Oxide Interfaces: Perspectives & New Physics

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“One should not work with semiconductors, that is a filthy mess; who knows if they really exist.” ---- Pauli 1931
A picture of the first transistor ever assembled, invented in Bell Labs in 1947. It was called a point contact transistor because amplification or transistor action occurred when two pointed metal contacts were pressed onto the surface of the semiconductor material. The contacts, which are supported by a wedge shaped piece of insulating material, are placed extremely close together so that they are separated by only a few thousandths of an inch. The contacts are made of gold and the semiconductor is germanium. The semiconductor rests on a metal base.
High-resolution scanning electron microscopy image of a lattice-matched SrTiO$_3$/LaTiO$_3$ superlattice, grown with pulsed laser deposition.

Ref: Ohtomo et al., Nature 419, 378 (2002)
Epitaxial Oxides

A platform that combines materials with very diverse bulk properties

A platform for which synthesis capabilities have been developed to a point where we can focus on intrinsic properties, not artifacts.
Theoretical Methods

Electronic structure of solids: Interacting many-body problem

- Density-Functional Theory
  - Local Density Approximation (LDA, LSDA)
  - Generalized Gradient approximation (GGA)
  - LDA/GGA + Hubbard U
- Models: Hartree-Fock, Dynamical mean field theory (DMFT)
- More accurate methods: exact diagonalization, Quantum Monte Carlo (Limited to small systems)
Density-functional Theory

- Key point (Kohn, Sham, Hohenberg, 1965): The ground-state energy of the interacting electrons can be found by solving a one-particle Schrödinger equation with an effective potential:

\[ H \Psi_i = \varepsilon_i \Psi_i \]

\[ H = -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(x, y, z) \]

Solution of the “mean-field” one-particle equations

- LMTO (Linear muffin-tin orbitals method)
  - {most physical, computationally fast}
- LAPW (Linear augmented plane waves)
  - {most accurate}
- Pseudopotential plane waves method
  - {easiest to formulate}

Different religions, same God.

Ohtomo et al., Nature 419, 378 (2002)
Superconducting interface between insulating oxides: 2DEG

Ref: Reyren et al., Science 317, 1196 (2007)
Quantum Hall effect in the 2DEG at the oxide interfaces

Ref: Tsukazaki et al., Science 315, 1388 (2007)

ZnO/Mg$_x$Zn$_{1-x}$O

![Graphs showing quantum Hall effect](image)
Bulk electronic structure of $\text{SrTiO}_3$ and $\text{LaTiO}_3$

$\text{LaTiO}_3$: Mott insulator - Occupied Ti($d^1$) -
Half-filled Hubbard band - antiferromagnetic insulator
$\text{SrTiO}_3$: Band insulator - Empty Ti($d^0$) band

$La^{+3}Ti^{+1}(d^1)(O^{−2})_2$
$Sr^{+2}Ti^{+2}(d^0)(O^{−2})_2$

FIG: Resistivity data indicating the Metal-Insulator transition as a small number of holes are doped via Sr substitution

Ref: Tokura et al, PRL 70, 2126 (1993)
The LaTiO$_3$/SrTiO$_3$ Interface: 2D Electron Gas

- Electronic Structure Calculations
- Density-Functional Theory
- Methods: LMTO, LAPW

Zoran Popovic

Paul Larson
SrTiO$_3$/(LaTiO$_3$)$_1$/SrTiO$_3$: Basic result from DFT

The V-shaped potential and the electron density profile near the interface from DFT

Popovic and Satpathy, PRL 94, 176805 (2005)
Electron density profile from EELS

Ref: Ohtomo et al., Nature 419, 378 (2002)
Electron confinement at the interface: No lattice relaxation

Electron charge-density contours
Effect of lattice relaxation

Ti and O atoms relax to generate a dipole moment that screens the interface electric field

LaO (Positively charged plane)

LAPW results: Larson et al, unpublished
Lattice Relaxation screens the electric field

SrTiO$_3$ is close to a ferroelectric transition, with very large dielectric constant.

DFT: Static dielectric constant
\[ \varepsilon \approx 23 \text{ (electrons only)} \] unrelaxed
\[ \varepsilon \approx 70 \text{ (electrons + lattice)} \] relaxed

Screening in solids: Electronic + lattice
The 2DEG at the interface

30 Å
Interface Subbands

(SrTiO₃)₉/LaTiO₃

Energy (eV)

X  Γ  M

Ti-1, Ti-2, Ti-3(xz)
Ti-3(xy)
Ti-1, Ti-2, Ti-3(xz,yz)
Ti-2(xy)
Ti-1(xy)

Energy (eV)
GaN/Al$_x$Ga$_{1-x}$N Interface: Highest-density 2DEG in the semiconductor system

$$E_1 + E_2 = \frac{\sigma}{\epsilon_0}$$

FIG: Electric fields calculated from DFT
2DEG at the GaN/Al$_x$Ga$_{1-x}$N Interface (Expt vs. Theory)

Density of the 2DEG

- $\sigma \sim 10^{12}$ cm$^{-2}$ (semiconductor interface)
- $\sim 1 \times 10^{13}$ cm$^{-2}$ (GaN/AlGaN)
- $\sim 3 \times 10^{14}$ cm$^{-2}$ (LaTiO$_3$/SrTiO$_3$ interface)

SS, Popovic, Mitchel, JAP 95, 5597 (2004)
Jellium model for the 2DEG at the Oxide Interface

Ref: Thulasi, Ph. D. thesis (MU, 2006); Thulasi and Satpathy, PRB (2006)

Sunita Thulasi

Schematics of the 2DEG formed at the oxide interface. The charged La atom forms a positive sheet charge, localizing a 2DEG in its neighborhood.

\[ H = H_{ke} + H_{ee} + H_{ext} + H_{eb} \]

V-shaped external potential: \[ H_{ext} = cE \mid z \]

Problem: Study the ground-state properties using Hartree-Fock and DFT methods.
Two-Dimensional Airy electron gas in the jellium model

\[ H = H_{ke} + H_{ee} + H_{ext} + H_{eb} = -\frac{\hbar^2}{2m^*} \sum_i \nabla_i^2 + \frac{e^2 \sigma}{2 \varepsilon} \sum_{i=1}^N |z_i| + H_{ee} \]

One-particle states are the Airy functions in the V-shaped potential well

\[ -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dz^2} + V(z)\psi = \varepsilon \psi, \quad V(z) = F |z| \]

\[ |\vec{k} n \lambda> = \frac{1}{\sqrt{A}} e^{i \vec{k} \cdot \vec{r}_n} \psi_n(z) \eta_\lambda \]

Hartree-Fock: \[ |F> = \prod_{\text{occ}}^{\text{occ}} a^+_n |\text{vac}> \]

\[ E_{HF} = <F \mid H \mid F> \]
DFT Calculation of the 2DEG

\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\vec{r}) \right] \psi_{\gamma k}(\vec{r}) = \epsilon_{\gamma k} \psi_{\gamma k}(\vec{r})
\]

Kohn-Sham equations

\[
V_{\text{eff}}(\vec{r}) = V_{\text{ext}}(\vec{r}) + V_H(n(\vec{r})) + V_{xc}(n(\vec{r}))
\]

Use von Barth-Hedin expression for \( V_{xc} \) and solve self-consistently

Ground-state Energy

Potential and electron density
Spatial extent of the 2DEG: Jellium model vs. Expt

Calculated density profile of the 2DEG, compared to the EELS data.
II. \( \text{CaRuO}_3/\text{CaMnO}_3 \): A metal-on-magnetic insulator interface

\[
\text{CaRuO}_3 \text{ thickness dependence of } [\text{CaMnO}_3(10 \text{ unit})/\text{CaRuO}_3(\text{N unit})]_{15}
\]

Ref: Tokura et al. (2006), Takahashi (2001)

\[
\text{Magnetization per interface atom (\( \mu_B \))}
\]

Q. Is the suppressed magnetic moment due to the formation of magnetic domains or something more interesting might be going on at the interface?
CaMnO$_3$/CaRuO$_3$ Interface

Q. What is the origin of the suppressed magnetization at the interface?

Q. Can we control the interface magnetism by controlling the leaked metallic electrons?


Ranjit Nanda
Potential barrier and charge leakage at the interface

- Exponential leakage of electron gas similar to a Jellium surface
- Potential is similar to that of metal-vacuum interface

\[ V(z) = \begin{cases} 
\frac{1 - \exp[-\lambda(z - z_0)]}{2\varepsilon_0 (z - z_0)}, & z > z_0 \\
-U_0 / \{ A \exp[-B(z_0 - z)] + 1 \}, & z < z_0 
\end{cases} \]

Lang and Kohn, PRB (1970)

W surface: Jones, Jennings, and Jepsen, PRB (1984)
Charge leakage from the metallic to the insulator side

- Interface Dipole moment
- Exponential leakage of electron gas similar to a Jellium surface

Lang and Kohn, PRB (1970)
Energetics (LSDA results)

<table>
<thead>
<tr>
<th>Structure</th>
<th>AFM</th>
<th>FM</th>
<th>FM-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total energy</td>
<td>11 meV</td>
<td>0</td>
<td>63 meV</td>
</tr>
</tbody>
</table>
DFT Results: Electron distribution at the interface

Leaked electrons
Mn (d) electron states in the solid

$\uparrow$ $e_g$

$\uparrow\uparrow\uparrow$ $t_{2g}$

Mn (d)
Magnetic Interactions: Superexchange and Double Exchange

- **Superexchange**

  \[
  J_{AF} = -\frac{2t^2}{U}
  \]

- **Double Exchange** (Anderson, Hasegawa, Zener, De Gennes, 1950s)

  \[
  J_F = t
  \]

  Canting angle of the Mn core spins

  Simple model: Anderson-Hasegawa (1950) \( \Rightarrow \)

  \[
  \theta = 2 \cos^{-1}\left(\frac{tx}{2J_{AF}}\right)
  \]
Canting does survive in a lattice and also Coulomb does not kill the canting

Two-site model: Anderson-Hasegawa (1950) \[ \theta = 2 \cos^{-1} \left( \frac{tx}{2J_{AF}} \right) \]

\[ \mathcal{H} = -t \sum_{<ij>,\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + \text{c.c.} + \sum_{<ij>} J_{ij} S_i \cdot S_j \]

\[ -2J_H \sum_i S_i \cdot s_i + U_0 \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + U_1 \sum_{<ij>,\sigma\nu} \hat{n}_{i\sigma} \hat{n}_{j\nu} \]

Results of exact diagonalization

Ref: Mishra, SS, Gunnarsson, PRB 55, 2725 (1997)
Buridan’s ass is the common name for the thought experiment which states that an entirely rational ass, placed exactly in the middle between two stacks of hay of equal size and quality, will starve since it cannot make any rational decision to start eating one rather than the other.
Q. How are the competing interactions accommodated at the interface layer?

Ans: A spin-canted state forms.

\[ H = -t \sum_{ij, \sigma} c_{i \sigma}^\dagger c_{j \sigma} + \text{h.c.} + \sum_{ij} \hat{J}_{ij} S_i \cdot S_j - 2J_H \sum_i S_i \cdot s_i \]

No. of electrons in eg level = x

Compute canting angle \( \theta \) by minimizing total energy:

\[ E = J \cos(\theta) + \sum_{nk} \epsilon_{nk}^{\text{occ}} \]

A single MnO\(_2\) plane at the interface

\[ H_k = \begin{bmatrix} \epsilon_{\uparrow \uparrow}(k) & \Delta_{\downarrow \downarrow}(k) \\ \Delta_{\uparrow \downarrow}(k) & \epsilon_{\downarrow \downarrow}(k) \end{bmatrix} \]

\[ \epsilon_{\uparrow \uparrow}(k) = 2t \cos(\theta/2) f(k) \]

\[ \Delta_{\uparrow \downarrow}(k) = 2t \sin(\theta/2) f(k) \]

\[ f(k) = \cos k_x a + \cos k_y a \]
Canted State in the interfacial CaMnO$_3$ layer

- **First layer:** electron concentration $x \sim 0.1$ 
  $\Rightarrow$ canted state
- **Second layer:** $x \sim 0.01$ 
  $\Rightarrow$ AFM state remains unchanged

Expt: Mag. Mom. at the interface is 0.85 $\mu_B \Rightarrow 115^0$ canting

Conclusion: Canted antiferromagnet at the interface.

Nanda, SS, Springborg, PRL (2007)
III. Spin polarized 2DEG: The LaMnO$_3$/SrMnO$_3$ system

Potential $V(z)$ seen by electrons near the interface

Spin-polarized 2DEG
Control of interface magnetism by strain

Double exchange $\sim t$ (Ferro)
Superexchange $\sim -t^2/U$ (Anti-ferro)

Coulomb divergence (Harrison 1978)

Coulomb divergence solved by atomic diffusion at the interface. But does that really happen or do we have "electronic reconstruction"?
LaAlO$_3$/SrTiO$_3$

**Q. What is the origin of the 2DEG at the interface? (polarity issues)**

**Q. How much of the effect is intrinsic to the interface and how much is extrinsic, such as oxygen vacancy?**

**Q. Why is 2DEG metallic, while 2DHG is insulating?**

**Q. Is the 2DEG any different from that in the semiconductor interfaces? (correlated system)**
• New class of perovskite oxide interfaces -- New physics of 2DEG?
• Examples:
  • SrTiO$_3$/LaTiO$_3$/SrTiO$_3$ (High density 2DEG at interface)
  • CaMnO$_3$/CaRuO$_3$ (Interfacial magnetism controlled by leaked electrons)
  • LaMnO$_3$/SrMnO$_3$/LaMnO$_3$ (spin polarized 2DEG --new system ever?)
  • LaAlO$_3$/SrTiO$_3$ (how does polarity affect interface states)
• Rapid progress in growth of high-quality, lattice-matched oxide interfaces is poised to bring in a new era
• Potential for new physics and new device applications