Integration of Functional Oxides and Semiconductors:

Magnetism and Epitaxy

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Outline of the talk

• Introduction
• Magnetism in Oxides
• Molecular Beam Epitaxy
• COX
• LaCoO$_3$ on Si
• Conclusions
Advances in Oxide Epitaxy

1 monolayer Sb in (100) Silicon

2 nm

1 monolayer La in (100) SrTiO₃

2 nm

La³⁺  Sr²⁺  Ti³⁺/Ti⁴⁺

500 nm

LaTiO₃ in SrTiO₃

Superlattices by design

Epitaxial oxide on semiconductors

SrTiO$_3$ on Si

Model

Experiment

BaTiO$_3$ on Ge

Fig. 1. Alkaline earth and perovskite oxides heteroepitaxy on silicon and germanium. The figure illustrates our ability to manipulate interface structure at the atomic level using our $(AC)_n(ABO_3)_m$ structure series. The $n/m$ ratio defines the electrical characteristics of this new physical system of COS in a MOS capacitor. In (A), $n = 3$, $m = 0$; in (B), $n = 1$, $m = 2$; in (C), $n = 0$, $m = 3$.

SrTiO$_3$/LaAlO$_3$ heterostructure:

Superconducting Interfaces Between Insulating Oxides


Magnetic effects at the interface between non-magnetic oxides

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Adaptive oxide devices

- Ferroelectricity
  - Ion diffusion
    - Polarization: Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$, BaTiO$_3$
    - Capacitor, Schottky diode, Tunnel junction
  - Conductive filament
    - Resistance: Cr: SrZrO$_3$, TaO$_x$
    - Capacitor
    - Tunnel junction, Spin-transfer torque MTJ

- Redox
  - Resistance: Gd$_2$O$_3$, NiO

- Ferromagnetism
  - Magnetization: La$_{1-x}$Sr$_x$MnO$_3$/SrTiO$_3$, CoFe/MgO
Conceptual structure of the 3-D heterogeneous optoelectronic integrated system-on-silicon for an intelligent vehicle system’s variable signal-processing functions depending on the moving speed of the car.
Diverse Accessible Heterogeneous Integration (DAHI):

- Compound Semiconductor Materials on Si,
- Electronic-photonic heterogeneous integration
Transition metals

A transition metal is one which forms one or more stable ions which have *incompletely filled d orbitals.*

\[
\text{[Ar]} = 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6
\]

\[
\text{[Ti]} = [\text{Ar}]3d^24s^2
\]

\[
\text{[V]} = [\text{Ar}]3d^34s^2
\]
Perovskite oxides $\text{ABO}_3$

CaTiO$_3$, BaTiO$_3$, SrHfO$_3$, ...

Octahedral symmetry ($O_h$):

Ligand field theory

High spin   Low spin
Fe$^{3+}$ (d$^5$)

$E^S - E^T = 2J$
Molecular Orbital Theory

Important energies:

- crystal field splitting $10Dq$
- exchange energy $J$
- charge transfer energy $\Delta_c$
Ferroelectricity

\[ \Delta E = \frac{1}{2} \alpha_0 (T - T_0) P_x^2 + \frac{1}{4} \alpha_{11} P_x^4 + \frac{1}{6} \alpha_{111} P_x^6 \]
Molecular Beam Epitaxy

Epitaxy: ordered growth on a monocrystalline substrate
From two Greek words: “epi”-above and “taxis”-in ordered manner
MBE was invented in the late 1960s at Bell Laboratories by J. R. Arthur and Alfred Y. Cho.
Making Nothing: Vacuum Pumps

10^-2 - 10^-3 Torr

10^-2 - 10^-10 Torr

10^-7 - 10^-11 Torr

10^-3 - 10^-7 Torr
Vacuum Chamber

Flanges

Manipulators

Vacuum gauges

Transfer rods
Knudsen Cell

Martin Hans Christian Knudsen (1871 -1949)

E-gun evaporator
Quartz Crystal Monitor

Piezoelectric Effect in Quartz

No Stress
T Tension
C Compression

Silicon Atom
Oxygen Atom
RHEED
Theoretical methods

\[
\left( -\frac{\hbar^2 \nabla^2}{2m} + V(r) \right) \psi_i(r) = \varepsilon_i \psi_i(r)
\]

\[
\Psi(R, r) = \sum_{k=1}^{K} \chi_k(r; R) \phi_k(R);
\]

\[
H_e \chi(r) = E_e \chi(r)
\]

\[
[T_n + E_e(R)] \phi(R) = E \phi(R)
\]

\[
E_{KS}[n] = \varepsilon \left| \Psi \right|^2 = E_{KS}[n] + E_{\text{ion-ion}}[n] + E_{\text{ion-\text{ion}}}[n] + E_{\text{xc}}[n]
\]

\[
-\frac{\hbar^2 \nabla^2}{2m} + V_{KS}(r) \psi_i(r) = \varepsilon_i \psi_i(r)
\]

\[
V_{KS}(r) = V_{\text{ext}}(r) + \int \frac{n(r')}{|r-r'|} dr' + V_{XC}(r)
\]

\[
F_i = -\frac{\partial E}{\partial R_i} \quad \rightarrow \quad F_i = m_i \ddot{x}_i
\]

\[
H = -t \sum_{<i,j>, \sigma} c_i^\dagger \sigma \瑞典 c_j^\sigma + U \sum_{i=1}^{N} n_i^\dagger n_i^1 \quad \rightarrow \quad E_i = \varepsilon_i + \left( \Phi_i \right| \Sigma(E_i) - V_{\text{xc}} \left| \Phi_i \right) \approx \varepsilon_i + \Sigma_{\sigma} \left( \Phi_i \right| \Sigma(\varepsilon_i) - V_{\text{xc}} \left| \Phi_i \right)
\]
SrTiO₃/LaAlO₃ heterostructure:

COX: Crystalline oxide on semiconductor

SrTiO$_3$ on Si

Model

Experiment

BaTiO$_3$ on Ge

Fig. 1. Alkaline earth and perovskite oxides heterojunctions on silicon and germanium. The figure illustrates our ability to manipulate interface structure at the atomic level using our \((\text{AO})_n(\text{ABO}_3)_m\) structure series. The \(n/m\) ratio defines the electrical characteristics of this new physical system of COS in a MOS capacitor. In (A), \(n = 3, m = 0\); in (B), \(n = 1, m = 2\); in (C), \(n = 0, m = 3\).

Si and STO are very different!

A. Geometry:

Silicon

45 ° “rotation”

ABO₃

A-layer

B-layer

a_{Si}/(2)^{0.5}=3.84 Å
a_{STO}=3.905 Å

B. Chemistry:
Zintl intermetallics: SrAl₂

Zintl Alchemy

Edward Zintl (1898-1941)

tI10 SrAl₄ structure

fcc Al metal

SrAl₂ structure
SrTiO₃ deposition on Si

- Sr-assisted SiO₂ desorption
- ½ monolayer Sr on Si
  (Zintl template layer)

- Initial amorphous SrTiO₃ seed layer at 200°C (4 unit cells)
  Crystallize at 550°C
- Main SrTiO₃ deposition
  4x10⁻⁷ torr O₂ at 550°C
  Co-evaporation of Sr and Ti at 1 monolayer per minute
  20 unit cells (fully relaxed)
Integrating ferromagnets on Si (001)
**Properties and applications** $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$

- **Properties**
  - $\text{Co}^{3+}$: $3d^6$
  - 0.6 eV gap semiconductor
  - Non-magnetic at low temperature but paramagnetic at room temperature
  - **Epitaxial strain induces ferromagnetism**
  - Spin state transitions
    - Low, intermediate, high-spin
  - Metal-insulator transition when doped

- **Possible applications**
  - Electrode (Sr-doped)
    - Cathode material for solid oxide fuel cells
    - Epitaxial oxide electrode for perovskite multilayers
  - Gas sensors / catalysis
  - Magnetic semiconductor
    - Spintronics

*Fig. 41. Phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ for $0 = x = 0.50$; adapted from [247]. $\text{Co(III)}$ = low-spin; $\text{Co(iii)}$ = intermediate-spin; $\text{Co}^{3+}$ = high-spin*

- Fuchs et al., PRB 75, 144402 (2007)
- Rondinelli & Spaldin, PRB 79, 054409 (2009)  NO
- Gupta & Mahadevan, PRB 79, 020406 (2009)  YES
LaCoO$_3$

- Low spin (LS); $S = 0$
- Intermediate spin (IS); $S = 1$
- High spin (HS); $S = 2$

$t_{2g}^*$ (W $\approx$ 1.5 eV)

$e_g^*$ (W $\approx$ 4 eV)

DOS (a.u.)

*Low spin (LS); $S = 0$
• Half-metallic IS is stabilized beyond 3.8%.
• Experimentally, strained LCO on STO is insulating.
• Experimental critical strain is less than 3.8%.
Issues related to MBE growth of LCO on Si

• Direct deposition of La, Co on Si in oxygen at high temperature will form CoSi$_2$ and SiO$_2$
  – Incommensurate or amorphous $\rightarrow$ Prevents epitaxy

• Phase formation range of LaCoO$_3$ requires both high oxygen chemical potential and high temperature
  – Typical MBE growth conditions using molecular oxygen (10$^{-6}$ torr) results in Co$^{2+}$ oxidation state

• To overcome these difficulties we will use an SrTiO$_3$/Si pseudo substrate
  – Use an epitaxial template layer $\rightarrow$ SrTiO$_3$ on Si
  – Use activated oxygen $\rightarrow$ atomic oxygen from rf plasma source
Growth of LaCoO$_3$ on STO/silicon

- Atomic oxygen
  - 300 W rf power
  - $1 \times 10^{-5}$ torr background oxygen pressure
- Substrate temperature 750°C
- Co-deposition of La and Co with matched fluxes
  - 2 unit cells per minute rate
- Slow cooling in oxygen
  - 10°C per minute to 100°C

![LCO <110>](image1)
![LCO <100>](image2)
Cross-section TEM

LaCoO$_3$

8 nm SrTiO$_3$

6 nm SiO$_2$

Si
X-ray diffraction

30 nm LCO/8 nm STO/Si

LaCoO$_3$ lattice parameters
(bulk $a = 3.80$ Å)
$c = 3.77$ Å
$a = 3.89$ Å  Strained to SrTiO$_3$ ($a = 3.90$ Å)

No secondary phases ($\text{La}_4\text{Co}_3\text{O}_{10}, \text{La}_2\text{CoO}_4, \text{CoO}$)

Core level spectra (XPS)

No Co metal detected in XPS
Spectra consistent with literature data for single crystal
Magnetization vs. temperature

Temperature (K)

Magnetic moment (emu)

$T_C = 85$ K

$H = 1$ kOe

Field cooled
Magnetization vs. field

\[ \text{Magnetic moment (} \mu_\text{B}/\text{Co}\text{)} \]

\[ \text{Magnetic field (kOe)} \]

\[ T = 10 \text{ K} \]

Half-metallic IS is stabilized beyond 3.8%.
- Experimentally, strained LCO on STO is insulating.
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Supercells

$\sqrt{2} \times \sqrt{2} \times 2$
- 4 independent Co sites
  2 in-plane, 2 out-of-plane

$\sqrt{2} \times \sqrt{2} \times 4$
- 8 independent Co sites
  2 in-plane, 4 out-of-plane

$2 \times 2 \times 2$
- 8 independent Co sites
  4 in-plane, 2 out-of-plane

Identical site
Energy vs. strain: HS/LS mixed states

Band gap change as a function of strain

Energy (eV) vs. strain (%)

-4 -2 0 2 4

dyz, dxz  dxy  d3z2-r2

Cubic, Oh

D4h

Tensile

Compressive

D4h
Strain accommodation

- Corner-sharing octahedral network with relatively rigid CoO$_6$ units under epitaxial stress

\[ \Delta_{TD} = \frac{(b_{in} - b_{out})}{|b_{in} + b_{out}|/2} \]
Bond lengths and angles

- **ΔTD (%)**

- **θ (°)**

- **θ₀ = 162.9°**

- **NM**

- **HS site**

- **LS site**

- **θ₀ = 162.9°**

- **θ in (°)**

- **θ out (°)**

- **strain (%)**
Voltage-switchable magnetoresistance in LaCoO₃

Normally nonmagnetic LaCoO₃ becomes ferromagnetic below 85 K under tensile strain.

No magnetoresistance above $T_C$ for both voltage polarities.

Magnetoresistance observed only below $T_C$ and for only positive voltage.

Critical voltage needed to observe magnetoresistance.

In collaboration with Ed Yu, UT Austin.
Summary

• First demonstration of epitaxial growth of magnetic LaCoO$_3$ on silicon.

• High quality crystalline LaCoO$_3$ layer epitaxially strained to underlying SrTiO$_3$ buffer (XRD, TEM, XPS), $T_C \sim 85$ K (SQUID)

• Beyond biaxial tensile strain of 2.5% local magnetic moments, originating from HS ($S=2$) states of Co$^{3+}$ ions, emerge in the LS Co$^{3+}$ matrix.

• The HS/LS state is insulating.

• The stabilization of the FM state is attributed to increased compliance of LCO when it has higher concentration of HS Co$^{3+}$ ions. Despite the energy cost to excite LS Co$^{3+}$ to HS state, LCO chooses this option and gains energy above tensile strain of 2.5% owing to the softness of the HS CoO$_6$ clusters.

• In contrast, compressive strain could not produce a magnetic state in LCO.