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First-principles calculations of capacitors at finite bias

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These are preliminary lecture notes, intended only for distribution to participants
First-principles calculations of capacitors at finite bias

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Why capacitors?

• Capacitors are omnipresent in electronic circuits and devices
• Often they are the largest components, and reducing their size is crucial
• Size and thickness have reached a regime where classical and phenomenological models are no longer reliable (<10 nm)
Outline

• Motivation from the experiments
• Theoretical methods
• Results
• Conclusions
Classical capacitor

$C/A = \varepsilon_0 \frac{\varepsilon}{t}$

- Miniaturization → we have to increase $C/A$
  - Thinner films
  - Materials with higher permittivity $\varepsilon$
Thin-film high-ε devices

Finite intercept for \( t \to 0 \): here \( C/A = 30 \text{ fF/μm}^2 \)

Linear behavior: \( 1/C = at + b \)

C. S. Hwang, JAP 92, 432 (2002).
Dielectric “dead” layer

- **Physical origin:** Intrinsic or defect-induced?
- **Role of the electrode:** elemental metals (Pt, Au) vs. metallic oxides (SrRuO$_3$)?
- **Practical question:** how can we avoid it?
Interfacial capacitance

- **Dead layer**
  - $C_{\text{interface}} \ll C_{\text{film}}$
  - $C \sim C_{\text{interface}}/2$

- **No dead layer**
  - $C_{\text{interface}} \gg C_{\text{film}}$
  - $C \sim C_{\text{film}}$

We want an interfacial capacitance as high as possible!
What is the origin of $C_i$?

- Imperfect screening at the interface
- Phenomenological model: metallic oxide electrodes ($\text{SrRuO}_3$) are intrinsically better than Pt because of lattice contribution to the screening

$C_{\text{SRO}} \sim 900 \text{ fF/um}^2$, $C_{\text{Pt}} \sim 200 \text{ fF/um}^2$

Many results support this model...

- Much higher $C_i$ with SrRuO$_3$ electrodes compared to Pt, in agreement with the model

- These results seem to confirm the importance of ionic screening, which is absent in Pt

R. Plonka et al., APL 86, 202908 (2005)
...but others don’t!

- No T shifts in BaTiO$_3$ single-crystal lamellae (as thin as t=75 nm) with Au electrodes!

\[
\frac{1}{\mathcal{C}(T)} = \frac{4\pi t}{\varepsilon_{\text{bulk}}(T)} + \frac{2}{C_i}
\]

**Curie-Weiss law**

\[
\frac{1}{\varepsilon_{\text{bulk}}(T)} = \frac{(T - T_0)}{\alpha}
\]

\[
\frac{1}{\mathcal{C}(T)} = \frac{4\pi t}{\varepsilon_{\text{bulk}}(T + \Delta T)}
\]

**Temperature shift**

\[
\Delta T = \frac{2\alpha}{4\pi t C_i}
\]

If $C_i=200$ fF/um2, $\Delta T \sim 150$ K!

Outline

- Motivation from the experiments
- **Theoretical methods**
- Results
- Conclusions
Computational setup

- Supercell technique + Periodic boundary conditions
- Finite electric fields

\[ E^\mathcal{E} = E_{KS} - \Omega \mathcal{E} \langle P \rangle = E_{KS} - e \mathcal{E} \langle x \rangle \]
Electric fields + PBC?

- An infinite crystal in a uniform external field *does not have a ground state*
- Scalar potential is *non-periodic*
- Recently solved for pure insulators*

*I. Souza, J. Iñiguez and D. Vanderbilt, PRL 2002
P. Umari and A. Pasquarello, PRL 2002*
Polarization in insulators

- The position operator in a pure insulator can be expressed in \textit{k-space} as a Berry phase*

\[
\langle x \rangle_{Berry} = \frac{L}{2\pi} \text{Im} \ln \det M
\]

\[
M_{mn} = \langle \psi_m | e^{i \frac{2\pi}{L} x} | \psi_n \rangle
\]

*R. D. King-Smith and D. Vanderbilt, PRB 47, 1651 (1993)
Metallic slab in vacuum

- Polarization (dipole moment) can be calculated in real space with a saw-tooth function

\[
\langle x \rangle = \int_{-L/2}^{L/2} x \rho(x) \, dx
\]
And a capacitor?

- Saw-tooth function has unphysical discontinuities where $\rho(x)$ is large
- Partially filled bands at the Fermi level → the Berry phase expression does not work
Polarization in insulators (again)

• In alternative to the Berry phase, the position operator can be written in \textit{real space} using Wannier functions

\[ \langle x \rangle = 2 \sum_i \langle w_i | x | w_i \rangle \]

• The goal is to find a \textit{localized representation} (always possible in insulators)
1D band structure: three energy windows

- $f=0$: Conduction band
- $0<f<2$: Metal
- $f=2$: Valence band

Fermi level

$E_{gap}$

Unit cell (x direction)
1. Conduction states are discarded
2. MIGS are already localized!
3. “Parallel transport” for fully occupied states

All states localized along $x$!

$\langle x \rangle = \sum_i f_i \langle w_i | x | w_i \rangle$
Finite bias potential

- Localized orbitals polarized individually by state-dependent saw-tooth potentials in real space

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Test: MgO/Ag(100)

- Favorable lattice matching
- Well-studied interface between a simple metal and a wide-gap insulator
Capacitance & permittivity profile

**Classical**

\[ C_{CL} = 30.3 \text{ fF/\(\mu m^2\)} \]

**Ab-initio**

\[ \varepsilon_{bulk} = 9.23 \]

**Ideal classical behavior in the ultrathin limit!**

\[ C_{AI} = 31.2 \text{ fF/\(\mu m^2\)} \]
SrTiO$_3$/SrRuO$_3$

- **STO**: insulating perovskite with high permittivity
  - $\varepsilon_{\text{exp}} \sim 20000$ (0 K), 290 (RT)
  - $\varepsilon_{\text{th}} = 490$

- **SRO**: metallic perovskite, very popular electrode for capacitor applications
SRO/STO: inv. permittivity profile

- $C_{cl} = 1610 \text{ fF/um}^2$, $C_{fp} = 258 \text{ fF/um}^2$
- No defects, ideal interface $\rightarrow$ “intrinsic” dead layer!

Influence of ionic relaxations in the SrRuO$_3$ electrodes

- Relaxation of electrode lattice reduces the dead layer by a factor of 2, but does not remove it!
Screening & depolarizing field

- Well-known concept for ferroelectric capacitors*
- At the electrode, the polarization charge of the dielectric is not completely screened
- The field contrasts $P$, thus suppressing the dielectric response

Soft-mode hardening effect

Dipolar-active optical modes shift to higher frequencies and mix

\[ \varepsilon \sim 1/\omega^2 \]
Pt or SrRuO$_3$?

$C_{SRO} = 0.26 \text{ F/m}^2$

$C_{Pt} = 1.0 \text{ F/m}^2$
Spin capacitors

- Ferromagnetic electrodes
- Spin-polarized carriers → storage of spin density!

J. Rondinelli, M. Stengel and N. A. Spaldin, in preparation
Conclusions

- New, powerful finite-field method
- Pt electrodes are intrinsically better than SrRuO$_3$ ones
- Bad performance of Pt in the experiments has to be ascribed to processing issues
- Challenge for the future: production of high-quality interfaces with free-electron metals