Two Mechanisms of Resistive Switching in Perovskite Oxide Thin Films

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Outline

- Background

- Ferroelectric Polarization Controlled Resistive Switching and Switchable Diode Effect in BFO films
  - Growth of BFO epitaxial thin films
  - Evidence for ferroelectric resistive switching
  - Switchable diode effect and selfconsistent calculation

- Evidence for a crucial role played by the oxygen vacancies in LaMnO$_3$ resistive switching memories
Resistive switching & Classification

Switching modes:

Unipolar switching ($V_{SET} > V_{RESET}$)

Bipolar switching ($V_{SET} \sim -V_{RESET}$)

Switching mechanisms:

- Nanomechanical Memory Effect
- Molecular Switching Effects
- Electrostatic/Electronic Effects
- Electrochemical Metallization Effect
- Valency Change Memory Effect
- Thermochemical Memory Effect
- Phase Change Memory Effect
- Magnetoresistive Memory Effect
- Ferroelectric Tunneling

Ferroelectric resistive switching

Non-Ferroelectric resistive switching

**Ferroelectric resistive switching**

**Ferroelectric resistive switching ≠ Resistive switching in ferroelectrics**

**Nonferroelectric** resistive switching  
(TiO$_2$, CuO, SrTiO$_3$, Pr$_{0.7}$Ca$_{0.3}$MnO$_3$, etc)

Related to redox reaction, migrating of ions and vacancies, etc

**Ferroelectric** resistive switching

- Ferroelectric tunneling effect (super thin films or FTJs)
- Switchable diode effect (thin films & bulks)

**Formation of conductive filaments**

**Polarization switching**

Bipolar
The forward direction of the diode is determined by the ferroelectric polarization, and it can be reproducibly switched by large external electric fields.

SCIENCE 324, 63(2009)
Our results observed in epitaxial BiFeO$_3$ thin films
Epitaxial growth of BFO/SRO/STO by Laser-MBE

A part RHEED intensity oscillation of SrTiO3 homoepitaxy (The oscillation cycle from 750 to 1050)
XRD and HRTEM characterization of BFO thin film
Current-voltage hysteresis loops

Bipolar resistive switching

Switchable diode effect

25 cycles
Current hysteresis & Ferroelectricity

IV curves measured with various sweeping voltage

Ferroelectric loops measured at 50 kHz with various voltages 6–30 V

Appl. Phys. Lett. 98, 192901 (2011)
Direct evidence for ferroelectric resistive switching

![Graphs](image)

Piezoelectric phase image of original preferred polarization patterns (downward) switched upward through PFM tip scanning of the film surface at $-8\,\text{V}$ within a square area of $3 \times 3\,\mu\text{m}^2$. After that, the polarization in the center $1 \times 1\,\mu\text{m}^2$ area is scanned downward at $+8\,\text{V}$. (c). The diode current mapping at $-3\,\text{V}$. (d)
Non-destructive readout nonvolatile RAM
This device has a memory that lasts for months, a sufficiently high on current and on/off ratio to permit ordinary sense amplifiers to measure “1” or “0”, and is fully compatible with complementary metal-oxide semiconductor processing.

Appl. Phys. Lett. 98, 192901 (2011)
Numerical calculation for the MFM structures

\[ \frac{d^2 \phi(x)}{dx^2} = -\frac{e}{\varepsilon(x)} \rho(x), \quad (1) \]

\[ \frac{1}{e} \frac{dj(x)}{dx} - R(x) = 0, \quad (2) \]

\[ j(x) = \frac{\sigma(x) d\kappa(x)}{e} , \quad (3) \]

\[ \kappa_m(x) = \frac{\hbar^2}{2m} \left[ 3\pi^2 n_m(x) \right]^{\frac{3}{2}} - e\phi(x), \quad (4) \]

\[ \kappa_s(x) = kT \ln \left[ \frac{n_s(x)}{Nc} \right] + E_c - e\phi(x), \quad (5) \]

\[ \varepsilon_s \varepsilon_0 \frac{d\phi(x)}{dx} \bigg|_{x_l} - \varepsilon_m \varepsilon_0 \frac{d\phi(x)}{dx} \bigg|_{x_l} = -\sigma(X_l) = P, \quad (6) \]

\[ \varepsilon_m \varepsilon_0 \frac{d\phi(x)}{dx} \bigg|_{x_r} - \varepsilon_s \varepsilon_0 \frac{d\phi(x)}{dx} \bigg|_{x_r} = -\sigma(X_r) = -P, \quad (7) \]

\[ \kappa(x) = \text{continuous.} \quad (8) \]
Non Polarization for Pt/BFO/Pt

Schematic Structures

Energy Band (eV)

Band Diagram

Charge Density (cm$^{-3}$)

I-V
Right Polarization for Pt/BFO/Pt

Schematic Structures

Energy Band (eV)

Charge Density I-V

Band Diagram

Charge Density (cm\(^{-3}\))

I-V

Current Density (mA/cm\(^2\))
Left Polarization for Pt/BFO/Pt

Schematic Structures

Energy Band (eV)

Band Diagram

Charge Density (cm$^{-3}$)

Charge Density

Current Density (mA/cm$^2$)

I-V
Calculated results for SrRuO$_3$/BiFeO$_3$/Pt


Theoretical proof for ferroelectric resistive switching
Interface barrier playing an important role in the Switchable diode effect
Doping density effect

Thickness of the film

Thickness of the film

Thickness effect

(a) Energy Band (eV)

(b) Density (cm$^{-3}$)

(c) Current Density (mA/cm$^2$)

(d) ON/OFF ratio

Conclusions

- Switchable diode effect & ferroelectric resistive switching were observed in the epitaxial BFO thin films.
- Direct evidence for the ferroelectric resistive switching.
- Our theoretical results verify that the ferroelectric polarization can modulate the interface barrier and dominate the switchable diode effect.
- Open a way to novel ferro-resistive memory
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- Evidence for a crucial role played by the oxygen vacancies in LaMnO$_3$ resistive switching memories
SXRD patterns for LaMnO$_3$ thin films

Thickness: ~100nm

substrate: SrTiO$_3$:Nb (0.8 wt%) (SNTO)

SXRD for films fabricated under the various oxygen pressures $10$, $5 \times 10^{-2}$, and $5 \times 10^{-4}$ Pa are 3.892, 3.973, and 4.014 Å, respectively.

c-axis lattice constant of the LMO films becomes larger, owing to the increase of the oxygen vacancies

high-resolution Synchrotron X-ray diffractometry by the BL14B1 beam line of Shanghai Synchrotron Radiation Facility (SSRF).
An aberration-corrected annular-bright-field scanning transmission electron micrographs of the LMO/SNTO interfaces along the [001] axis corresponding to oxygen pressures of 10 Pa, $5 \times 10^{-2}$ Pa, and $5 \times 10^{-4}$ Pa,

Films fabricated in lower oxygen pressure are with more oxygen vacancies.
LaMnO$_3$ resistive switching memories

Typical $I$-$V$ curves for Pt/LMO/SNTO devices under various oxygen pressure

Small 8, 1279–1284 (2012)
LaMnO$_3$ resistive switching memories

Pulse measurements of the Pt/LMO/SNTO devices with fabrication oxygen pressure of $5 \times 10^{-4}$ Pa. The pulse condition for HRS is $+5$ V with a pulse width of 1 ms and for LRS is $-5$ V with a pulse width of 1 ms. The resistance was readout at 0.1 $\mu$A.

The $R_{\text{OFF}}/R_{\text{ON}}$ ratios are indicated by numbers.

None obvious decay was observed within 10000 cycles.
Theoretical modelling

\[
\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{q}{\varepsilon_s} (p(x) - n(x) + Nd)
\]  \hspace{1cm} (1)

\[
\frac{\partial n(x)}{\partial t} = \frac{1}{q} \frac{\partial J_n(x)}{\partial x} - U(x)
\]  \hspace{1cm} (2)

\[
\frac{\partial p(x)}{\partial t} = -\frac{1}{q} \frac{\partial J_p(x)}{\partial x} - U(x)
\]  \hspace{1cm} (3)

\[
J_n(x) = -qu_n n(x) \frac{\partial \phi_n(x)}{\partial x}
\]  \hspace{1cm} (4)

\[
J_p(x) = -qu_p p(x) \frac{\partial \phi_p(x)}{\partial x}
\]  \hspace{1cm} (5)

\[
J(x) = J_n(x) + J_p(x)
\]  \hspace{1cm} (6)

\[
n(x) = n_i \exp\left(\frac{q}{kT} (\psi(x) - \phi_n(x))\right)
\]  \hspace{1cm} (7)

\[
p(x) = n_i \exp\left(\frac{q}{kT} (\phi_p(x) - \psi(x))\right)
\]  \hspace{1cm} (8)
different states for Pt/LMO/SNTO at the Pt/LMO Schottky interface. When negative voltage applied on the TE, the oxygen vacancies will accumulate at the Pt/LMO interface, making the doping density at the Pt/LMO increase, while the oxygen vacancies will migrate away from the Pt/LMO interface, giving rise to the decrease of doping density under the forward bias.

Oxygen                 –
Oxygen vacancy         +
Negative bias          + moving to the interface S2
Forward bias           + moving away from interface S3

Small 8, 1279–1284 (2012)
Conclusion

1. The results of X-ray diffraction verify that with the decrease of the oxygen pressures, the $c$-axis lattice constant of the LMO films becomes larger, owing to the increase of the oxygen vacancies.

2. An ABF STEM with atomic resolution and sensitivity for light elements is used, which clearly shows that the number of oxygen vacancies increases with the decrease of oxygen pressures during fabrication.

3. The resistive switching property becomes more pronounced with more oxygen vacancies contained in LMO films.

4. A numerical model based on the modification of the interface property induced by the migration of oxygen vacancies in these structures is proposed to elucidate the underlying physical origins.
Thank you for your attention!

Acknowledgement:
People in L03 group

http://L03.iphy.ac.cn
Dielectric constant: $10 \varepsilon_0$

Carrier lifetime: $10^{-9} \text{s}$
Electron mass: $3m_0$
Hole mass: $5m_0$

<table>
<thead>
<tr>
<th></th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
</tr>
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<tbody>
<tr>
<td>Concentration (cm$^{-3}$)</td>
<td>$9.8 \times 10^{19}$</td>
<td>$3.5 \times 10^{19}$</td>
<td>$5 \times 10^{18}$</td>
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<tr>
<td>Mobility (cm$^2$/V.s)</td>
<td>1.5</td>
<td>2</td>
<td>7</td>
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<tr>
<td>Band Gap (eV)</td>
<td>1.55</td>
<td>1.6</td>
<td>2.0</td>
</tr>
<tr>
<td>Conduction band (eV)</td>
<td>4.6</td>
<td>4.35</td>
<td>3.4</td>
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</table>
The experimental (diamonds) and calculated (lines) I-V in the case of RP (a) and LP (b) for the SrRuO$_3$/BiFeO$_3$/Pt structure.

<table>
<thead>
<tr>
<th></th>
<th>SRO</th>
<th>Pt (M)</th>
<th>BFO</th>
<th>F1 (F2)</th>
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<tbody>
<tr>
<td>Dielectric constant ($\varepsilon_0$)</td>
<td>8</td>
<td>2</td>
<td>100</td>
<td>100</td>
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<tr>
<td>Mobility (cm$^2$/V·s)</td>
<td>10</td>
<td>60</td>
<td>5</td>
<td>5</td>
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<tr>
<td>Effective mass ($m_0$)</td>
<td>5</td>
<td>1</td>
<td>5</td>
<td>5</td>
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<tr>
<td>Concentration (cm$^{-3}$)</td>
<td>$1.2 \times 10^{22}$</td>
<td>$1.5 \times 10^{22}$</td>
<td>$4 \times 10^{16}$</td>
<td>$3 \times 10^{17}$</td>
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<tr>
<td>Work function (eV)</td>
<td>5.0</td>
<td>5.55</td>
<td>4.7</td>
<td>5.43 (5.03)</td>
</tr>
</tbody>
</table>

The parameters used in our calculations

铁电薄膜介电常数的影响

Ferromagnetic property at room temperature

![Graph showing the magnetization (emu/cm³) vs. magnetic field (Oe) for BFO/STO(001) with different orientations at room temperature. The graph indicates the magnetic saturation at various field strengths for different orientations, demonstrating the ferromagnetic behavior.]
Growth of oxide thin films by Laser Molecular Beam Epitaxy

Schematic illustration of laser MBE system

SrRuO₃ on STO substrate at 2*10⁻⁴ Pa, 300 pulses
Giant resistive switching in FTJs?

“… ferroelectric tunnel junctions, which take advantage of a ferroelectric as the barrier potential…may have a profound effect on the conductance leading to a resistive switching…”

Switchable diode effect in bulk ferroelectrics

Science, 324 (2009) 63

JAP, 109 (2011) 084108
Switchable diode effect in thin film ferroelectrics


材料体系分类

过渡金属氧化物：NiO\textsubscript{x}, TiO\textsubscript{x}, Nb\textsubscript{2}O\textsubscript{5}, Ta\textsubscript{2}O\textsubscript{5}, CuO\textsubscript{x}, WO\textsubscript{x}, CoO\textsubscript{x}...

钙钛矿氧化物：SrTiO\textsubscript{3}, La\textsubscript{1-x}Ca\textsubscript{x}MnO\textsubscript{3}, Pr\textsubscript{1-x}Ca\textsubscript{x}MnO\textsubscript{3}...

单极性RS效应
双极性RS效应

R. Waser Nat. Mater, 6 833 (2007)
Tunneling electroresistance effect

A combination of PFM and C-AFM techniques on nanometer-thick epitaxial BaTiO$_3$ (4.8 nm) single crystal thin films

Nature 460, 81 (Jul. 2009)

Giant TER in ultrathin BTO/LSMO films (PFM phase image and C-AFM resistance mapping)