# ENTER THE OXIDES

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Thin films of oxygen-bearing compounds could have myriad practical applications, finds **Joerg Heber**, if a few problems can be overcome.

In late 1996, a young Bell Labs physicist named Harold Hwang told his lab director that he wanted to start a radical programme of research into oxides — the ubiquitous, oxygen-bearing compounds found in everything from granite and glass to ceramics, chalk and rust. Hwang was convinced that even the most familiar oxides might show surprising and useful properties if different ones could be stacked up into 'heterostructures': layer-cake-like arrangements in which each level is an ultrathin film just a few atoms thick.

The lab director, Horst Störmer, was slightly dubious — not about the potential, but about the practicality. "Have you ever grown a thin film in your life?" he asked. He knew all too well what Hwang was getting himself into. Störmer had made his own reputation by growing and studying thin films of a very different class of materials: semiconductors. Those films had shown some remarkable properties — including a phenomenon called the fractional quantum Hall effect, in which the free-roaming electrons inside a layer condense into a liquid-like state. That discovery would later earn Störmer a share of the 1998 Nobel Prize in Physics. But such phenomena appeared only if the layers were absolutely uniform in height, with a crystalline structure that was so pure and defect-free that electrons could race along without crashing into imperfections. It had taken Störmer and his colleagues at Bell Labs more than 10 years to invent and perfect the techniques for fabricating such films. And oxides, he knew, would be even more difficult to master. The compounds, which form 99% of Earth's outer crust, typically consist of a larger number of chemical elements than semiconductors, and have more complex crystal structures.

Still, Störmer told Hwang to go ahead, and the younger man did not disappoint. In time, Hwang and others doing research in the field succeeded in growing high-quality oxide thin films with the same atomic precision as semiconductors. And those films do indeed exhibit interesting phenomena. In 2004, for example, Hwang co-discovered the existence of a two-dimensional (2D) electron gas, in which electrons at the interface of two oxide thin films show an extremely high mobility[1] — an effect that is particularly striking because the two oxides involved are electrical insulators.

> "Have you ever grown a thin film in your life?"
> — Horst Störmer

Now oxide thin films are at roughly the same stage of development as semiconductor thin-films were in the early 1970s — a period when researchers were finally learning how to work with them well enough to fabricate devices such as the thin-film lasers, which would later have their commercial breakthrough in compact-disc players. For example, the 2D electron gas that Hwang and his colleagues discovered is being explored for use in a new type of fast transistor, a device that can amplify or switch electronic signals. Another use of oxide films could be as the basis for very high-density data-storage devices in which the magnetic information is controlled with electrical fields.

And that's just the beginning, says Hwang. "The great opportunity we have now is to design and grow artificial thin film structures down to the atomic scale — using multilayers of superconductors, ferromagnets, or even a combination — and to engineer systems that may one day be used for electronics or sensing applications."

## The power of oxygen

The rich array of phenomena found in oxides is largely due to the oxygen, says Yoshinori Tokura, a physicist from the University of Tokyo who has worked in this field for more than 20 years. Oxygen tends to pull electrons away from other atoms in the compound, says Tokura, resulting in strong electrical fields at the interatomic scale. These fields can give rise to substantial correlations in behaviour between the electrons of one atom and those of its neighbours. And the correlations in turn can lead to effects such as ferromagnetism, in which a material's electrons spontaneously line up and produce a magnetic field.

Nevertheless, for many years researchers tended to shy away from using oxides in advanced applications, because they are far more difficult to fabricate than metals and semiconductors. This situation changed in 1986 with the discovery of high-temperature superconductivity in certain oxides. The work kicked off an intense, worldwide focus on oxides that led to other discoveries. In 1993, for example, researchers encountered 'colossal magnetoresistance', in which a slight shift in the external magnetic field causes certain oxides to undergo an orders-of-magnitude change in electrical resistance[2].

**"You can imagine controlling the states at phase boundaries by making small modifications." — Stuart Parkin**

Another example is the 2D electron gas that Hwang and his co-worker Akira Ohtomo stumbled on when they were studying the interface between two insulators[3], lanthanum aluminate ($LaAlO_3$) and strontium titanate ($SrTiO_3$). "We started to fabricate very crude-looking transistors that should not have been conducting by themselves, but found they were already conducting," recalls Hwang, who is now at the University of Tokyo. "We started thinking, 'What is going on here?'"

They soon found that everything depended on the precise crystalline structure of the interface: only when the right atomic layers met would the internal electrical fields on each side push electrons towards the junction, so that they could form the electron gas. Otherwise, no charge layer develops[4]. The interface electrons also turned out to be surprisingly mobile. In fact, as discovered in 2007 by the groups of Jochen Mannhart from the University of Augsburg in Germany and Jean-Marc Triscone from the University of Geneva in Switzerland[5], these structures can become superconducting, meaning that the electrons can travel without resistance — albeit only below the very low temperature of about 200 millikelvin.

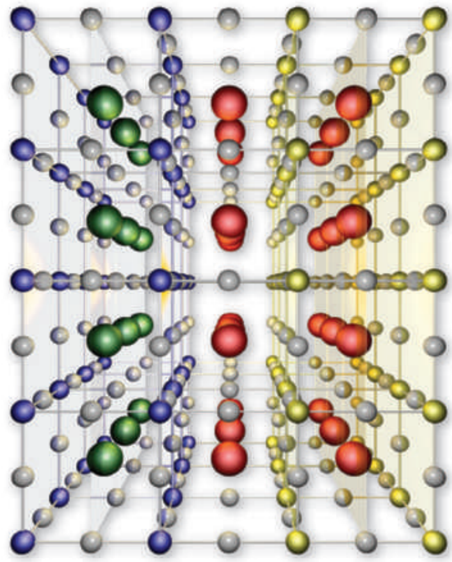
Researchers have also been studying potential applications that would exploit the thin-film interface. One way to do that would be to place a ferromagnetic oxide next to an insulating oxide that isn't ferromagnetic. If an external electrical field is applied, it causes an electrical polarization to develop at the interface. But the field also shifts the number of electrons in the ferromagnetic material, which changes the magnetic field. As a result, electrical polarization and magnetism are both controlled by the same electrical field, and are therefore cross-linked — a coupling of properties that defines multiferroic materials[6]. Such materials are of interest both as magnetic field sensors and as memory devices, in which information is written by electrical voltages and read by magnetic read head — with the benefit that no electrical current flows through the device, significantly reducing heat generation. Indeed, says Tokura, "the route via thin films offers the most straightforward fabrication method to realize a multiferroic material".

As well as looking at the coupling of two different properties at an oxide interface, researchers are looking for applications in which a single property, such as magnetic field[7,8] or electrical conductivity, is controllably turned on and off. "Controlling conductivity as a whole, rather than electrical current itself, in some sense is the most exciting area," says Stuart Parkin, a physicist at IBM's Almaden Research Center in San Jose, California. "Contrary to conventional transistors, the required current densities could be quite small, and this is what you want for applications."

Consider, for example, the superconducting 2D electron gas. Through the application of an electrical field it is easy to push electrons away from the interface, destroying the superconducting state and making it impossible for current to flow[9]. This is analogous to what happens in conventional transistors, in which the flow of electrons can likewise be switched on or off by an external electrical field. Conceivably, researchers could use local voltages to write complex patterns into this 2D electron gas. Where a voltage is applied, the interface would be insulating, and elsewhere it would be superconducting — potentially allowing the definition of entire electronic circuits. "It will be exciting to see the realization of small devices such as logic and memory circuits, or even small amplifiers," says Mannhart. Amplifiers written into the superconducting film could enable fast switching with extremely low noise levels and thus could detect and amplify weak electronic signals. Even the logic gates used for quantum information processing could be etched into the superconducting layer this way.

Stuart Parkin: excited by controlling conductivity.

IBM



J. MANNHART/GERMAN HAMMERL

The interface between lanthanum aluminate and strontium titanate.

## Just one small push

Unfortunately, the switching of superconductivity in the $LaAlO_3/SrTiO_3$ system occurs at temperatures far too low to be relevant for most applications. So one alternative is to look at the different phases many oxides show at various temperatures or pressures. Conductivity often changes dramatically at the transition from one phase to another. "If you go to phase boundaries, that's where you often get extremely large instabilities," says Parkin. "Then you can imagine controlling those states by small modifications." Such a small trigger impulse can push the system from one phase to the other. This is what happens in colossal magnetoresistance — a small external magnetic field induces huge variations in electrical resistance during a phase transition.

To realize high-quality oxide heterostructures for applications, researchers have had to overcome substantial obstacles to the development of suitable thin-film growth techniques. Oxides often have complex crystal structures, and films refuse to grow properly unless the right crystal layer is exposed on the top surface. Otherwise, the incoming atoms will not be able to stick to the proper chemical bonds. In 1994, this problem was identified and solved for $SrTiO_3$ by Masashi Kawasaki, a materials scientist then at the Tokyo Institute of Technology, now at Tohoku University in Japan, who developed a pre-growth treatment involving various acids that strip the crystal substrate down to the desired atomic layer[10]. With this advance, says Kawasaki, "people could finally grow complex oxides".

Unfortunately, it is still impossible to obtain oxide heterostructures anywhere near as large as those used in silicon technology. "Scaling up $SrTiO_3$ wafers to realistic sizes is out of the question," says Darrell Schlom, a materials scientist from Cornell University in Ithaca, New York. So, many researchers are now trying to integrate oxide heterostructures into silicon wafers. "The plan is not only to integrate oxides with silicon electronics, but even more importantly to take advantage of the processing infrastructure of silicon technology," says Schlom.

This is an arduous task, not least because there are substantial differences in crystal structure between most oxides and silicon. And worse, oxide thin films are grown by condensing a high-temperature vapour that includes oxygen — which can turn silicon into silicon dioxide at the slightest contact. This can be avoided only by carefully adjusting growth temperatures and supplying just the right amount of oxygen at precisely the right time. Still, progress has been made and the quality of oxide films on silicon has been improving steadily[11]. "Even advanced oxide films such as $LaAlO_3/SrTiO_3$ heterostructures have now been grown on silicon," says Mannhart.

## Not so crazy

Particularly promising in this regard is zinc oxide (ZnO), which is itself a semiconductor with a wide range of potential applications. "In ZnO, electrons can travel up to a micrometre without scattering," says Kawasaki. Kawasaki and his colleagues have even observed the quantum Hall effect in ZnO — a first for an oxide[12]. The presence of such quantum phenomena suggests the use of ZnO for 'spintronics' applications, which promise ultrahigh-density storage and ultrafast processing of information using the electron's tiny magnetic moment, or spin.

This isn't the end of the possible uses of oxides. "This might be a very crazy idea, but we are wondering whether these heterostructures can be applied to new types of solar cells," says Tokura. Solar cells are currently made of semiconductors, he explains, and function through the absorption of light with energies larger than a certain threshold known as the band gap. If the light has an energy much larger than this band gap, the excess is wasted into heat. But if electrons are confined, for example, in semiconductor nanoparticles, they begin to interact strongly with each other, which amplifies a process in which the excess energy is not wasted but rather used to excite multiple electrons. The entire process becomes more efficient.

In complex oxides, with their strong electron correlations, such an amplification could be very strong, says Tokura. Indeed, researchers already know of certain oxides in which light can excite so many electrons that the material becomes metallic. But that would still leave the problem of extracting these electrons from the oxide to put their energy to use. Even here, oxide thin-film structures may offer a solution. The layers are generally very thin, which means that electrons generated in one film could easily be extracted to an adjacent layer. "If we can make this work, it would be really exciting," says Kawasaki, who is investigating this idea with Tokura.

> "This might be a crazy idea, but maybe these heterostructures can be applied to solar cells."
> — Yoshinori Tokura

Parkin has an even more ambitious idea. He is looking for layered oxide systems in which superconductivity sets in at unprecedentedly high temperatures. "Room temperature is, of course, the ultimate goal," Parkin says. "In my mind this is entirely feasible." He thinks that such superconductivity might be found at interfaces similar to $LaAlO_3/SrTiO_3$, and might also involve the use of oxide compounds that do not normally exist in nature and can only be stabilized as thin films.

After more than 20 years of research into oxide thin films, efforts are bearing fruit. Progress is becoming fast-paced. Thin-film-growth technology has been adapted for oxide compounds, suitable substrates have been developed and complex heterostructures are being studied for new functionality. "Although what we have achieved as a community is still at the very early stages, we now know a lot more about the basic rules of engagement," says Hwang.

At the same time, Hwang sounds a note of caution. "Now the hard questions come," he says. Even seemingly mundane issues such as sample quality need to be tackled. "Oxide heterostructures are still loaded with defects. Understanding how to control these is key to taking oxide heterostructures from scientific curiosity — their current position in various scientific sandboxes — to real technologies," says Schlom.

Nevertheless, the achievements so far are strong testament to the fact that researchers in the field have begun to predict and control the phenomena that can exist in oxide heterostructures. Whether as new electronic compounds, as sensors, as memory devices, as solar cells or simply for their exciting science, oxide heterostructures are here to stay. The journey has merely begun. ■

**Joerg Heber is a senior editor of *Nature Materials*.**

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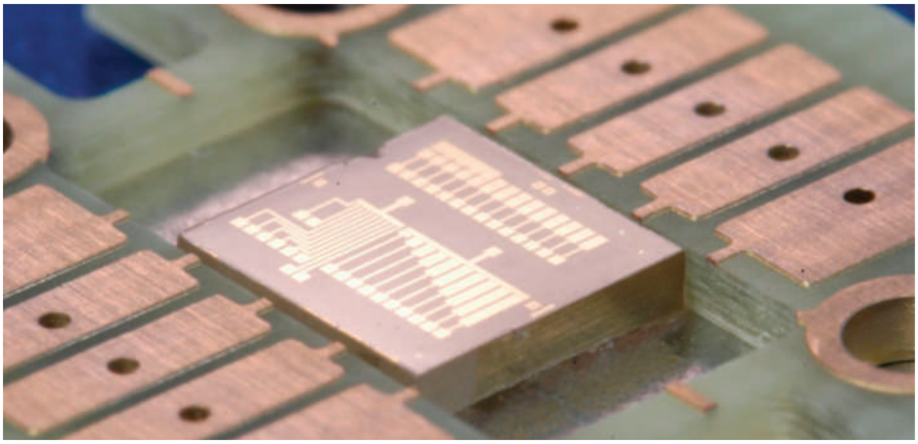
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Electronic circuits made from thin oxide layers are only starting to tap the potential of oxides.