Thin films: new physics and applications?

Oberseminar 2007

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Lehrstuhl für Angewandte Physik
II. Physikalisches Institut, Universität zu Köln
Can we use thin films to create new materials, new properties and new devices?

Yes, but one needs to understand the ‘physics’, i.e. need to understand what happens to the electronic structure!

• Modification of material properties due to proximity of substrate:
  - strain
  - screening
  - charge donation

• New material compositions:
  non-existent in bulk, but stabilized in film

• New sample preparation routes:
  MBE combined with distillation and control of stoichiometry during growth by resistivity measurements
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Doubling the critical temperature of $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ using epitaxial strain


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Figure 4 Resistivity versus temperature for the two films grown simultaneously and for the bulk $\chi = 0.10$ sample. Data were obtained using a four-point method. Inset, Real and imaginary parts of the a.c. susceptibility of the film on SLAO, which reveals a sharp, single-phase transition $\Delta T_c = 0.7\,\text{K}$; the transition width of the film on STO is $\Delta T_c = 4\,\text{K}$. 
O-1s X-ray Absorption measurements (Tjong, Abbanon, Scutsky)
ESRF - Feb '00

15 nm La$_{1.92}$ Sr$_{0.08}$ CuO$_4$

Fluorescence Yield (a. u.)

Ti peak
ZR
UHB

Photon Energy (eV)

on STO and on SLAO: same oxygen hole concentration

x = 0.07

concentration from HALL-effect is not reliable!
Novel Electronic Properties on Ferroelectric / Ferrimagnetic Heterostructures

Hiteshi TABATA* and Tomoji KAWAI†, Nonmembers

Fig. 7 Temperature vs. resistance of the (La, Sr) MnO₃ layer without (A) and with a gate voltage of 3 V (B).

Fig. 8 Relation between the resistivity of ferroelectric LSMO layer and the gate voltage applied at a gate electrode (a) without magnetic field and (b) with magnetic field of 0.3 T (3000 G).
**tensile** in-plane strain

\[ c/a < 1 \]

CoO sandwiched by MnO

\[
\text{MnO}/(14\text{Å})\text{CoO}/(100\text{Å})\text{MnO}/\text{Ag}(100)
\]

CoO: \( a = 4.424 \text{ Å} \)
\( c = 4.15 \text{ Å} \)

\( L_z = 1.36 \mu_B \)
\( 2S_z = 2.46 \mu_B \)

anisotropy: +4.8 meV

**slightly compressive** in-plane strain

\[ c/a \approx 1 \]

CoO on Ag

\[
(90\text{Å})\text{CoO}/\text{Ag}(100)
\]

CoO: \( a = 4.235 \text{ Å} \)
\( c = 4.285 \text{ Å} \)

\( L_x = 1.00 \mu_B \)
\( 2S_x = 2.14 \mu_B \)

anisotropy: - 1.6 meV

from best fit of cluster calculations to Co L_{23} XAS data
Cluster calculations establish orientation and magnitude of magnetic moments.
Orbital occupation and magnetic moment

CoO: high spin 3d$^7$ ion

\[ d_1 = \sqrt{\frac{1}{2}}(-id_{yz} - d_{zx}) \]
\[ d_{-1} = \sqrt{\frac{1}{2}}(-id_{yz} + d_{zx}) \]
\[ d_2 = \sqrt{\frac{1}{2}}(id_{xy} + d_{x^2-y^2}) \]
\[ d_{-2} = \sqrt{\frac{1}{2}}(-id_{xy} + d_{x^2-y^2}) \]
\[ d_0 = d_{z^2} \]

degenerate real-space orbitals
\( d_{yz}/d_{zx} \)- hole \( \rightarrow d_{-1} \)
\( L_z = 1 \ \mu_B , \ 2S_z = 3 \ \mu_B \)

non-degenerate real-space orbitals
\( d_{xy} \)- hole
\( L_z = 0 , \ S \ in \ x-y \ plane \)
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Ferromagnetism in LaFeO$_3$-LaCrO$_3$ Superlattices

Kenji Ueda, Hitoshi Tabata, Tomoji Kawai

Ferromagnetic spin order has been realized in the LaCrO$_3$-LaFeO$_3$ superlattices. Ferromagnetic coupling between Fe$^{3+}$ and Cr$^{3+}$ through oxygen has long been expected on the basis of Anderson, Goodenough, and Kanamori rules. Despite many studies of Fe-O-Cr-based compounds, random positioning of Fe$^{3+}$ and Cr$^{3+}$ ions has frustrated the observation of ferromagnetic properties. By creating artificial superlattices of Fe$^{3+}$ and Cr$^{3+}$ layer along the [111] direction, ferromagnetic ordering has been achieved.

Fig. 3. Temperature dependence of magnetization of LaCrO$_3$-LaFeO$_3$ superlattice on SrTiO$_3$ (111) (●) and that of LaCr$_{0.5}$Fe$_{0.5}$O$_3$ solid solution film (○), measured in a 0.1-T magnetic field applied parallel to the substrate surface.
Stabilizing rocksalt \( \text{Cr}_{1-x} \text{O} \) by epitaxial growth

RHEED on 18 ML \( \text{Cr}_{1-x} \text{O} \) on MgO(100)

- \( 0 < x < 0.3 \)
- defect structure (ordered)
- multilayers \( \text{Cr}_{1-x} \text{O}/\text{MgO} \)
- with NO\(_2\): \( \text{CrO}_{2/3} \text{N}_{1/3} \)?!
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Modification of material properties using image charge screening

Reduction of charge excitation energies:

• Coulomb energy: \( U = U_0 - 2E_{\text{image}} \)
• Charge transfer energy: \( \Delta = \Delta_0 - 2E_{\text{image}} \)
• Bandgap: \( E_g = E_{g0} - 2E_{\text{image}} \)

Examples from experiments:

• Monolayer \( \text{C}_60 \) on Ag: \( U \) and \( E_g \) reduced by 1 eV
• Thin oxide film on Ag: \( U \) and \( \Delta \) reduced by 1-2 eV

Expectations:

• Stronger (super)exchange interactions: \( \sim t^2/U; \sim t^4/\Delta^2(1/U-1/\Delta) \)
• Higher \( T_C \) and \( T_N \)?!!
Bandgap is reduced! Rigidly!
Molecular orbital structure is conserved!

MgO monolayer on Ag(100):
U and $\Delta$ reduced by 2 eV!
Multiplet splittings are conserved!
Bandgap is reduced because on-site Coulomb energy $U$ is reduced!
Fig. 3. - Photocession and inverse photocession processes for a monolayer of C_{60} on metal (a) and for the surface of bulk C_{60} (b). In both cases, the final state charges and polarizations of the bucky-balls are indicated.

\[ E_g = E_g^{at} - 2 E_P (C_{60}) - 2 E_P (\text{metal}) \]

\[ \begin{array}{cccc}
2.2 \text{ eV} & 5.0 \text{ eV} & 1.2 \text{ eV} & \rightarrow 1.6 \text{ eV} \\
(6 \text{ nearest neighbors})
\end{array} \]

\[ E_g = E_g^{at} - 2 E_P (C_{60}) \]

\[ \begin{array}{cccc}
3.3 \text{ eV} & 5.0 \text{ eV} & 1.7 \text{ eV} \\
(9 \text{ nearest neighbors})
\end{array} \]

\[ 2 E_P (\text{metal = image charge}) = \frac{e^2}{2D} = 1.44 \text{ eV} \quad (D \approx 5 \text{ Å}) \]
What happens at a semiconductor – metal interface

\[ E_F - E_{\text{gap}} = \text{constant?} \]
Bending

\[ \Delta E_{\text{gap}} \sim 1 \text{eV} \]

Depends on Orientation!

Orientation changes the gap at interface
Orientation disorder is really bad
Influence of STM tip on bandgap of solid $C_{60}$ ?!
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Electronic reconstruction at an interface between a Mott insulator and a band insulator

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Surface science is an important and well-established branch of materials science involving the study of changes in material properties near a surface or interface. A fundamental issue has been atomic reconstruction: how the surface lattice symmetry differs from the bulk. ‘Correlated-electron compounds’ are materials in which strong electron–electron and electron–lattice interactions produce new electronic phases, including interaction-induced (Mott) insulators, many forms of spin, charge and orbital ordering, and (presumably) high-transition-temperature superconductivity\textsuperscript{1,2}. Here we propose that the fundamental issue for the new field of correlated-electron surface/interface science is ‘electronic reconstruction’: how does the surface/interface electronic phase differ from that in the bulk? As a step towards a general understanding of such phenomena, we present a theoretical study of an interface between a strongly correlated Mott insulator and a band insulator. We find dramatic interface-induced electronic reconstructions: in wide parameter
Figure 1: Ground-state phase diagram computed in Hartree–Fock approximation as a function of the on-site Coulomb interaction $U$ and the inverse of the La layer number $n$. For small $U$ values the ground state is a paramagnetic metal with no orbital ordering (PMM region; shaded blue). The solid line marked with squares denotes a second-order transition to a orbitally disordered magnetic state (M-OD; shaded yellow) that is ferromagnetic for $n = 1$; for $n > 1$ each (001) Ti layer is uniformly polarized, but the magnetization direction alternates from layer to layer, leading to a ferrimagnetic state ($n = 2, 4, 6, \ldots$; odd number of occupied Ti layers) or antiferromagnetic state ($n = 3, 5, 7, \ldots$; even number of occupied Ti layers). The solid line marked with circles denotes a first-order transition to a fully polarized ferromagnetic state with (00$\pi$) orbital order (FM-OO; shaded green). For sufficiently thick samples (bulk, shaded pink), the latter transition is preempted by a first-order transition to the bulk state, which, in the Hartree–Fock approximation used here, has ferromagnetic spin order and G-type ($\pi\pi\pi\pi$) antiferromagnetic order. The actual materials exhibit a G-type AF order and a complicated orbital order$^{20}$, apparently due to subtle lattice distortions neglected here$^{21}$. Inset, schematic of plane perpendicular to (010) direction of (001) superlattice for the $n = 2$ case. Circles show the positions of Sr (white) and La (red) ions respectively; small black dots show the positions of Ti ions.

Figure 2: Spin and orbitally resolved charge densities as function of transverse (001) coordinate $z$ for heterostructure with one La layer. La plane is at $z = 0$. Filled (open) symbols indicate majority (minority) spin densities for $xz$, $yz$ and $xy$ orbitals (see key on figure). a, Intermediate $U/(M-OD)$ regime; full spin polarization but all three orbitals equally occupied. b, Large $U$ (FM-OO) regime. Full spin polarization persists, orbital disproportionation occurs. In the Ti layer at $z = 1/2$, the $xz$ orbital is dominant; in the Ti layer at $z = -1/2$, the $xy$ orbital is dominant; at larger $|z|$ the $xy$ orbital is dominant, but the electron density is low.
ranges, the near-interface region is metallic and ferromagnetic, whereas the bulk phase on either side is insulating and antiferromagnetic. Extending the analysis to a wider range of interfaces and surfaces is a fundamental scientific challenge and may lead to new applications for correlated electron materials.

To assess the effects of a surface or interface on correlated-electron behaviour we require to understand the changes in the parameters governing bulk correlated-electron behaviour. The three key factors are interaction strengths, bandwidths and electron densities\[1,3\], all of which may change near a surface or interface. In most cases, surface- or interface-induced changes in all three factors will contribute, but in developing a general understanding it is desirable first to study the different effects in isolation. Here we focus on the effect of electron-density variation caused by the spreading of charge across an interface. A different charge distribution effect—the compensation of a polar surface by electronic charge rearrangement—was argued to change the behaviour of C\(_{60}\) films\[4\]. (Indeed, Hesper \textit{et al.}\[4\] coined the term “electronic reconstruction” in reference to this specific effect; we suggest that this useful phrase be applied more generally to denote electronic phase behaviour that is fundamentally different at a surface from in bulk.) Proximity to a surface or interface can also change the electron interaction parameters\[5,6\], the electron bandwidth\[7\], and level degeneracy\[8\]. Experimental studies of surfaces\[9-12\] and heterostructures\[13\]


Photoemission evidence of electronic stabilization of polar surfaces in $K_3C_{60}$

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Polar Surfaces

- Existence of non-neutral or charged planes in crystal structures
- Rocksalt (111) surfaces: MgO, NiO
\[ \Delta V = 57.9 \text{ Volt} \] per MgO or NiO double layer

IMPOSSIBLE !!
Surface
- facets: pyramids with (100) surfaces
- reconstructs: octopolar at NiO (111)
- attracts charged contaminants: OH\(^-\), I\(^-\)
- Zener-breakdown: ionic charge at surface ≠ in bulk

MnS(111): I\(^-\)
ZnO(0001): OH\(^-\), Na\(^+\)
MgO(111) in Cu
K\(_3\)C\(_{60}\)(111): C\(_{60}\)\(^{1.5-}\)
EuO(111): Eu\(^{1+}\)

Surfactants !!
Photoemission evidence of electronic stabilization of polar surfaces in K$_3$C$_{60}$

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Fig. 21. The crystal structures of the fulleride family. The top row shows the fcc structure of undoped $C_{60}$, the $A_1C_{60}$ structure with octahedral site occupancy, the $A_2C_{60}$ structure with tetrahedral site occupancy, and the $A_3C_{60}$ structure with tetrahedral and octahedral site occupancy. The bottom row shows $C_{60}$ molecules arranged in the bcc structure, the filling of tetrahedral sites producing $A_4C_{60}$ and $A_6C_{60}$. The bottom-right structure corresponds to superconductors $K_3C_{60}: T_c = 19 \text{K}$ and $Rb_2C_{60}: T_c = 30 \text{K}$. 
Elektronische Struktur eines C$_{60}$ Moleküls

- $t_{1u}$ Orbital ist LUMO
  (Lowest Unoccupied Molecular Orbital)
- $h_u$ Orbital ist HOMO
  (Highest Occupied Molecular Orbital)
- HOMO vollständig gefüllt
Bandstruktur eines C\textsubscript{60} Festkörpers

- $t_{1u}$ Band ist LUMO
- $t_{1u}$ Band ist dreifach entartet, kann 6 Elektronen aufnehmen
- $h_u$ Band ist HOMO, vollständig gefüllt
* Valence of $C_{60}$ at surface is $2.5^-$ and not $3^-$ as in bulk!
PHOTOEMISSION: $h\nu = 21.2$ eV

$K_xC_{60}$: thin film on $Al_2O_3$ single crystal

COUNTS

BINDING ENERGY (eV)

$LUMO$
Electronic Structure of $K_3C_{60}$ fcc (111) surface

- Surface has larger $U$ and smaller $W$ than bulk!
  - Naive expectation: bulk is just metallic $\rightarrow$ surface is insulating

- Integer valence $\rightarrow \frac{1}{2}$ band filling non-degenerate Hubbard model
  Metal - Insulator: $U \geq W$

- Integer $+\frac{1}{2}$ valence $\rightarrow \frac{1}{4}$ band filling non-degenerate Hubbard model
  Metal - Insulator: $V \geq W$ ($U \gg V$)

$U$: on-site Coulomb interaction = 1.7 eV
$V$: nearest neighbor Coulomb interaction = 0.3-0.5 eV
$W$: one-electron bandwidth = 0.2-0.3 eV

- Triangular lattice, $\frac{1}{4}$ band filling $\Rightarrow$ Frustrated!

Photoemission: $E_g = 2V$ $E_g = 0$ $E_F$ $??$
Photoemission from Buried Interfaces in SrTiO$_3$/LaTiO$_3$ Superlattices

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![Schematic diagrams](image)

**FIG. 1** (color online). Schematic views of the SrTiO$_3$/LaTiO$_3$ superlattice samples: capping layer only sample A; 1 uc capping sample B; 2 uc capping sample C; 2 uc capping and annealing sample D. Growth temperatures are also indicated.

![Graphs](image)

**FIG. 2** (color online). UPS spectra of the SrTiO$_3$/LaTiO$_3$ superlattice samples: the capping layer only sample A, the 1 uc capping sample B, the 2 uc capping sample C, and the 2 uc capping and annealing sample D. (a) Valence-band spectra over a wide energy range. (b) Near Fermi-level spectra after background subtraction (see text).
$\text{Fe}_3\text{O}_4 : \text{Magnetite}$

- Ältestes bekanntes magnetisches Material
- Natürlich gewachsener Kristall zeigt Oktaederflächen
- Inverse Spinell-Struktur
- Sauerstoff bildet kubisch dichteste Packung
- Eisen füllt Löcher:
  - Trivalente Eisenionen ($\text{Fe}^{3+}$) sind gleichmäßig auf Oktaeder- & Tetraeder-Plätze verteilt
  - Divalente Eisenionen ($\text{Fe}^{2+}$) sind oktaedrisch von $\text{O}$ umgeben
- $a = 8.394 \, \text{Å}$
Polar Surface of Fe$_3$O$_4$ (100)

Typ I

z.B. MgO (100)

Typ II

z.B. Fe$_2$O$_3$ (001)

Typ III

z.B. Fe$_3$O$_4$ (100)
FIG. 7. Three possible surface structures for the $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstructed Fe$_3$O$_4(100)$ surface, in top view. (a) A termination at a half-filled $A$ layer of Fe$^{3+}$ ions. (b) A termination at a $B$ layer of oxygen anions and octahedral Fe$^{2.5+}$ ions. There is one oxygen vacancy per unit cell, accompanied by the oxidation of two Fe$^{2.5+}$ ions to Fe$^{3+}$. The remaining Fe$^{2.5+}$ ions are trapped by the oxygen vacancies, resulting in charge ordering. (c) An alternative termination at a $B$ layer. Here, the surface does not contain oxygen vacancies, but one hydroxyl group per unit cell. Furthermore, the surface is fully oxidized, containing only Fe$^{3+}$ ions. Large open circles: oxygen anions; small open circles: missing Fe$^{3+}$ ions; black filled circles: Fe$^{3+}$ ions; large gray filled circles: Fe$^{2.5+}$ ions; small gray filled circles: hydrogen. In each case, the bulk unit cell is outlined.
Thin films:
Lehrstuhl fur Angewandte Physik, II. Physikalisches Institut

Materials: binary oxides with precise stoichiometry control

Technique: Molecular Beam Epitaxy
- control of oxygen stoichiometry
- compatible with electron spectroscopies

- ultra high vacuum (1x10^{-10} mbar)
- effusion cells and e-beam evaporators
- oxidizers: O_2, O_3, NO_2, O-radicals
- co-evaporation and distillation
- resistivity monitoring during growth
- in-situ RHEED and LEED
- in-situ XPS and XAS
MBE + in-situ $\rho(T)$

**HBFG-MBE**

HBFG-MBE: We have designed and constructed a new more versatile MBE system for the growth of binary oxide systems. It adds to the mini-MBE systems the capability to measure the resistivity of the thin films in situ and during growth for a wide range of temperatures. This allows to control the growth condition very accurately and to characterize the temperature-dependent transport properties of the thin films.

The system is equipped with a He flow cryostat, a RHEED gun and screen, and the system can accommodate up to 6 different effusion cells or e-beam evaporators. The design allows a full 360° azimuthal rotation of the sample in order to cover the angular range needed for a complete RHEED analysis.

For maximal flexibility both MBE systems are coupled via a sample-transfer system to each other, to an XPS system and to a loadlock.
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