Interfaces in Complex Functional Oxides

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Background

Epitaxial heterostructures as model systems
Role of defects
Reliability and Yield
A huge range of oxide crystals: pyrochlores, layered structures, spinels, rock salt, …

Complex Oxides: Many Possibilities

A-site (La) Oxygen

- Superconductors (YBCO)
- Ferroelectrics (BaTiO$_3$)
- Colossal Magnetoresistance ((La,Sr)MnO$_3$)
- Multiferroics (BiFeO$_3$)
- Topological Insulators (Y$_2$Ir$_2$O$_7$)
- Thermoelectrics (doped SrTiO$_3$)
- Ferromagnets (SrRuO$_3$)
- Photovoltaics (copper oxides)
Creating Coupled Systems

I. Interface-mediated functionality

II. Functional interfaces

Energy Conversion/Transduction
Field Tunable Photonic Bandgap Structures
Information Storage
Radiation Sensing
Energy Storage
Bismuth Ferrite, BiFeO$_3$: Model Multiferroic

BiFeO$_3$
Rhombohedral, $R3c$

$a_{\text{hex}} = 5.58$ Å; $c_{\text{hex}} = 13.86$ Å
$a = 3.96$ Å, $a_r = 0.6^\circ$

G-type Antiferromagnetic Order

Weak Ferromagnetic Moment
what's the coupling mechanism at the interface?
--- Role of Orbital physics?
--- can we use an electric field to control this coupling?
Creating and Understanding Interfaces

MBE
- e.g., Schlom Group
- Highly controlled growth
- Extremely high structural quality

Laser-MBE
- Highly controlled growth
- Controlled interfaces

RHEED, TOF-ISARS
- Highly controlled growth
- Interface chemistry
Atomic Control of Oxide Heterostructures

J. Huijben, …, D. Blank, Univ. of Twente
All Oxide Interfaces: BFO/LSMO

AFM: SrTiO₃

All Oxide Interfaces: BFO/LSMO

Rheed Intensity (a.u.)

Time (Second)
Controlling Surface Termination

Time Of Flight-Mass Spectroscopy of Recoil Ion (TOF-MSRI)

La O Sr O La O Sr O
La O Mn O Mn O Mn O
Sr O Sr O Sr O Sr O
O O Ru O Ru O Ru O
Sr O Sr O Sr O Sr O
O O Ru O Ru O Ru O
Sr O Sr O Sr O Sr O
O O Ti O Ti O Ti O
Sr O Sr O Sr O Sr O
O O Ti O Ti O Ti O

Substrate holder & manipulator
Sample transfer (Load-lock)
Laser-in
Ion source
DRS
Oxygen gas
Target carouse
RHEED gun
RHEED screen
Ion screen

$\alpha$ K ion

$60^\circ$ MSRI
Probing Surface Termination

MSRI Intensity

Atomic Weight

$\alpha = 5^0$

$^{55}$Mn

$^{88}$Sr

$^{139}$La
Atomic Structure of interfaces

BiO Interface

La$_{0.7}$Sr$_{0.3}$O Interface

SRO
Structure and Composition of Interfaces (STEM-EELS)

BiO Interface

La$_{0.7}$Sr$_{0.3}$O Interface

Normalized Intensity

Distance [nm]

Normalized Intensity

Distance [nm]
Interface Termination Controls Bulk properties

\( \text{MnO}_2 \text{ interface} \)

\( (\text{BiO})^+ \)

\( (\text{FeO}_2)^- \)

\( (\text{MnO}_2)^{-0.7} \)

\( (\text{La},\text{SrO})^{+0.7} \)

\( \text{La}_{0.7}\text{Sr}_{0.3}\text{O} \text{ interface} \)

\( (\text{BiO})^+ \)

\( (\text{FeO}_2)^- \)

\( (\text{MnO}_2)^{-0.7} \)

\( (\text{La},\text{SrO})^{+0.7} \)

Out of plane PFM image

+0.15 e

-0.15 e

P. Yu et al., under review (2011)
Experimental Probe of Interface Induced Potential Step.

- Internal field: shift of piezoresponse hysteresis loop;
- Interface induced electrostatic potential step ~ difference between internal fields ~ 1.2 Volts.
Interface Termination Controls Bulk properties

Interface induced electrostatic potential step ~1.3V

Collaboration with Dr. Luo, W. D., Prof. Pennycook, S. J. and Prof. Pantelides, S.T. at ORNL.
Exchange coupling changes with Interface termination!!

**BiO Interface**

![BiO Interface Structure]

**La$_{0.7}$Sr$_{0.3}$O Interface**

![La$_{0.7}$Sr$_{0.3}$O Interface Structure]
Probing Exchange Coupling with XMCD

- 5nm LSMO + 30nm BFO
- 0.2T FC
- -0.2T FC
- 5nm LSMO
- 0.2T FC

Intensity (Arb. Units)

Magnetization ($\mu_B / \text{Mn}$)

Magnetic Field (Oe)

Photon Energy (eV)
## FeRAMs: Solving Technology Challenges through Science

<table>
<thead>
<tr>
<th>Memory Parameter</th>
<th>DRAM</th>
<th>FeRAM</th>
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<tr>
<td></td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>Supply Voltage</td>
<td>3.15 V</td>
<td>3.45 V</td>
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<tr>
<td>Low Power Standby</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Operating Active Current</td>
<td>-</td>
<td>25 mA</td>
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<tr>
<td>Operating Temperature</td>
<td>0°C</td>
<td>70°C</td>
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<tr>
<td>Storage Temperature</td>
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<td>125°C</td>
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<tr>
<td>Non-Volatile Data Storage</td>
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<td>-</td>
</tr>
<tr>
<td>Read Cycle Time</td>
<td>50 ns</td>
<td>-</td>
</tr>
<tr>
<td>Address Access Time</td>
<td>-</td>
<td>26 ns</td>
</tr>
<tr>
<td>Read Cycles Per Byte</td>
<td>&gt;$10^{15}$</td>
<td>-</td>
</tr>
<tr>
<td>Write Cycle Time</td>
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<tr>
<td>Non-Volatile Data Retention</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Write Cycles Per Byte</td>
<td>&gt;$10^{15}$</td>
<td>-</td>
</tr>
</tbody>
</table>

Basic Science Solves Applied Problems

Old Process – Fatigue is an issue

Binary Metallic Oxides
- IrO$_2$
- RuO$_2$
- PoO$_2$
- OsO$_2$
- ReO$_3$

Metallic Perovskites
- (La,Sr)CoO$_3$
- SrRuO$_3$
- Bi$_2$Sr$_2$CaCu$_2$O$_8$
- Bi$_2$SrCaTiO$_3$
- (La,Sr)MnO$_3$
- LaNiO$_3$
- YBa$_2$Cu$_3$O$_7$

New Approach – LSCO/PNZT/LSCO

Polarization – $\Delta P$ ($\mu C/cm^2$)

Epitaxial
- Oriented
- Polycrystalline

Fatigue Cycles
- $10^4$
- $10^6$
- $10^8$
- $10^{10}$
- $10^{12}$

Remnant Polarization
- $10$
- $10^2$
- $10^4$
- $10^6$
- $10^8$
- $10^{10}$
- $10^{12}$

Fatigue Cycles
- $10^4$
- $10^6$
- $10^8$
- $10^{10}$
- $10^{12}$

References:
- Ramesh, et al., APL 61, 1537 (1992)
- Ramesh, et al., APL 63, 3592 (1993)
- Kingon, et al., JMR 9, 2988 (1994)
Oxide Electrodes: Eliminate Imprint

Pt/PZT/Pt

LSCO/PZT/LSCO

Polarization (μC/cm²)

Voltage (V)

Polarization (μC/cm²)

Voltage (V)

Oxide Electrodes Solve the Imprint (Internal Field) Problem

**Processing Issues in CVD: Role of Composition**

**Graph (I):**
- Bi/(Bi+Fe) atomic ratio in film (%) vs. Bi/(Bi+Fe) solution mixing ratio (%)
- Data points indicate the relationship between the atomic ratio and the mixing ratio.
- Substrate temperature: 650 °C
- Vaporizer temperature: 190 °C

**Graphs (II) and (III):**
- X-ray diffraction patterns showing intensity vs. 2θ (degree) for different phases.
- Peaks for STO, SRO, BFO, Fe₂O₃, and Bi₂O₃ are indicated.

**Processing Issues:**
- Detailed analysis of the role of composition in CVD processes.
Composition effect

Topography (3\times3 \mu m^2)

Out-of-plane piezoresponse

Fe-rich

Bi-rich

Need for careful composition control!!
High quality epitaxial BFO films
Possible conduction mechanisms

\[ J_S = RT^2 \exp \left( -\frac{\Phi}{k_B T} - \frac{1}{k_B T} \left( \frac{q^3 E}{4 \pi \varepsilon_0 K d} \right)^{1/2} \right) \]

Schottky emission

\[ J_{SCLC} = \frac{9 \mu \varepsilon_0 K V^2}{8} \frac{1}{d^3} \]

Space charge limited conduction

\[ \sigma_{PF} = c \exp \left( -\frac{E_I}{k_B T} - \frac{1}{k_B T} \left( \frac{q^3 E}{\pi \varepsilon_0 K d} \right)^{1/2} \right) \]

Poole-Frenkel emission

\[ I = A_{eff} \frac{e^3 m_{Pt}}{8\pi h m_{BFO} \phi_B} \times E^2 \exp \left( -\frac{8\pi \sqrt{2m_{BFO} \phi_B^{3/2}}}{3he} \frac{\phi_B^{3/2}}{E} \right) \]

Fowler-Nordheim tunneling
Critical Issue #2
How to reduce leakage?
Understand leakage mechanisms
Chemical doping

Leakage Current [A] vs. Applied Voltage [V]
- 20C (Positive)
- 20C (Negative)
- 40C
- 60C
- 80C
- 100C

Poole-Frenkel Emission: Fe$^{3+} \rightarrow$ Fe$^{2+}$ + h$^+$
Schottky Emission
Electron Hopping: From Fe$^{2+}$ to Fe$^{3+}$
Space-Charge-Limited Conduction

Area: 8e$^{-6}$cm$^2$

Leakage [A] vs. Voltage [V]
- Positive
- Negative

$d=240$nm
$A=8E^{-6}$cm$^2$
Identifying the leakage mechanism

**Poole-Frenkel Plot**

The extracted dielectric constant is too high, about twice that of the expected 6.25-6.5

**Schottky**

The extracted dielectric constant is too low for the negative direction, but not far off for higher fields

**Space Charge Limited**

Log-log plots (not shown) do not follow the expected trend

**Need more thickness, T and E dependent measurements**