
This copy is for your personal, non-commercial use only.

If you wish to distribute this article to others, you can order high-quality copies for your colleagues, clients, or customers by [clicking here](#).

Permission to republish or repurpose articles or portions of articles can be obtained by following the guidelines [here](#).

The following resources related to this article are available online at www.sciencemag.org (this information is current as of January 7, 2012):

Updated information and services, including high-resolution figures, can be found in the online version of this article at:

<http://www.sciencemag.org/content/313/5795/1895.full.html>

A list of selected additional articles on the Science Web sites **related to this article** can be found at:

<http://www.sciencemag.org/content/313/5795/1895.full.html#related>

This article **cites 7 articles**, 1 of which can be accessed free:

<http://www.sciencemag.org/content/313/5795/1895.full.html#ref-list-1>

This article has been **cited by** 16 article(s) on the ISI Web of Science

This article appears in the following **subject collections**:

Physics, Applied

http://www.sciencemag.org/cgi/collection/app_physics

APPLIED PHYSICS

Tuning Interface States

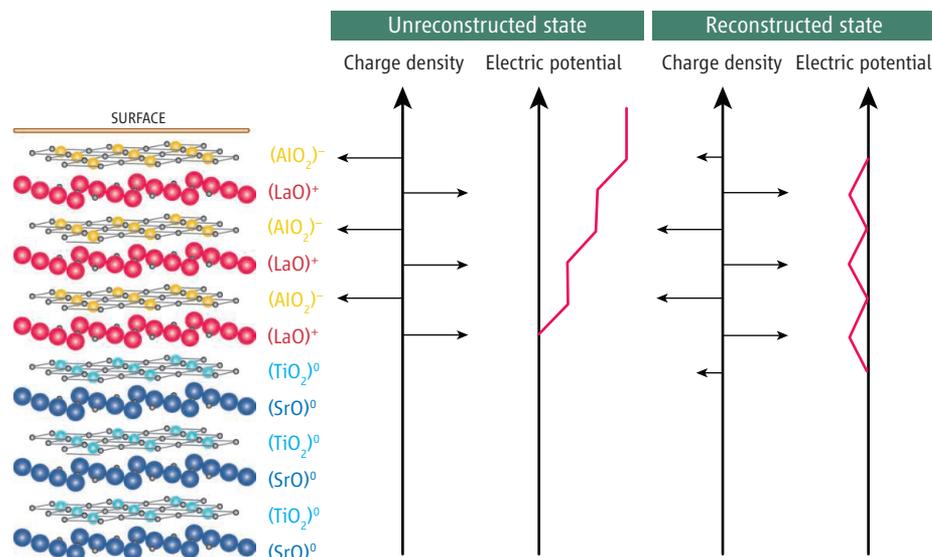
Harold Y. Hwang

An important goal of nanoscience research is the creation of new functionality by controlling materials down to the atomic level. An emerging example can be found in recent studies of the electronic structure at the interface between perovskite oxides. Modern atomic-scale growth and probe techniques enable the formation and study of new artificial interface states that are quite distinct from the bulk state. For example, the interface between two insulators, LaAlO_3 and SrTiO_3 , sustains a metallic phase with high carrier mobility for an appropriate atomic arrangement of the interface (1). This is analogous to modulation doping in GaAs heterostructures and provides a new avenue for doping perovskite interfaces, accessing the diverse physical properties of these materials, including superconductivity, magnetism, ferroelectricity, and their intercouplings. On page 1942 of this issue, Thiel *et al.* (2) report that this interface can be dynamically tuned across a metal-insulator transition by applying an external gate field. The result is a system that can be switched from highly insulating to highly conducting for a wide range of potential device applications.

The interface in question represents the border between stacks of charge-neutral atomic layers in SrTiO_3 , and alternately charged atomic layers in LaAlO_3 (see the figure). The electrostatic potential produced by the charges diverges with LaAlO_3 thickness (assuming that there are no charge rearrangements compared to the bulk structure). This divergence represents a truly energetically unfavorable circumstance—it quickly becomes the dominant energy in the system, and some reconstruction must occur.

Such a polar discontinuity is not at all new; it has been much discussed for semiconductor heterointerfaces (3–5). In those cases, the interface atomically reconstructs, changing the interface stoichiometry (usually accompanied by considerable roughening and diffusion) to remove the diverging potential. What is new here is the realization that the potential divergence can be overcome by an electronic reconstruction. Unlike

When grown with atomic precision, materials that are normally insulators can form a conducting interface with properties that can be controlled by an external field.



Polar discontinuities. (Left) The unreconstructed interface examined by Thiel *et al.* (Middle) This charge configuration leads to an electric potential that diverges with LaAlO_3 thickness. (Right) Above a threshold thickness, the charge distribution reconstructs, removing the divergence. This is shown as a layer of $\text{Ti}^{3.5+}$ at the interface, and a simple reconstruction of the polar surface of LaAlO_3 . More realistic charge distributions can be described by incorporating additional dipoles, but the overall structure remains unchanged.

semiconductors, transition metal ions at the interface can acquire a mixed-valence ionic character, whose charge balances the polar discontinuity. In the specific case shown in the figure, the titanium ions, normally Ti^{4+} elsewhere, tend toward Ti^{3+} at the interface, inducing a quasi-two dimensional electron gas (6). It should also be noted that the polar surface must also reconstruct, although the detailed configuration is not currently known.

Thiel *et al.* initially observe that there is a threshold thickness for the electronic reconstruction to occur. For LaAlO_3 layers that are up to three unit cells thick, the interface is insulating. When one or more unit cells of LaAlO_3 are added, the interface becomes abruptly metallic. Their results imply a crossover between the unreconstructed and reconstructed state as a function of interface thickness (7). This is similar to recent observations of proximity coupling of polar discontinuities with opposite sign (8)—that is, coupling between two interfaces, rather than between an interface and a surface. Next, Thiel *et al.* find that this balance point can be shifted by applying an external gate voltage, inducing a metal-insulator transition observed both at room temperature and at 4.2 K. This shift is quite dramatic, with

changes in interface conductance exceeding seven orders of magnitude (limited by detection of the insulating state).

Taken together, these results demonstrate substantial progress in the manipulation of new artificial low-dimensional charge states formed at oxide heterointerfaces. What is exciting is that extremely high doping levels can be achieved by polar discontinuities, notably exceeding the largest values obtained for field effect transistors, ferroelectric gate devices, and photocarrier generation. The figure implies an interface carrier density of $\sim 6 \times 10^{14} \text{ cm}^{-2}$; although such values have been observed, the carrier density can be varied very widely depending on growth conditions (the structures of Thiel *et al.* show an interface carrier density of $\sim 2 \times 10^{13} \text{ cm}^{-2}$, and were optimized for lower carrier density). Growth kinetics and defect chemistry are important for any experimentally realized interface, in which local rearrangements and vacancies can partially compensate the anticipated electronic structure. Indeed, it has been reported that in different growth conditions, the interface carrier density can be dominated by growth-induced oxygen vacancies (9, 10).

The author is in the Department of Advanced Materials Science and the Department of Applied Physics, University of Tokyo, Kashiwa, Chiba 277-8561, Japan. E-mail: hyhwang@k.u-tokyo.ac.jp

By growing precise structures incorporating an external gate, the interface can be statically and dynamically tuned over many orders of magnitude. At the high end, the doping levels should allow access to phase transitions that have not been previously reachable. These phase transitions can be precisely traversed and studied, as demonstrated by Thiel *et al.* Control of the interface electronic structure is central to the function and improvement of virtually all existing oxide device characteristics—similar considerations have

already played a role in enhancing magnetic tunnel junctions, as an example (11). These and other advances are rapidly opening a new frontier in the science and technology of oxide heterostructures.

References and Notes

1. A. Ohtomo, H. Y. Hwang, *Nature* **427**, 423 (2004).
2. S. Thiel, G. Hammerl, A. Schmehl, C. W. Schneider, J. Mannhart, *Science* **313**, 1942 (2006); published online 24 August 2006 (10.1126/science.1131091).
3. G. A. Baraff, J. A. Appelbaum, D. R. Hamann, *Phys. Rev. Lett.* **38**, 237 (1977).
4. W. A. Harrison, E. A. Kraut, J. R. Waldrop, R. W. Grant, *Phys. Rev. B* **18**, 4402 (1978).
5. H. Kroemer, *J. Cryst. Growth* **81**, 193 (1987).
6. N. Nakagawa, H. Y. Hwang, D. A. Muller, *Nat. Mater.* **5**, 204 (2006).
7. An alternative scenario is a different kind of reconstruction at short length scales, perhaps via charge transfer from the interface to the surface; these distinctions are not yet experimentally established.
8. M. Huijben *et al.*, *Nat. Mater.* **5**, 556 (2006).
9. A. S. Kalabukhov *et al.*, <http://arxiv.org/cond-mat/0603501>.
10. W. Siemons *et al.*, <http://arxiv.org/cond-mat/0603598>.
11. H. Yamada *et al.*, *Science* **305**, 646 (2004).

10.1126/science.1133138

GEOCHEMISTRY

Manganese Redox Chemistry Revisited

Kenneth S. Johnson

Manganese is an important component of some marine reduction-oxidation cycles. It is usually assumed that only the Mn(II) and Mn(IV) oxidation states play an important role in these cycles. But recently, Webb *et al.* (1) suggested that during the oxidation of Mn(II) by bacteria, Mn(III) is formed as an intermediate. Large concentrations of Mn(III) would then accumulate and leak into the environment. On page 1955 of this issue, Trouwborst *et al.* (2) show that in regions of the Black Sea and Chesapeake Bay where the concentration of molecular oxygen is extremely low (suboxic regions), much of the dissolved manganese is indeed present as Mn(III). This discovery will alter the paradigm on which our understanding of manganese aqueous geochemistry is based.

Manganese acts as a catalyst that shapes chemical gradients in the oxygen-deficient zones found throughout the coastal ocean and marginal seas. It can perform this role because it exists in multiple oxidation states and is recycled rapidly between these states by bacterial processes. These transformations serve as an electron-transfer system for other chemical cycles. For example, oxidized manganese consumes upwelling hydrogen sulfide in the Black Sea, which contains the world's largest mass of anoxic water (3). The reduced manganese produced during oxidation then diffuses upward, where it consumes down-

welling oxygen (see the figure). This reaction resupplies the pool of oxidized manganese, thereby creating a catalytic cycle and a suboxic zone in which molecular oxygen and sulfide concentrations are very low.

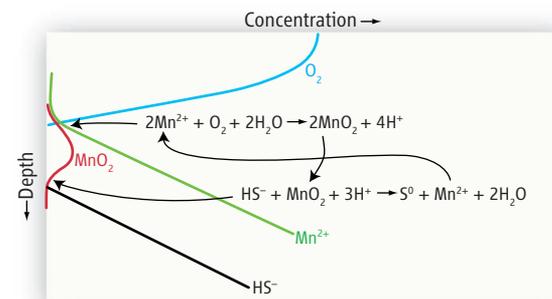
Our understanding of how manganese mediates chemistry in these suboxic areas has been based on the paradigm that there are two predominant forms of manganese in the environment: dissolved, reduced Mn(II) and particulate, oxidized MnO_x [where *x* is near 2 and most of the manganese is in the +4 oxidation state, although particulate Mn(III) also exists]. The vertical or lateral gradients in dissolved or particulate manganese set limits on the rates of reaction that can occur. These gradients,

Manganese in natural oxygen-poor waters can persist in a +3 oxidation state, a state previously seen only in the lab, necessitating a major revision of the current understanding of manganese aqueous geochemistry.

multiplied by the appropriate diffusion coefficient or, in the case of particulate MnO_x, the appropriate settling velocity, define the flux of electron donors and acceptors available for reaction.

Dissolved Mn(III) has been largely ignored, because it is both a very strong oxidant and reductant that is expected to rapidly disproportionate to Mn(II) and MnO₂. The Mn(III) detected by Trouwborst *et al.* persists because it is stabilized by dissolved ligands, perhaps pyrophosphate. The authors measured the Mn(III) concentration by using desferrioxamine-B (DEF-B), an Fe³⁺-binding ligand that is produced by bacteria. DEF-B also strongly binds Mn(III) and can out-compete natural ligands to sequester all of the dissolved Mn(III) in a filtered sample. The concentration of the DEF-B–Mn(III) complex can then be determined electrochemically.

In the Black Sea, water below a depth of about 100 m is permanently anoxic. The Chesapeake Bay is much shallower (~20 m), and anoxic zones form below ~15 m in the summer in response to nutrient-stimulated inputs of decaying phytoplankton. These two environments represent the extremes in anoxic conditions found in natural waters, one permanent and the other temporary. Dissolved Mn(III) was observed in both loca-



How manganese catalyzes chemical cycles in the Black Sea. In subsurface waters, Mn(II) reacts with oxygen, depleting its concentration and forming manganese oxide (MnO₂) particles. The particles sink into deeper waters, where they react with upwelling hydrogen sulfide, resulting in the regeneration of Mn(II). Trouwborst *et al.* report that much of the dissolved manganese in the suboxic zone is Mn(III), rather than Mn(II). This finding will require a reevaluation of how such cycles operate.

The author is at the Monterey Bay Aquarium Research Institute, Moss Landing, CA 95039, USA. E-mail: johnson@mbari.org