Band-alignment issues in the *ab initio* simulation of ferroelectric nanocapacitors

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Oxide interfaces in a momentous stage
One of the Science Top 10 breakthroughs of 2007

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 conditions vary.

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, 1844 (2007)
Role of DFT simulations in the advance of science of oxide interfaces

- DFT has played a determinant role in the advance of oxide interfaces science in the last years.

Improper FE in PTO/STO

2DEG at the interface of insulating materials


Theoretical review: Pentcheva, JPCM 22, 043001 (2010)
Band alignment in ferroelectric capacitors

Real world

Conduction Band

Fermi Level

Valence Band

\[ \Phi_n \]

\[ \Phi_p \]

\[ E_{gap}^{\text{exp}} \]
Band alignment in ferroelectric capacitors

Real world

Conduction Band

Fermi Level

Valence Band

DFT (LDA or GGA)

- “Normal” case

Metal

Insulator

Metal

$E_{\text{gap}}^{\text{exp}}$

$\Phi_n$

$\Phi_p$

$E_{\text{gap}}^{\text{DFT}}$
Calculating the Schottky barriers using the PDOS

- Unpolarized capacitor
- LDA gap < experimental gap

<table>
<thead>
<tr>
<th>$E_{\text{gap}}^{\text{LDA}}$ (eV)</th>
<th>$E_{\text{gap}}^{\text{exp}}$ (eV)</th>
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<tbody>
<tr>
<td>1.8</td>
<td>3.4</td>
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$\Phi_p = 1.27 \text{ eV}$  $\Phi_n = 0.52 \text{ eV}$
Band alignment in ferroelectric capacitors
Pathological case

**Real world**

- Conduction Band
- Fermi Level
- Valence Band

**DFT (LDA or GGA)**

- Pathological case
- Transfer of charge

Metal | Ferroelectric | Metal
Pathological band alignment in ferroelectric capacitors

- Unpolarized capacitor
- LDA gap < experimental gap

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$\Phi_n = -0.25 \text{ eV}$

$E_F$
Transfer of charge from the electrodes to the FE

\[ \rho(\mathbf{r}, E \in [E_F - \delta E, E_F + \delta E]) = \int_{E_F - \delta E}^{E_F + \delta E} \rho(\mathbf{r}, E) dE \]

CB

\[ E_F - \delta E \]

\[ E_F + \delta E \]

VB

\[ E_F \]
Transfer of charge from the electrodes to the FE

\[ \rho(r, E \in [E_F - \delta E, E_F + \delta E]) = \int_{E_F - \delta E}^{E_F + \delta E} \rho(r, E) dE \]
Screening of the charge injection by ionic displacements

- Local charge neutrality is lost
- High electrostatic cost

 Integral in $[E_F-0.5eV, E_F+0.5eV]$
Screening of the charge injection by ionic displacements

- Local charge neutrality is lost
- High electrostatic cost

- System relax to screen charge injection \( \rho_B = -\nabla P \)

- Wrong band alignment \( \rightarrow \) charge injection \( \rightarrow \) inhomogeneous P
Band alignment in ferroelectric capacitors
Polarized configuration case

Real world:
- Conduction Band
- Fermi Level
- Valence Band
- \( \Phi_n \)
- \( \Phi_p \)

DFT (LDA or GGA):
- Pathological case
- Transfer of charge at \( P \neq 0 \)
PbTiO$_3$/SrRuO$_3$ nanocapacitor: Well behaved unpolarized configuration

- Positive Schottky barriers
- Absence conduction charge in the insulator
- Homogeneous $P(z)$
Band tilting under polarization of FE layer

$[\text{PbTiO}_3]_{12.5}/[\text{SrRuO}_3]_{5.5}$

Fully relaxed

$P \approx 0.53 \, \mu\text{C/cm}^2$
Band tilting under polarization of FE layer

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

Fully relaxed

\[ P \approx 0.53 \mu\text{C/cm}^2 \]
Band tilting under polarization of FE layer

$\text{PbTiO}_3$ $\text{/[SrRuO}_3\text{]}_{5.5}$

Fully relaxed

$P \approx 0.53 \mu\text{C/cm}^2$
**Band tilting under polarization of FE layer**

Fully relaxed

\[
\text{[PbTiO}_3\text{]}_{12.5}/[\text{SrRuO}_3\text{]}_{5.5}
\]

\[P \approx 0.53 \, \mu\text{C/cm}^2\]
PbTiO$_3$/SrRuO$_3$ polar nanocapacitor: Band tilting

Electronic smearing

\[ T = 0.075 \text{ eV} \]

\[ P \approx 0.53 \mu \text{C/cm}^2 \]

\[ [\text{PbTiO}_3]_{12.5}/[\text{SrRuO}_3]_{5.5} \]

Fully relaxed
PbTiO$_3$/SrRuO$_3$ polar nanocapacitor: Transfer of charge

\[ \rho(r, E \in [E_F - \delta E, E_F + \delta E]) = \int_{E_F - \delta E}^{E_F + \delta E} \rho(r, E) \, dE \]

Integrated in 
\[ [E_F - 0.5 \text{ eV}, E_F + 0.5 \text{ eV}] \]

Spurious transfer of charge to the PTO layer

\[ [\text{PbTiO}_3]_{12.5}/[\text{SrRuO}_3]_{5.5} \]

Fully relaxed

\[ P \approx 0.53 \mu\text{C/cm}^2 \]
**PbTiO$_3$/SrRuO$_3$ polar nanocapacitor:**

Transfer of charge

\[[\text{PbTiO}_3]_{12.5}/[\text{SrRuO}_3]_{5.5}\]

Fully relaxed

\[P \approx 0.53 \, \mu\text{C/cm}^2\]

Unphysical distortion

Bound charge screens spurious charge transfer
Conclusions

• DFT is an invaluable tool in material oxide interfaces physics
• but has some limitations, for instance, the band alignment in FE nanocapacitors.
  • Check correct band alignment from PDOS.
  • Possible artifacts if CB is below/close to the Fermi level.

• Inhomogeneous polarization provides perfect screening of charge injection.