Opportunity for Electronics

Oxide Interfaces—An Opportunity for Electronics

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Extraordinary electron systems can be generated at well-defined interfaces between complex oxides. In recent years, progress has been achieved in exploring and making use of the fundamental properties of such interfaces, and it has become clear that these electron systems offer the potential for possible future devices. We trace the state of the art of this emerging field of fundamental science. Curiously, stating, “Often, it may be said that the interface is the device” (1). Transistors, lasers, and solar cells all exploit interfacial phenomena. Interfaces enable data processing, memory, and electronic communication. Moreover, interfaces in semiconductor structures are the birthplace of a multitude of semiconductor multilayers; it is possible to precisely create interfaces connecting different oxide materials provides a wealth of new possibilities to generate novel electronic phases. The chemical abruptness and crystalline perfection of oxide multilayers now rival those of semiconductor multilayers; it is possible to change from one material to another over a distance of a single unit cell (6, 7) (Fig. 1B). Such oxide heterostructures can also be patterned laterally (8) (Fig. 1D), even with nanometer resolution (9). The ability to precisely create interfaces connecting different oxide materials provides a wealth of new possibilities to generate novel electronic phases.

The same phenomena that control interfaces in standard semiconductors, such as the formation of space charge layers, are also relevant at oxide interfaces. Mobilities of charge carriers have reached values so high that the quantum Hall effect (QHE) has been achieved at interfaces between oxides, an effect previously limited to interfaces between high-purity semiconductors and to interfaces involving graphene sheets. As a result of improvements in film growth, the mobility of two-dimensional ele-

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Fig. 1. Micrographs of LaAlO$_3$-SrTiO$_3$ heterostructures. (A) Top view of a LaAlO$_3$-SrTiO$_3$ bilayer containing eight monolayers of LaAlO$_3$, taken by scanning force microscopy (figure courtesy of S. Paetel). (B) Cross-sectional view of a corresponding sample containing five monolayers of LaAlO$_3$ (figure courtesy of L. Fitting Kourkoutis and D. A. Muller). (C) Optical photograph of a complete sample (figure courtesy of G. Hammerl and K. Wiedenmann). (D) Scanning force microscopy image of a conducting ring patterned by electron beam lithography into a LaAlO$_3$-SrTiO$_3$ structure (from (8)).

These phenomena arise in oxides from regularly spaced ions interacting with the electrons, from the unique electronic character of oxygen ions, and from the electronic correlations—interactions among the electrons, which make them deviate from free-particle behavior.

Interfaces Matter

The introduction of interfaces into semiconductor structures spawned numerous semiconductor devices of immense utility and interesting physics. By analogy, it is tantalizing to incorporate well-defined interfaces into oxides to generate novel phenomena. Because oxide multilayers are far more difficult to grow than semiconductor heterostructures, progress in this direction was thwarted for many years. Intensive efforts over the past two decades to grow oxide superconductors, however, led to decisive progress in the growth of oxide multilayers (Fig. 1). Key steps were the ability to terminate oxide substrates at well-defined ionic planes (2), the application of pulsed-laser deposition (PLD) (3) and molecular-beam epitaxy (MBE) (4) to the growth of multicomponent oxides containing difficult-to-oxidize constituents, and the development of high-pressure reflection high-energy electron diffraction (5) to monitor the deposition of individual atomic layers. As a result, epitaxial heterostructures of oxides can now be grown with atomic-layer precision. The chemical abruptness and crystalline perfection of oxide multilayers now rival those of semiconductor multilayers; it is possible to change from one material to another over a distance of a single unit cell (6, 7) (Fig. 1B).

The ability to precisely create interfaces connecting different oxide materials provides a wealth of new possibilities to generate novel electronic phases. The same phenomena that control interfaces in standard semiconductors, such as the formation of space charge layers, are also relevant at oxide interfaces. Mobilities of charge carriers have reached values so high that the quantum Hall effect (QHE) has been achieved at interfaces between oxides, an effect previously limited to interfaces between high-purity semiconductors and to interfaces involving graphene sheets. As a result of improvements in film growth, the mobility of two-dimensional ele-
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electron gases (2DEGs) at ZnO-Mg0.05Zn0.95O interfaces has now surpassed 20,000 cm² V⁻¹ s⁻¹ (0.5 K) (10). The QHE found in ZnO-Mg0.05Zn0.95O (Fig. 2) closely resembles the QHE of GaAs-Al0.3Ga0.7As interfaces because ZnO is, like GaAs, devoid of strong electronic correlations [Zn2⁺ in ZnO has a full shell electron configuration (3d⁰)]. Strong correlations may be added, however, by altering the material—for example, by incorporating monolayers with strong electronic correlations close to the interface. An exciting prospect for future research is to find out which phases the 2DEGs will generate if, for example, the QHE and fractional QHE states are coupled to superconducting or magnetic states.

The physical phenomena possible at oxide interfaces go well beyond those exhibited by conventional semiconductor interfaces because new and largely unexplored physics becomes relevant, enabling novel electronic phases. The key factors controlling the electronic behavior that can arise at precisely tailored interfaces between transition metal oxides, an important class of materials for emerging electronics, are described next.

Ionicity and Oxygen

Because of the strongly ionic character of transition metal oxides, the Coulomb interaction of an ion with the host lattice, the Madelung energy, plays an important role in determining interface properties. The Madelung energies of interface ions differ appreciably from those of the same ions well away from the interface in the bulk of the material, altering the energies of electronic states in the vicinity of the interface. Moreover, as a result of the ionic character of the lattice, electronic orbitals in oxides tend to overlap less than the hybridized s- and p-orbitals characteristic of standard semiconductors. The characteristic bandwidths of transition metal oxides are therefore smaller than those of conventional semiconductors. As a result, the effective masses of the charge carriers in oxides exceed those of electrons in conventional semiconductors by an order of magnitude or more; the carriers move more slowly, thereby coupling more strongly to (slow) polarization effects of the lattice, and are more localized.

The energies by which bands bend at interfaces involving transition metal oxides are thus comparable to the bandwidths of the oxides themselves. This enables built-in potentials at interfaces to shift the Fermi energy through and beyond complete bands, causing phase transitions or otherwise markedly altering the electronic properties. By the same token, the Fermi energy of planes parallel and close to the oxide interface (e.g., the planes one and two unit cells away from the interface) may reside at rather different levels with respect to the band edges. Therefore, in different planes the electronic states at the Fermi energy may, for example, originate from different atomic orbitals, causing such planes to have disparate electronic characters and to be only weakly coupled with each other, even though these planes are all chemically identical.

Many oxide interfaces become electronically active by altering the hybridization of the ionic orbitals and by modifying the orbital and spin ordering that can occur in oxides and are coupled to the lattice structure. The d-orbital lobes of the transition metals, for example, tend to align with the crystallographic axes. Orbital and spin ordering may be frustrated or even generated at interfaces. Such effects are again unknown in conventional semiconductors.

The unique character of oxygen ions is another key factor in generating novel electronic properties at oxide interfaces [see, e.g., (11)]. O²⁻ ions are exquisitely polarizable, typically causing a large, non-linear, and nonuniform polarizability of the lattice. Because the carrier density at oxide interfaces is high (~10¹⁵ to 10¹⁶cm⁻², as opposed to the 10¹⁰ to 10¹¹/cm² found in semiconductor heterostructures), this polarizability often leads to electrostatic screening lengths in complex oxides of 1 to 100 nm, which are smaller than typical screening lengths in semiconductors, again giving rise to more local, more confined novel interfacial properties. Oxygen is also special because holes in the oxygen 2p band give rise to magnetism, which, for example, is predicted to occur at the step edges of NiO surfaces (12).

Electronic Correlations

The most exciting phenomena arising at or awaiting discovery at customized oxide interfaces result from correlated electron effects. In correlated electron systems, the interaction of an electron with other electrons can no longer be described by the Coulomb interaction of a virtually free, independent particle with an average background charge that represents the other electrons. In a highly complex, nonlinear manner, electronic correlations determine the phases an electron system possesses, and thereby its characteristic properties. The strengths and relevance of the correlations among electrons are characterized by parameters such as the on-site Coulomb repulsion energy U and exchange energies J. As these parameters are sensitive to the local ionic structure, they are usually highly susceptible to change at interfaces (13). One example is an interface-driven reduction of the electronic screening, possibly caused by the broken periodicity of the ion lattice, leading to an enhanced on-site Coulomb energy U.

Figure 3 illustrates this key issue by sketching the electronic systems at interfaces between conventional semiconductors and between correlated materials. Semiconductor interfaces are characterized by band bending and space charge layers. At such interfaces the semiconductors’ carrier densities n are altered, as drawn for an exemplary case in Fig. 3A. In contrast, the electronic system of a material with correlated electrons may show several electronic phases already in its bulk (Fig. 3B, bulk phase diagram at the left). At the interface, space charge layers are induced and the carrier density changes. The interface may consequently undergo an “electronic reconstruction” (14) in which the resulting electronic phases now correspond to those of the bulk at the altered carrier density. As a result, the single-electron picture used to construct band diagrams at semiconductor interfaces collapses. It fails by not including electronic reconstruction, a key aspect of the physics of interfaces in correlated materials.

The difference between interfaces involving strong electronic correlations and semiconductor interfaces can, however, be even more striking. At interfaces in strongly correlated systems, the correlation parameters may be changed to values that are unachievable in the bulk. Because electron correlation parameters underlie all electronic properties, completely novel electronic systems with unique electronic properties can thus be generated at interfaces (15–18) (Fig. 3C). Correlated electron systems may even emerge at interfaces between uncorrelated host materials. Although experimental evidence for the emergence of truly novel phases is currently sparse, there is no doubt that they do exist, and the exploitation of oxide interfaces to create such novel phases holds promise as a route to new, exciting, and useful properties. Because this effect creates electronic phases wholly absent in the parent material regardless of electron concentration, we distinguish it from electronic reconstruction by calling it “electronic metamorphosis” [in (15, 17) the term “electronic reconstruction” has also been used to describe such effects].

A Route to New or Improved Technologies?

As a result of these and other phenomena, interfaces in oxides can harbor surprising electronic systems with remarkable properties. These systems are still topics of fundamental research. Yet for some of them the relevance to possible applications is already apparent, either because the interfaces provide potentially useful electronic properties or because the interfaces determine the electronic behavior of tech-

![Fig. 2. Measured longitudinal resistance ρₓₓ (red) and Hall resistance ρᵧᵧ (blue) of a two-dimensional electron gas formed at a ZnO-Mg₀.₀₅Zn₀.₉₅O interface, where v is the Landau filling index. The data were measured at 0.5 K. Data courtesy of A. Tsukazaki and M. Kawasaki [after (10)].](http://science.sciencemag.org/)
Grain boundary interfaces in the high-critical temperature \( T_c \) superconducting cuprates are one of the most important examples of the latter. These boundaries are charged, and the space-charge-induced carrier density change triggers a phase transition of the superconductor into an insulating phase (19). As a result, nanometer-wide highly resistive layers are created at the boundaries—a textbook example of electronic reconstruction (Fig. 3B). Although these insulating layers are exploited to make high-quality Josephson junctions, they were a key problem for the fabrication of high-\( T_c \) superconducting cables, because the supercurrent flow is impaired by these regions, causing resistive losses in the superconductor. This technological roadblock was overcome in two ways: (i) by using grain shapes that provide large boundary areas and therefore wide current paths, as used for cables fabricated from Bi-based cuprates, or (ii) by aligning the grains to reduce the width of the insulating layer, as implemented in the second generation of high-\( T_c \) cables, the coated conductors fabricated from the 123-cuprates.

Electronic reconstruction has been used to generate interfacial superconductivity (20, 21) and also in the design and fabrication of ultrathin magnetic layers. Heterostructures of antiferromagnets were grown that electronically recon-struct to induce a ferromagnetic state precisely at the interface (22). Pushing ultrathin magnetic layers to the limit, strategies to generate two-dimensional electron systems that are fully spin-polarized have been conceived. These are based, for example, on LaAlO\(_3\)-EuO interfaces (23).

Interfaces involving manganites have been intensively investigated to exploit the colossal magnetoresistance for which these materials are famous. Although manganites are already highly magnetoresistive in the bulk, the magnetoresistivity is enhanced by orders of magnitude at grain boundary interfaces (24). Space charge is once more important; it suppresses the local Curie temperature (25) and thereby enhances the magnetoresistance. These experiments highlight the extraordinary sensitivity with which interfacial electronic systems can react to external parameters—the basis of a sensor.

In contrast to the comparatively simple ferromagnetic interfaces in manganites used to enhance their magnetoresistivity, the interface between La\(_{2/3}\)Sr\(_{1/3}\)MnO\(_3\) and the high-\( T_c \) superconductor YBa\(_2\)Cu\(_3\)O\(_7\) has truly surprising properties (26). Across this interface covalent bonds are formed, which modify the electronic structure of the CuO\(_2\) layers of the YBa\(_2\)Cu\(_3\)O\(_7\). As a result, the Cu ions in the YBa\(_2\)Cu\(_3\)O\(_7\) at the interface are ferromagnetically magnetized. Such order is impossible for bulk YBa\(_2\)Cu\(_3\)O\(_7\). The possibility of using interfaces to alter materials is an intriguing means to design novel superconductors (27–29).

Conducting sheets at interfaces—which are generated between insulators, work at room temperature, can be tuned by electric fields applied by gate electrodes, and feature high carrier mobilities—represent an ideal configuration for electronic applications. The seminal discovery of conducting electron systems at interfaces between the band insulators LaAlO\(_3\) and SrTiO\(_3\) comes close to realizing this (30). If LaAlO\(_3\) is epitaxially grown on the TiO\(_2\)-terminated and (100)-oriented surface of SrTiO\(_3\), a conducting electron-doped (n-type) sheet is generated at the interface. Remarkably, this happens only if the insulating LaAlO\(_3\) is at least four unit cells thick (31). As a result, the conductivity can be precisely switched by adding or etching away single monolayers of the overlying LaAlO\(_3\) insulator when the LaAlO\(_3\) thickness in such heterostructures is just below or above the critical thickness for conductivity.

Typical sheet conductances of the electron system at the LaAlO\(_3\)-SrTiO\(_3\) interface are \( 5 \times 10^{-2} \) S and \( 5 \times 10^{-3} \) S at 300 K and 4.2 K, respectively. Mobilities are \(~7\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) at 300 K and \(~700\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) at 4.2 K. Carrier densities are usually in the range of \(10^3\) cm\(^{-2}\). In the direction perpendicular to the interface, the conducting sheet is at most a few nanometers thick (32–36). These characteristics, which differ remarkably from the typical properties of semiconductor interfaces (table S1), are shown by samples that are grown at oxygen pressures of \(5 \times 10^{-5}\) mbar and are subsequently oxidized (e.g., during cooling) at close to 1 bar of oxygen. Under these conditions, the conducting sheet generated by electronic reconstruction is not shunted by electrons arising from doping of SrTiO\(_3\) by oxygen vacancies (37). Yet even if such effects are avoided, the interfaces can be influenced by a variety of defects that depend on growth conditions, such as defect complexes involving oxygen vacancies, intermixing, and other off-stoichiometries that may even be inhomogeneous (38, 39).

**Catastrophe and Reconstruction**

Equivalent interfaces have also been found for several other material combinations, which, like LaVO\(_3\)-SrTiO\(_3\) multilayers (40), all involve SrTiO\(_3\) as one component. A generic mechanism has been proposed to drive the generation of the conducting layers (41). This mechanism has acquired fame as the “polar catastrophe.” In growing, for example, a (100)-oriented LaAlO\(_3\) film, an electrostatic voltage is built up as the charged La\^O\(^+\) and AlO\(^-\) planes of the LaAlO\(_3\) are stacked in series. The voltage grows with the LaAlO\(_3\) thickness to such large values that electrons reduce their Coulomb...
energy by moving from the LaAlO$_3$ sheet to the interface, to occupy Ti 3d states there. These 3d states form two-dimensional bands extended parallel to the interface. As many degrees of freedom are involved, the generation of the conducting electron system is a complex process. It involves, for example, orbital reconstruction of the Ti 3d states (35) and subtle yet critical shifts of the ion positions (42, 43). Even if the possible defects listed above are not considered, the generation of the electron system can only be described with completeness numerically, such as by methods based on density functional theory (DFT) [see, e.g., (42–45)].

Scanning tunneling spectroscopy measurements of the density of states at the LaAlO$_3$-SrTiO$_3$ interface (46) have revealed remarkable differences between this two-dimensional electron system and the 2DEGs formed at interfaces between conventional semiconductors. As sketched in Fig. 4A, at the semiconductor interface the mobile electrons move in two-dimensional subbands within the quantum well generated by band bending. At the oxide interface, however, there are multiple quantum wells given by the ionic potentials of the TiO$_6$ octahedra, and within each quantum well are subbands that are a subset of the Ti 3d states (Fig. 4B). In these bands, the electrons are subject to the correlations of the Ti 3d orbitals and form a two-dimensional electron liquid rather than an electron gas (46). Being a metal at room temperature, the electron liquid condenses below ~250 mK into a two-dimensional superconducting state (20).

At all temperatures, the carrier density in these sheets reacts sensitively to gate fields with concomitant changes of the conductivity. Indeed, large, depleting gate fields switch the systems into a completely insulating phase. Even the superconducting ground state can be switched into an insulating one, crossing a quantum critical point at several multiples of $10^{10}$/cm$^2$. As small variations of gate voltage cause drastic resistance changes, electric field–driven phase transitions are of interest for use in drain source channels of field-effect transistors to enhance the channels' transport response to gate fields.

The electron liquid at the LaAlO$_3$-SrTiO$_3$ interfaces is robust and stable up to several hundred degrees Celsius. This enables samples to be contacted and patterned with standard lithography techniques (8) (Fig. 1D). This electron system can also be patterned on the nanometer scale, well beyond the limits of standard lithography, using an atomic force microscope (AFM) (9). By biasing an AFM tip with a positive voltage of 10 V, conducting lines have been written in 3-monolayer-thick LaAlO$_3$-SrTiO$_3$ (by default an insulating electron system) with a spatial resolution as fine as 2 nm. With the use of negative voltages, the lines can be erased again. Lifetimes of days have been achieved, and nanometer-sized exploratory devices have been written (9).

Quantum confinement has also been predicted for vanadate-based interfaces, and this phenomenon is expected to generate electronic properties even more peculiar than those of LaAlO$_3$-SrTiO$_3$ interfaces: Quantum confinement in half-metallic VO$_2$ layers embedded within insulating TiO$_2$ is predicted to produce an unprecedented two-dimensional state characterized by a (semi-Dirac) point Fermi surface. This state comprises spinless charge carriers that have a finite effective mass along one principal axis of the lattice but are massless along the other (47).

Oxide interfaces are also of interest for their possible multiferroic behavior and for their thermoelectric properties. Large thermoelectric voltages have been reported for two-dimensional electron systems in (Nb,Sr)TiO$_3$-SrTiO$_3$ quantum wells (48). The stated Seebeck voltages are very high (850 μV/K). For applications, such large voltages are highly desirable. In principle, the use of superlattices enables many interfaces to be added in parallel to achieve sizable power output. Novel device architectures are desired, in order to decrease the thermal conduction of the materials forming the interfaces.

**Fig. 4.** (A and B) Comparison between two-dimensional electron systems generated at interfaces between standard semiconductors, for example, between GaAs and Al$_x$Ga$_{1-x}$As (A) and between LaAlO$_3$ and SrTiO$_3$ (B). At the semiconductor interface, two-dimensional electronic subbands are formed within the quantum well generated by band bending. At the oxide interface, the two-dimensional bands are generated in the potential wells arising predominantly from the ionic charges. For the LaAlO$_3$-SrTiO$_3$ interface, these are 3d bands of Ti ions. The overall band bending lowers the electronic energies of the unit cells next to the interface, such that the mobile electron system that forms a two-dimensional electronic liquid (2DEL) resides predominantly in the oxide planes next to the interface [after (46)]. (C) Illustration of the situation in (B): The LaAlO$_3$ is grown on top of the SrTiO$_3$; the mobile electron system is depicted in yellow.
Incorporation of functional oxides into electronic devices and circuits or their use in other applications requires mastering these interfaces. Today we are in the midst of learning how to meet this challenge; once mastered, these interfaces will provide vast and unforeseen opportunities, technologies, and science for decades to come.

References and Notes
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