Field effect experiments on transition metal oxides

E. Bellingeri
CNR-INFM - LAMIA Corso Perrone 24 16152 Genova Italy

Oxide Electronics Group
Director A.S. Siri*
D. Marre*, I. Pallecchi, L. Pellegrino
G. Canu, A. Caviglia

*Università di Genova Dipartimento di Fisica
Via Dodecaneso 33 16146 Genova
Italy
Superconductivity & technological transfer

Superconducting fault current limiter fabricated at LAMIA for CESI SpA

Superconducting resonator fabricated at LAMIA for ESAOTE SpA

Thin films of superconducting materials - MgB₂ with extremely high upper critical fields

Spin-off company for MgB₂:
Columbus Superconductors srl:
Km length MgB₂ superconducting tapes and wires
Synthesis of superconducting oxides
Structural refinement and HRTEM analysis

Single crystal growth of superconducting and magnetic oxides

HPHT Combustion synthesis of nitrides

Mechanical alloying of metallic and ceramic nanopowders

Synthesis of intermetallic alloys for hydrogen storage and ceramics for fuel cells
Oxide Electronics: new materials and nanodevices

Field Effect Nanotransistors on Functional Oxides

Channel dim: 0.7 μm x 8 μm

Ferroelectric Memories

Colossal Magnetoresistance based devices

\[ T_{\text{mi}} = 134.33 K \]
\[ V_{\text{gate}} = \pm 40 \text{ Volts} \Rightarrow \Delta T \approx 1K \]
Outline

- Transition metal oxides
  - Perovskite
  - Wurzite
  - Traditional
    - Stacked
    - Back Gate
    - Side Gate
  - Ferroelectric
    - Stacked
    - Local (AFM)
- Field effect geometries
- Experiments
  - Oxide Semiconductor
  - Manganites
  - Superconductor
Transition Metal oxides

**Wurzite**
- zinc (II) oxide
- Hexagonal
- Lattice parameters: \(a=3.24 \, \text{Å}, c=5.19 \, \text{Å}\)
- Transparent semiconductor
- High mobility
- Wide-band gap
- Doped with magnetic ions (Co, Mn...): dilute magnetic semiconductors

**Perovskite**
- \(ABO_3\)
- (Pseudo)cubic
- Many physical properties depending on cations
- High Tc superconductivity
- Ferroelectricity
- Ferromagnetism, Colossal Magnetoresistance
- Semiconductors, Insulators
Dielectrics and semiconductors:

$\text{SrTiO}_3, \text{LaVO}_3, \text{ZnO}$

M-I transition in titanates
Colossal magnetoresistance:

La$_{1-x}$Sr$_x$MnO$_3$, La$_{1-x}$Ba$_x$MnO$_3$

Continuos flow

- $P(O_2)$ 10$^2$ mbar
- $P(O_2)$ 10$^3$ mbar
- $P(O_2)$ 10$^4$ mbar

$R$ (Ω) vs. $T$ (K)

- $B=0$
- $B=0.1$ T
- $B=0.2$ T
- $B=0.5$ T
- $B=1$ T
- $B=2$ T
- $B=3$ T
- $B=5$ T
- $B=7$ T
- $B=9$ T

$R$ (KΩ) vs. $T$ (K)
Superconductivity:

YBCO, LaSCO, infinite layers...
Properties are controlled by:

\[ n \text{ Band filling factor} \rightarrow \text{proportional to the charge} \]
\[ W \text{ Band width} \rightarrow \text{proportional to } d \text{ and } p \text{ orbital overlapping} \]

How to change \( n \) and \( W \)?

**BANDWIDTH CONTROL**
- Cell deformation
  - Orbital overlapping
- Isovalent atomic substitution (different radius)
- Pressure

**FILLING CONTROL**
- Fermi level variation
- Eterovalent atomic substitution
- Field effect

Problem: the phase diagram depends not only on the carrier concentration but also on the lattice structure; chemical doping affects both carrier concentration and lattice structure and it is very difficult to discriminate between these two contributions. **Field effect** tunes the carrier concentration only, thereby it is a powerful tool to study this correlated system.
Illustration of the zero-temperature behaviour of various correlated materials as a function of charge density. Silicon is shown as a reference. The examples for high-$T_c$ superconductors and for colossal magnetoresistive (CMR) manganites reflect YBa$_2$Cu$_3$O$_{7-\delta}$ and (La,Sr)MnO$_3$, respectively.

AF, antiferromagnetic; FM, ferromagnetic; I, insulator; M, metal; SC, superconductor; FQHE, fractional quantum Hall effect; Wigner, Wigner crystal.

**Electric field effect in correlated oxide systems**
Nature 424, 1015-1018 (28 August 2003) doi: 10.1038/nature01878
Many of interesting physical properties in these material occur at $10^{19-21}$ e-/cm$^3$ (for 100 nm film => $10^{14-16}$ e/cm$^2$ => 10 – 1000 μC/cm$^2$)

Very high q value!

High polarization
Ultrathin films

**Figure 2** Cross-section of a typical sample geometry used for field-effect studies. S, source; G, gate; D, drain.
The characteristic width of accumulation or depletion layer is given by the electrostatic screening length

Thomas-Fermi for metal

\[ k_{TF} = \sqrt{\frac{3ne^2}{\varepsilon_0\varepsilon_r E_F}} \]

\[ \lambda_{TF} = \frac{2\pi}{k_{TF}} = \sqrt{\frac{4\pi^2 \varepsilon_0 \varepsilon_r E_F}{3ne^2}} \]

Debye for semiconductors

\[ \lambda_D = \sqrt{\frac{kT\varepsilon_0 \varepsilon_S}{e^2 n_{ext}}} \]

Lower carrier density ➞ larger \( \lambda \)

<table>
<thead>
<tr>
<th>Debye length at room temperature</th>
<th>( N(e/cm^3) )</th>
<th>( \varepsilon_r =300 )</th>
<th>( \varepsilon_r =100 )</th>
<th>( \varepsilon_r =10 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{20} (e/cm^3) )</td>
<td>2.0 nm</td>
<td>1.2 nm</td>
<td>0.38 nm</td>
<td></td>
</tr>
<tr>
<td>( 10^{19} (e/cm^3) )</td>
<td>6.5 nm</td>
<td>3.8 nm</td>
<td>1.2 nm</td>
<td></td>
</tr>
<tr>
<td>( 10^{18} (e/cm^3) )</td>
<td>20 nm</td>
<td>12 nm</td>
<td>3.8 nm</td>
<td></td>
</tr>
</tbody>
</table>
Field effect devices: Stacked Geometry

MIS heterostructure
Metal-Insulator-Semiconductor

- Growth of the dielectric layer on the channel
- Compatibility problems
- Leakage

Back gate geometry

- Very good dielectric properties of the oxide (single x-tal)
- Very thick ➔ High voltage
Advantages of the side gate geometry

- Easy: 2-layers structure (film/substrate)
- High quality substrates → Best Dielectric Properties
- Low voltage required
- Possibility to study the surface by Scanning Probe Microscopy
Side gate field effect devices fabrication by AFM

First step: patterning by optical lithography and wet etching in 10-20 \( \mu \text{m} \) wide crossing channels with bond pads

Second step: sub-micron patterning by Atomic Force Microscope anodization: the AFM biased tip triggers a local chemical and morphological transformation.

Conducting silicon
\( W_2C \) coated tip
0.12N/m

Nanoxidation of silicon
Fabrication of constrictions as narrow as 40 nm.

- Nanoscale GaAs/AlGaAs heterostructures

Local “anodic oxidation” of oxides:

The modified regions are swollen, porous and electrically insulating

Fabrication of constrictions as narrow as 40 nm.
Modified regions are selectively etched in HCl solution

Voltage controlled etching depth !!!
Etched sub-micron wide insulating barriers can sustain applied voltages up to ±80 Volts without appreciable leakage (<100pA).

Side gate field effect devices by AFM
Electric field profile and capacitance calculation

Channel width 600 nm
Gap 1200 nm, Thickness 10 nm
Applied Voltage V = 10V

Estimated capacitance:
\[ C/m = 8.8 \times \varepsilon_r \text{pF/m} \]

\[ \frac{dn_{\text{sheet}}}{dV_g} = \varepsilon_r \times 10^{10} (e/cm^2V) \]

\[ \varepsilon_r = 25 \text{ (LAO)} \]
\[ \Rightarrow dn_{\text{sheet}} = 2.5 \times 10^{12} (e/cm^2) \]
\[ \varepsilon_r = 1000 \text{ (STO)} \]
\[ \Rightarrow dn_{\text{sheet}} = 10^{14} (e/cm^2) \]
Ferroelectric Field effect

Induced charge proportional to the ferroelectric remnant polarization

- Remnant polarization $P_r \sim 10^{-60} \, \mu \text{C/cm}^2$
- Coercive field $E_c \sim 100 \, \text{kV/cm}$
- $P_b(Zr_{0.20}, Ti_{0.80})O_3$
- $c$-axis = 4.13-4.16 Å
- $\sigma \approx 10^{14}$ charges/cm$^2$

- No V applied during measurements
- No leakage
- Only 2 states available

$P$ ($\mu$C/cm$^2$) vs. $V$ (V) graph
Perovskite films growth and structural properties

Layer by layer growth

Atomically smooth surfaces

“Sharp” interface reflectivity

“Cube on cube” epitaxial growth
Oxides Semiconductors
Easy case : ZnO Back-gate devices

Double side polished SrTiO$_3$ 110 substrate

Channel thickness 70 nm

Channel thickness 270 nm

- More than 5 order of magnitude $R_{SD}$ modulation at 50K

$\mathbf{n} = 5 \times 10^{16}$ e/cm$^3$

$T=300 \text{ K}$

$T=50 \text{ K}$
ZnO Side gate devices

Transfer characteristics & field effect mobility

300K

\( I_{SD} \) [A] vs. \( V_G \) [V]

\( n = 6 \times 10^{18} \) e/cm\(^3\)

77K

\( I_{SD} \) [A] vs. \( V_G \) [V]

\( V_{ds} = 0.3 \) V

Characteristic curves

77 K

\( I_{SD} \) [μA] vs. \( V_{sd} \) [V]

\( V_G \) [V]: 0, 0.25, 0.5, 1, 2, 3

20 nm thick ZnO film by two-step method

20 nm thick ZnO film by two-step method

Gate

Source Drain

5 μm Gate

Transfer characteristics & field effect mobility

77K

\( I_{SD} \) [A] vs. \( V_G \) [V]

\( V_{ds} = 0.3 \) V

Characteristic curves

77 K

\( I_{SD} \) [μA] vs. \( V_{sd} \) [V]

\( V_G \) [V]: 0, 0.25, 0.5, 1, 2, 3
Thermal activated behaviour

MIT driven $\varepsilon_r$ of the STO substrate

Competition between $T$ and $V$

dependences of $\varepsilon_r$

Estimation of the density of state
(impurity band)

$$D(E) \propto \frac{1}{(E-E_c)}$$
Ferroelectric field effect on SrTiO$_3$ channel

Time stable 20% change in channel resistance modulated by polarization pulses

Consistent with channel thickness and channel carrier density

Ferroelectric SrTiO$_3$:La Channel

Strontium titanate resistance modulation by ferroelectric field effect
D. Marré, A. Tumino, E. Bellingeri, I. Pallecchi, L. Pellegrino, A.S. Siri,
First example of side gate devices (SrTiO$_3$ on LaAlO$_3$)


Successive Modification of the channel by the AFM tip
Temperature characterization of the side FET

- Resistance ($R(V)/R(0)$) vs. Temperature (K)
- Resistance ($R(V)/R(0)$) vs. Applied Voltage (V)
- Resistance ($R(V)/R(0)$) vs. Temperature (K)
- Resistance ($R(V)/R(0)$) vs. Applied Gate Voltage (V)

HCl solutions

11 μm x 11 μm
Nonlinearities in the $I$ vs $V$ channel behavior

Linear to Nonlinear transition of the SD characteristics at low $T$

Gate modulation of the SD linearity
Observation of E-Field Induced Drift

Low Gate field
No hysteresis

High Gate field
Memory effects
...Exploiting the Dielectric Constant of the Substrate

Maximum resistance modulation observed on homoepitaxial STO devices

- Homoepitaxial thin films have better conductivity
- Higher effect at lower gate voltages
Field-effect transistor on SrTiO$_3$ with sputtered Al$_2$O$_3$ gate insulator

K. Ueno,$^{a)}$ I. H. Inoue, H. Akoh, M. Kawasaki,$^{b)}$ Y. Tokura,$^{c)}$ and H. Takagi$^{d)}$

Correlated Electron Research Center (CERC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8562, Japan

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A field-effect transistor has been constructed that employs a perovskite-type SrTiO$_3$ single crystal as the semiconducting channel. This device functions as an n-type accumulation-mode device. The device was fabricated at room temperature by sputter-deposition of amorphous Al$_2$O$_3$ films as a gate insulator on the SrTiO$_3$ substrate. The field-effect (FE) mobility is 0.1 cm$^2$/V·s and on-off ratio exceeds 100 at room temperature. The temperature dependence of the FE mobility down to 2 K shows a thermal-activation-type behavior with an activation energy of 0.6 eV. © 2003 American Institute of Physics. [DOI: 10.1063/1.1605806]

Drain-source current $I_{DS}$ plotted against the drain-source bias $V_{DS}$ of the Al$_2$O$_3$/SrTiO$_3$ FET at 300 K. A channel length and a width of the FET device were 25 and 300 µm, respectively. The inset shows the blow-up of the $I_{DS}$–$V_{DS}$ curve for $V_{GS} = 0$ V.

(a) The gate-source bias $V_{GS}$ dependence of the drain-source current $I_{DS}$ for a fixed drain-source bias $V_{DS} = +1$ V of the same device used for Fig. 2. The on–off ratio between $V_{GS}$ of 0 and 4 V for $V_{DS}$ of 1 V exceeds 100. (b) $V_{GS}$ dependence of the field effect mobility $\mu_{FE}$. $\mu$ and $\mu_{FE}$ were deduced from Fig. 3(a) by using Eqs. (1) and (2), respectively. Both increase monotonically with $V_{GS}$ and no saturation was observed even for large gate bias.
Field-effect transistor based on KTaO$_3$ perovskite

K. Ueno, I. H. Inoue, T. Yamada, H. Akoh, Y. Tokura, and H. Takagi
Correlated Electron Research Center (CERC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8562, Japan

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An $n$-channel accumulation-type field-effect transistor (FET) has been fabricated utilizing a KTaO$_3$ single crystal as an active element and a sputtered amorphous Al$_2$O$_3$ film as a gate insulator. The device demonstrated an ON/OFF ratio of $10^4$ and a field-effect mobility of 0.4 cm$^2$/V·s at room temperature, both of which are much better than those of the SrTiO$_3$ FETs reported previously. The field-effect mobility was almost temperature independent down to 200 K. Our results indicate that the Al$_2$O$_3$/KTaO$_3$ interface is worthy of further investigations as an alternative system of future oxide electronics. © 2004 American Institute of Physics. [DOI: 10.1063/1.1703841]

Fig. 1. (a) Drain-source current $I_{DS}$ plotted against the drain-source bias $V_{DS}$ of the Al$_2$O$_3$/KTaO$_3$ FET for various gate voltages $V_{GS}$ at 300 K. The KTaO$_3$ single crystal was annealed at 700 °C prior to the device fabrication.
Manganites
Ferroelectric-field-induced tuning of magnetism in the colossal magnetoresistive oxide 
La$_{1-x}$Sr$_x$MnO$_3$

X. Hong, A. Posadas, A. Lin, and C. H. Ahn
Department of Applied Physics, Yale University, New Haven, Connecticut 06520-8284, USA
(Received 28 July 2003; published 8 October 2003)

A ferroelectric field effect approach is presented for modulating magnetism in the colossal magnetoresistive oxide La$_{1-x}$Sr$_x$MnO$_3$ (LSMO). The ferromagnetic Curie temperature of ultrathin LSMO films was shifted by 35 K reversibly using the polarization field of the ferroelectric oxide Pb(Zr$_x$Ti$_{1-x}$)O$_3$ in a field effect structure. This shift was also observed in magnetoresistance measurements, with the maximum magnetoresistance ratio at 6 T increasing from 64% to 77%. This model system approach does not introduce substitutional disorder or structural distortion, demonstrating that regulating the carrier concentration alone changes the magnetic phase transition temperature and leads to colossal effects.

DOI: 10.1103/PhysRevB.68.134415

PACS number(s): 73.50.-h, 75.47.Gk

FIG. 2. Schematic view of a PZT/LSMO heterostructure deposited on a SrTiO$_3$ (STO) substrate. Gold electrodes are deposited for electrical transport measurements.

FIG. 6. Resistivity as a function of temperature for the two polarization states of the PZT layer. The upper curve corresponds to depletion of holes and is termed the depletion state; the lower curve corresponds to accumulation of holes and is termed the accumulation state. The resistivity peak temperatures are 165 K and 200 K for the depletion and accumulation states, respectively.
Side-gate devices in a La$_{0.67}$Ba$_{0.33}$MnO$_3$ exhibiting metallic behavior

Reversible shift of the transition temperature of manganites in planar field-effect devices

Field effect on planar devices made of epitaxial manganite perovskites I. Pallecchi et al., J. Appl. Phys. 95, 8079 (2004)

Channel width 2.3 mm
Gate barrier width 1.4 mm
Film thickness 22 nm ⇒ C ≈ 7.6·ε$_r$ pF/m

For ε$_r$ ≈ 1000, the equivalent charge per unit volume accumulated/depleted by a gate voltage of ±66 V in the channel is 6.2·10$^{19}$ cm$^{-3}$

Comparison of the effects of electric and magnetic fields

Reversible shift of the metal-semiconductor transition temperature by 3.2 K

For ε$_r$ ≈ 1000, the equivalent charge per unit volume accumulated/depleted by a gate voltage of ±66 V in the channel is 6.2·10$^{19}$ cm$^{-3}$
The relative change in channel resistance behavior as a function of the applied electric field is **odd** and **linear** at T>100K; at lower temperature the observed non-linearities may be due to non-linear dielectric permittivity of the SrTiO$_3$ substrate.

**Sheet charge or volume charge?**
How much in depth does the electric field penetrate in a film with more than 10$^{20}$ carriers/cm$^3$? Shall we invoke a **phase separation** scenario?
Semiconducting behavior with incipient metallic transition

In a phase-separation scenario, metallic ferromagnetic regions are embedded in a semiconducting paramagnetic matrix and their volume fraction is below the percolation threshold.

The electric field enlarges or shrinks the metallic ferromagnetic domains, while the magnetic field enlarges and also polarizes them.
High Temperature Superconductors
Field effects in superconducting films. Change of the DS resistance of an 8-nm-thick $\text{YBa}_2\text{Cu}_3\text{O}_7$ channel with a 300-nm-thick $\text{Ba}_{0.15}\text{Sr}_{0.85}\text{TiO}_3$ gate insulator. The blue curve corresponds to depletion of the carrier density, and the red curve corresponds to enhancement of the carrier density in the DS (drain–source) channel.
We report on the electrostatic modulation of superconductivity in very thin films of cuprate superconductors using a field-effect device based on a SrTiO$_3$ single-crystal gate insulator. A $T_c$ modulation of 3.5 K and a 37% change of the normal state resistance have been observed in an epitaxial bilayer composed of an insulating PbBa$_2$Cu$_3$O$_{7-\delta}$ layer deposited on top of a superconducting NdBa$_2$Cu$_3$O$_{7-\delta}$ film, two unit cells thick. To achieve large electric fields, the thickness of the commercial dielectric single-crystal SrTiO$_3$ substrate (also used as the gate insulator) was reduced to 110 μm. The dielectric properties of the gate insulator were characterized as a function of temperature and electric field and the magnitude of the field effect was quantified. A $T_c$ enhancement of 2.8 K was obtained for an applied field of $-1.8 \times 10^6$ V/m, corresponding to a polarization of $-4 \mu C/cm^2$. © 2003 American Institute of Physics. [DOI: 10.1063/1.1624635]

Temperature and electric field dependence of the capacitance and dielectric constant of the STO single-crystal gate insulator. Inset: schematic of the device.

Resistivity as a function of temperature of the PBCO/NBCO heterostructure close to the foot of the transition and over the whole temperature range (inset) for different applied fields across the gate dielectric. The resistivity was calculated using the thickness of the NBCO layer. The arrow indicates the value of $T_{KT}$ for zero applied field.

Critical temperature $T_{KT}$ (the Kosterlitz–Thouless temperature), and $T_{c0}$, the temperature at which $R=0.1$ of the NBCO layer as a function of the measured polarization at $T_{KT}$ or $T_{c0}$. 
Electrostatic Modulation of Superconductivity in Ultrathin GdBa$_2$Cu$_3$O$_{7-x}$ Films


The polarization field of the ferroelectric oxide lead zirconate titanate [Pb(Zr$_{x}$Ti$_{1-x}$)O$_3$] was used to tune the critical temperature of the high-temperature superconducting cuprate gadolinium barium copper oxide (GdBa$_2$Cu$_3$O$_{7-x}$) in a reversible, nonvolatile fashion. For slightly underdoped samples, a uniform shift of several Kelvin in the critical temperature was observed, whereas for more underdoped samples, an insulating state was induced. This transition from superconducting to insulating behavior does not involve chemical or crystalline modification of the material.
Temperature dependence of the resistivity of Nd$_{1.2}$Ba$_{1.8}$Cu$_3$O$_y$ films having different thicknesses: 4 u.c. (closed squares), 8 u.c. (open squares), 10 u.c. (closed circles), and 110 cells (open triangles). In the inset a sketch of the field effect device is shown.

Sheet resistance measured as a function of temperature on an 8 u.c. FET for $V_g = 0$ (closed circles), $V_g = -30$ V (open diamonds), and $V_g = -34$ V (open circles). The dashed line indicates the value of the quantum resistance $R_Q = 6.45$ kΩ. In the inset the insulating–superconducting transition is shown.
Conclusions

• Field effect in transition metal oxides is possible adopting new geometries and high-\(\kappa\) materials.

• Back and side gate geometry allow direct access to the channel under FE

• In ZnO the application is close

• FE proved to be a powerful tools for the study of strongly correlated electron system:
  - Magnetic transition and phase separation in manganites
  - Superconducting properties in HTCS