage, comparable to that of semiconductors 60 years ago.

Despite recent activity, the field of oxide interfaces remains virtually unexplored. What might happen if we could mix materials with vastly different properties such as ferromagnets, antiferromagnets, superconductors, ferroelectrics, multiferroics, geometrically frustrated spin systems, heavy fermions, and others? Considering this enormous number of...
First-principles modeling of ferroelectric oxide nanostructures

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](image1)

![Double well energy](image2)
Perovskite oxides $\text{ABO}_3$: prototypes of ferroelectric materials

- First ferroelectric without hydrogen bonds
- First ferroelectric with a paraelectric phase
- First ferroelectric with more than one ferroelectric phase
- Very simple (5 atoms per unit cell)

$\Rightarrow$ lot of theoretical models

**Diagram:**
- BaTiO$_3$
- Cation A
- O octahedra
- Cation B
Phase transitions of BaTiO$_3$ as a function of the temperature

- **High T**
  - High Temperature Cubic
  - Paraelectric

- **130 °C**
  - Tetragonal
  - P along [001]

- **5 °C**
  - Orthorhombic
  - P along [110]

- **-90 °C**
  - Rhombohedral
  - P along [111]
Phase transitions from cubic to tetragonal, pattern of cooperative polar atomic displacements

Paraelectric

$\xi = 0$

$\xi = 1$

Continuum evolution of $\xi$

$\text{Energy (meV)}$

$\text{bulk}$
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)

... is there a fundamental limit?

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

100 nm
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.

A few unit cells might be ferroelectric!
Recent reviews on state-of-the-art on size effects in ferroelectric nanostructures


First-principles study of ferroelectric oxide epitaxial thin films and superlattices: role of the mechanical and electrical boundary conditions

Javier Junquera

Departamento de Ciencias de la Tierra y Física de la Materia Condensada,
Universidad de Cantabria, Avda. de los Castros s/n, E-39005 Santander, Spain

Philippe Ghosez

Physique Théorique des Matériaux, Université de Liège, B-4000 Sart Tilman, Belgium

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

Experimental measurements, global result
Experimental: small changes in boundary conditions, great changes in stable 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)

C. Lichtensteiger et al. (2007)

D. D. Fong et al. (2005)

V. Nagarajan et al. (2006)
First-principles calculations allow to isolate their respective influence.
Surface effects
Some questions that might be answered *ab-initio*

- Missing of Ti 3d-O 2p hybridization
- Intrinsic degradation of the polarization?
- Coupling of the polarization with surface-induced relaxations and reconstructions
- Influence of surface termination
The presence of a surface induces atomic relaxations

(001) TiO$_2$-terminated

<table>
<thead>
<tr>
<th></th>
<th>SrTiO$_3$</th>
<th>BaTiO$_3$</th>
<th>PbTiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Ti</td>
<td>O</td>
<td>Ti</td>
</tr>
<tr>
<td>Sr</td>
<td>-0.13</td>
<td>$\eta = +0.06$</td>
<td>O</td>
</tr>
<tr>
<td>Ti</td>
<td>+0.06</td>
<td>$\eta = -0.00$</td>
<td>Ti</td>
</tr>
<tr>
<td>Sr</td>
<td>-0.03</td>
<td>$\eta = -0.11$</td>
<td>Ba</td>
</tr>
<tr>
<td>Ti</td>
<td>-0.12</td>
<td>$\eta = +0.04$</td>
<td>Ti</td>
</tr>
<tr>
<td>Pb</td>
<td>-0.17</td>
<td>$\eta = +0.08$</td>
<td>O</td>
</tr>
</tbody>
</table>

Paraelectric structure
Cubic
Theoretical in-plane lattice param.
(1×1) surface reconstruction
Units in Å

(001) AO-terminated

<table>
<thead>
<tr>
<th></th>
<th>SrTiO$_3$</th>
<th>BaTiO$_3$</th>
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<tr>
<td>(a)</td>
<td>Sr</td>
<td>Ti</td>
<td>Pb</td>
</tr>
<tr>
<td>Ti</td>
<td>-0.13</td>
<td>$\eta = -0.03$</td>
<td>Ti</td>
</tr>
<tr>
<td>Sr</td>
<td>+0.04</td>
<td>$\eta = +0.02$</td>
<td>Ba</td>
</tr>
<tr>
<td>Ti</td>
<td>-0.03</td>
<td>$\eta = -0.02$</td>
<td>Ti</td>
</tr>
<tr>
<td>Pb</td>
<td>$\eta = -0.08$</td>
<td>$\eta = +0.02$</td>
<td>O</td>
</tr>
</tbody>
</table>

- Largest relaxations: surface atoms
- Surface layer contracts inwards
- Rumpling of the layers gives rise to ionic surface dipole
- Oscillating relaxation pattern

Relaxation energy (100 meV) $>>$ bulk ferroelectric well (30-50 meV)

J. Padilla and D. Vanderbilt, Surface Science 418, 64 (1998)
Coupling of the surface with in-plane polarization

Small influence of surface relaxation on in-plane ferroelectricity

<table>
<thead>
<tr>
<th>Material</th>
<th>TiO$_2$-terminated</th>
<th>AO-terminated</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$</td>
<td>Slightly↑</td>
<td>Slightly↓</td>
</tr>
<tr>
<td>PbTiO$_3$</td>
<td>Slightly↓</td>
<td>Slightly↑</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td></td>
<td>Very modest</td>
</tr>
</tbody>
</table>

(likely destroyed by T)

J. Padilla and D. Vanderbilt, Surface Science 418, 64 (1998)
Surface might induced reconstructions to saturate dangling bonds

(001) PbTiO₃

c(2×2) reconstructions in PbO-terminated
substantial enhancement of the AFD distortion
Driving force: shorter PbO bonds

Not observed neither in TiO₂ termination nor BaTiO₃ surface


(001) SrTiO₃

Experimentally: (2×1) reconstruction

Theoretically: (1×1) reconstruction
Mechanical effects
Some questions that might be answered *ab-initio*

- Strong coupling of homogeneous and inhomogeneous strain with P
- Strain engineering
  - tune specific properties by choosing substrate
  - appearance of new phases
- Role of misfit dislocation

SrTiO$_3$/LaTiO$_3$

(5×n)

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

Strain imposed by the substrate affects the properties of ferroelectric materials

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

Example:

BaTiO\textsubscript{3}  \( a_o = 4.00 \) Å
SrTiO\textsubscript{3}  \( a = 3.91 \) Å

\( u_m = -22.5 \times 10^{-3} \)

Pertsev et al. mapping the equilibrium structure as a function of $T$ and strain

- The free energy is written as a function of polarization and strain.
- Temperature incorporated via a linear dependence of some expansion coefficients.
- Infinite solid (no interface nor surface) subject to homogeneous strain.
- Parameters are taken from experiments near bulk FE transition.
- The most stable phase is found by minimizing the free energy.

$$
\tilde{G} = a_1^*(P_1^2 + P_2^2) + a_3^*P_3^2 + a_{11}^*(P_1^4 + P_2^4) + a_{12}^*P_1^2P_2^2
$$
$$
+ a_{13}^*(P_1^2P_3^2 + P_2^2P_3^2) + a_{33}^*P_3^4 + a_{111}^*(P_1^6 + P_2^6 + P_3^6) + a_{123}P_1^2P_2^2P_3^2
$$
$$
+ a_{113}^*[P_1^4(P_2^2 + P_3^2) + P_2^4(P_2^2 + P_1^2) + P_3^4(P_1^2 + P_2^2)] + u_m^2/(s_{11} + s_{13})
$$

$a_1^* = a_1^*(T, u_m); \ a_3^* = a_3^*(T, u_m); \ a_{11}^* = a_{11}^*(T); \ a_{33}^* = a_{33}^*(T); \ a_{123} = a_{123}(T)$

Pertsev et al. obtained a semiempirical phase diagram for epitaxial BaTiO$_3$
The scattering in the reported parameters produces “range of transitions” rather than clean boundaries.
First-principles phase diagram for epitaxial BaTiO$_3$ resolve earlier discrepancy

No ac phase


Courtesy of O. Diéguez
Other perovskites epitaxially grown on a cubic substrate theoretically explored


A. Antons et al., PRB 71, 024102 (2005)


Electrostatic effects
Some questions that might be answered *ab-initio*

- Finite depolarizing field
  - imperfect screening
  - polarization gradient
  - dead layer at the interface
couples with the polarization.
- Dependence of
  - density of free carriers
  - metal/ferroelectric interface
  - partial screening inside the ferroelectric
on the screening mechanism?

Different mechanisms for the appearance of a depolarizing field

- Inhomogeneity of the polarization distribution
  

- Existence of a dead layer at the ferroelectric/electrode interface
  

- Incomplete screening by real metallic electrode
  
  I. P. Batra et al., J. Vac. Sci. Technol. 10, 687 (1973)
Imperfect screening by real metallic electrodes produces a depolarizing field.

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

Vacuum
no screening

Screening by free charges
(electrodes or adsorbates)
Imperfect screening by real metallic electrodes produces a depolarizing field

Depolarizing field $\mathcal{E}_d$:

- Vacuum (no screening): $\mathcal{E}_d = -4\pi P$
- Real electrodes (imperfect screening): $\mathcal{E}_d = -4\pi \alpha P$
- Ideal electrodes (perfect screening): $\mathcal{E}_d = 0$

Depolarizing field $\mathcal{E}_d$ depends on:
- the metal and interface chemistry: screening length $\lambda_{\text{eff}}$
- the ferroelectric: the spontaneous polarization $P$
- the film thickness $d$

$\Delta V = 4\pi \sigma_{\text{pol}} \lambda_{\text{eff}}$

$\sigma_{\text{pol}} = P \cdot n$
High-resolution TEM of a typical ferroelectric capacitor

13 unit cells BaTiO$_3$ grown by MBE

J. Rodriguez Contreras, C. Jia, H. Kohlstedt, D. G. Schlom

Forschungszentrum Jülich
Institut für Festkörperforschung – Elektrokeramische Materialien
Simulations of ferroelectric nanocapacitors from first-principles: Building the paraelectric unit cell

Short-circuit boundary conditions

Mirror symmetry plane

SrRuO$_3$

BaTiO$_3$

SrRuO$_3$

SrTiO$_3$

$c$

$a = a_{SrTiO_3}$

$N_{at} = 40$ atoms
Simulations of ferroelectric nanocapacitors from first-principles


Thickness:
\( m \) number of BTO cells

Polarization control:
\( \xi \) percentage bulk soft mode

\( \xi = 0 \)
\( \xi = 1 \)
The depolarizing field is directly proportional to the induced polarization

- **Charge density changes** for $\xi \neq 0$:

  Complex pattern of charge at the interface
  Beyond simple Thomas-Fermi screening
  (with screening length $\lambda$)

- **Electrostatic potential changes**
  (electrons + ions) for $\xi \neq 0$:

  Potential drop at the interface:  
  $\Delta V$ *linear* with $\sigma_{\text{pol}} = P \cdot n$
  Effective screening length:
  $\Delta V = 4\pi \lambda_{\text{eff}} \cdot \sigma_{\text{pol}}$  
  ($\lambda_{\text{eff}} \sim 0.23$ Å)
  Depolarizing field:
  $\varepsilon_d = -2 \cdot \Delta V / (m \cdot a_{\text{cell}})$

The depolarizing field is inversely proportional to the thickness:

- **Depolarizing field** $\varepsilon_d$ evolves with thickness $m$:
  \[
  \varepsilon_d = -2 \cdot \frac{\Delta V}{m \cdot a_{cell}}
  \]

- **Potential drop** $\Delta V$:
  \[
  \Delta V = 4\pi \lambda_{eff} \cdot \sigma_{pol}
  \]
The depolarizing field depends on the interface

\[ \text{SrRuO}_3 / \text{BaTiO}_3 \]
\[ \text{SrRuO}_3 / \text{PbTiO}_3 \]  \quad \text{Incomplete screening}

\[ \text{Pt} / \text{PbTiO}_3 \]
\[ \text{Pt} / \text{BaTiO}_3 \]  \quad \text{“Perfect” screening}

Existence of a critical thickness in monodomain films

DFT results

$m = 2$ : full atomic relaxation starting from a ferroelectric state

$\Rightarrow$ the structure went back to the paraelectric state

Critical thickness for $m \approx 6$

Smaller $t_c$ if relaxation of all the atoms is allowed

Existence of a critical thickness in monodomain films

Electrostatic model

Bulk:

\[ U = A \xi^2 + B \xi^4 \]

Thin film:

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

\[ U \approx \text{bulk double-well energy} \]

\[ \mathcal{E}_d \approx 2.\Delta V/(m \cdot a_{\text{cell}}) \]
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 $\xi_{\text{min}}$

Two fold 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

**PHYSICAL REVIEW B** 72, 020101(R) (2005)

**Ferroelectricity in ultrathin perovskite films**

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

**PHYSICAL REVIEW LETTERS** 96, 107603 (2006)

**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$^{2}$

**PHYSICAL REVIEW B** 74, 060101(R) (2006)

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

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

**NANO LETTERS** 2006 Vol. 6, No. 3 483–487

**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. Tsybalskii$^{1,5}$

**PHYSICAL REVIEW LETTERS** 96, 127601 (2006)

**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,$^{3}$
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

| Reference        | Heterostructure                          | Method | Functional | Interface     | $a_{||}$ (Å) | $t_c$ |
|------------------|-----------------------------------------|--------|------------|---------------|--------------|-------|
|                  | SrRuO$_3$/PbTiO$_3$/SrRuO$_3$            | NAO    | LDA (CA)   | SrO-TiO$_2$   | 3.874        | 6     |
| Umeno et al.     | Pt/PbTiO$_3$/Pt                          | MBPP   | LDA (CA)   | Pt-PbO        | 3.845        | 4     |
|                  |                                         |        |            | Pt-TiO$_2$    |              | 6     |
|                  |                                         |        |            | GGA (PW91)    | 3.905 ($d_{\text{exp}}^{\text{SrTiO}_3}$) | No   |
|                  |                                         |        |            | Pt-PbO        |              | No   |
|                  | Pt/TiO$_2$                               |        |            |               |              |      |
| Duan et al.      | SrRuO$_3$/KNbO$_3$/SrRuO$_3$             | PW     | LDA (CA)   | SrO-NbO$_2$   | 3.905        | 4     |
|                  | Pt/KNbO$_3$/Pt                           |        |            | Pt-NbO$_2$    |              | 2     |
|                  | Pt/BaTiO$_3$/Pt                          |        |            | RuO$_2$/BaO   |              | >4    |
|                  |                                         |        |            | Pt-TiO$_2$    |              | >4    |
|                  |                                         |        |            | Pt-BaO        |              | >4    |
|                  | SrRuO$_3$/PbTiO$_3$/SrRuO$_3$            |        |            | SrO-TiO$_2$   | 3.905        | No    |
|                  | Pt/PbTiO$_3$/Pt                          |        |            | RuO$_2$/PbO   |              | No    |
|                  |                                         |        |            | Pt-TiO$_2$    |              | No    |
|                  |                                         |        |            | Pt-PbO        |              | No    |
|                  | D. D. Fong et al.                        | PW     | GGA        | SrO-TiO$_2$   | $a_{\text{PbTiO}_3}^{\text{th}}$ | >3    |
|                  | SrRuO$_3$/PbTiO$_3$/vacuum               |        |            |               |              | <3    |
|                  | SrRuO$_3$/PbTiO$_3$/OH, O or H          |        |            |               |              | ~3    |
|                  | SrRuO$_3$/PbTiO$_3$/CO$_2$               |        |            |               |              | >3    |
|                  | SrRuO$_3$/PbTiO$_3$/H$_2$O               |        |            |               |              |      |
Be careful with the functional used…
GGA overestimates tetragonality and double-well depth in bulk PbTiO$_3$

...responsible for the absence of critical thickness in PbTiO$_3$ nanocapacitors?

Until today, monodomain studies, goal of this work: multidomain simulations

Real electrodes
imperfect screening

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

Screening by free charges
(electrodes or adsorbates)

Formation of domains
(no net charge at surface)

Goal of this work
Main questions addressed in this work

• Is the phase transition as a function of thickness from... homogeneous polarization to paraelectric? homogeneous polarization to inhomogeneous polarization?

“It is not certain yet whether this instability in a single-domain ground state results in paraelectricity or in many small domains”


• If the second is true, do the domains have a defined structure?
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.

\[ N_{at} = N_x \cdot 40 \text{ atoms} \]
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 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 $\text{BaTiO}_3$ 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
($\alpha$ and $\beta$ 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

C. Kittel (1946)
Polydomain phases adopt the form of a “domain of closure”, common in ferromagnets.
Domains of closure recently predicted using a model hamiltonian approach

48 Å thick PbZr$_{0.4}$Ti$_{0.6}$O$_3$ thin films
sandwiched with a nongrounded metallic plate (top) and a non-conductive substrate (bottom)

Dead layer thickness

Domains of closure recently predicted using a phenomenological thermodynamic potential

242 Å thick PbTiO$_3$ thin films
sandwiched with a nonconducting SrTiO$_3$ electrodes @ 700 K
stripe period 132 Å

Full first-principles simulations: the domains of closure structure is more general than expected

Domains of closure appear even with symmetric metallic electrode

This work

Domains of closure appear even in BaTiO$_3$ ferroelectric capacitors

“BaTiO$_3$ profoundly dislike significantly rotating and in-plane dipole”

“BaTiO$_3$ with the PZT configuration is thermodinamically unstable because it directly transforms into 180 stripe domains after a couple of Monte Carlo sweeps”

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 very important 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
Relevant energy differences increase with thickness

\[ N_x = 4 \]

Monodomain

Ti-centered domains

Ba-centered domains
Transition from vortices to standard 180° domains. 4-unit-cell thick layer, great increase in polarization
Transition from vortices to standard $180^\circ$ domains. 4-unit-cell thick layer, great increase in polarization
In-plane displacements, contribute to stabilize domains

\[ N_x = 4 \]

Monodomain

In-plane constraint

Ti-centered domains

Ba-centered domains

\[ N_x = 4 \]
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 $z$

Pinning of charged defects at interface?

role on fatigue?

Two unit cells thick of BaTiO$_3$
Preliminary results on SrRuO$_3$/PbTiO$_3$/SrRuO$_3$

$m = 2$, $N_x = 6$ remain paraelectric

Good agreement with experiment

Ferroelectricity in Ultrathin Perovskite Films

Dillon D. Fong, G. Brian Stephenson, Stephen K. Streiffer, Jeffrey A. Eastman, Orlando Auciello, Paul H. Fuoss, Carol Thompson

At 1 and 2 unit cells, no satellites are observed at any temperature, indicating that the samples remain in the paraelectric phase.
Conclusions

• Many effects affect the delicate balance between short and long range forces in thin films:
  
  Surface
  Mechanical (epitaxial strain)
  Electrical (depolarizing field)
  Chemical

• As a result of the different interactions, wealthy of phase diagrams

• The question of suppression of ferroelectricity in ultrathin films cannot be answered in general but, instead, must be addressed independently for each individual system.

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

Polydomains phases have a structure: Closure domains

Slides available at: http://personales.unican.es/junqueraj
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Philippe Ghosez
Alberto García

Experimental collaborators

Céline Lichtensteiger, Jean-Marc Triscone
Valanoor Nagarajan, R. Ramesh
More information ...
Size effects in ferroelectrics
Two works that challenged the standard viewpoint

10 unit-cells thick Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$

2 monolayers thick random copolymer

Th. Tybell, Ch. Ahn and J.-M. Triscone

A.V. Bune et al.
Size effects in ferroelectrics
Standard view until the end of the nineties

\[ \text{PbTiO}_3 \text{ ultrafine particles} \quad \text{ABO}_3 \text{ ultrathin films} \]

**Experiment**

- **PbTiO\(_3\)**: ~ 80Å @ RT
- **Pb(Zr\(_{0.5}\)Ti\(_{0.5}\))O\(_3\)**: ~ 200Å @ RT

**Anisotropic mean-field calculations**

\[ \frac{T_c}{T_{co}} \]

Critical thickness:

- **Pb(Zr\(_{0.5}\)Ti\(_{0.5}\))O\(_3\)**: ~ 200Å @ RT
- **PbTiO\(_3\)**: ~ 80Å @ RT

K. Ishikawa, K. Yoshikawa, and N. Okada,

S. Li et al.
PbTiO$_3$ free standing slabs under stress free and short-circuit boundary conditions are ferroelectric.

First-principles simulations on ferroelectric thin films: full first-principles simulations

BaTiO$_3$ and PbTiO$_3$ free-standing slabs under external electric fields to screen the depolarizing field