

## OXIDE INTERFACES

# Instrumental insights

A powerful new set of tools combining artificial synthesis and *in situ* characterization of correlated oxides unites the processes of materials discovery and understanding, and reveals the origin of a dimensionality-induced metal-insulator transition.

James M. Rondinelli and Steven J. May

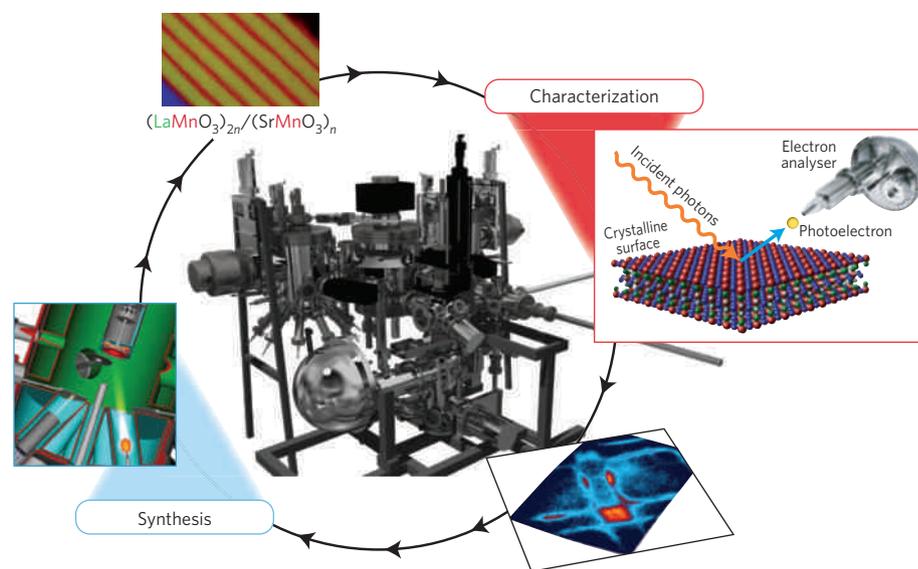
Sir Arthur Stanley Eddington said, “We used to think that if we knew one, we knew two, because one and one are two. We are finding that we must learn a great deal more about ‘and’.” Combining multiple materials with desirable properties is an oft-pursued route to achieve artificial composite materials with functionalities superior to any of their parts. When the dimensions at which the constituents are interleaved in the composite reach that of the wavelength of the electrons travelling within the material, unanticipated behaviour can occur<sup>1</sup>. Considerable efforts over the past decade have focused on how to stabilize those new states by forming superlattices with nanometre- to subnanometre-scale periodicities in a class of materials known as complex transition metal oxides<sup>2</sup>. These oxides contain correlated electrons, which means that every electron simultaneously is influenced by all other electrons in the system, owing to the open electronic shell configuration of the transition metal cations. This aspect makes predicting their properties a challenge. The uncertain meaning of ‘and’ in two-component atomic-scale oxide superlattices further compounds the problem of rational control of interface-derived phases, because simple sum rules rarely apply.

To surmount such challenges requires advanced instruments — atomic-level structure and electronic property interrelationships are essential in navigating the vast phase space of chemistries, strains and periodicities available to artificial oxide superlattices. Writing in *Nature Materials*, Eric Monkman and colleagues<sup>3</sup> demonstrate the powerful insights that can be gained from an integrated materials discovery instrument (Fig. 1) that combines atomic-level control over oxide superlattice growth with the capability to explore the interfacial electronic structure without ever breaching vacuum. The unprecedented capabilities of the consolidated tool enable Monkman and colleagues to reveal how the metal–insulator transition<sup>4</sup> in a systematic series of manganite superlattices

with different interleaving sequences arises from strong quantum many-body interactions induced by the dimensionality of the superlattice.

The unique instrument used by Monkman *et al.* for the growth and study of correlated oxide superlattices consists of molecular beam epitaxy (MBE) and angle-resolved photoemission spectroscopy (ARPES), respectively. The former technique provides the ability to create oxide superlattices with subnanometre periodicities and atomically sharp interfaces. The latter enables the electronic band structure and interactions of a system to be pieced together. ARPES relies on a momentum conservation book-keeping exercise, which exploits Einstein’s

photoelectric effect underpinning the quantum nature of all matter: electrons emitted by a material that are excited by light will occur only over certain energies. Both techniques have made seminal contributions to understanding and engineering multiferroicity<sup>5</sup> and high-temperature superconductivity<sup>6</sup>; however, their combined application is rare in perovskite-based superlattices — both techniques require sophisticated instrumentation and ultrahigh vacuum operation, and are typically performed in separate laboratories. Removing an oxide superlattice from the growth chamber, exposing it to the atmosphere and moving it to the ARPES system contaminates the surface of the sample, which can be



**Figure 1** | Innovation in the oxide superlattice design cycle is brought full circle through a concerted oxide superlattice growth and characterization approach. The monolayer precision of oxide MBE (bottom left) for the synthesis of atomic-scale heterostructures (top left) is enhanced by the capability of ARPES (top right) to probe the intrinsic electronic structure arising at interfaces providing access to fundamental insights into the *k*-space electronic band structure of complex materials (bottom right). The process provides an avenue to identify the critical structure–property relationships needed for engineering new phases. By varying the atomic structure and probing the electronic response, Monkman and colleagues iterated the materials discovery-and-understanding cycle to glean the mechanism for an unusual metal–insulator transition in a correlated oxide superlattice. Images courtesy of D. Schlom, D. Muller, J. Mundy, E. Monkman, K. Shen (Cornell University) and A. Schmehl (Universität Augsburg).

a significant impediment to meaningful electronic structure studies. Although this complication is usually circumvented in other materials by cleaving the sample in vacuum, the dense perovskite structure makes cleaving bulk oxides, let alone superlattices, exceedingly difficult.

Monkman *et al.* leverage the capabilities of both techniques in their integrated MBE–ARPES approach to investigate the interfacial electronic structure in  $(\text{LaMnO}_3)_{2n}/(\text{SrMnO}_3)_n$  superlattices as a function of dimensionality,  $n$ . The digital superlattice samples are compositionally equivalent to bulk  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ , a canonical metallic ferromagnetic oxide<sup>7</sup>. However, the ordered atomic layers of the superlattices display physical properties that differ dramatically from the random alloy. Previously, electronic transport measurements<sup>4</sup> demonstrated a metal–insulator transition as a function of  $n$ , with insulating behaviour observed when  $n$  is larger than three. Although these earlier resistivity measurements<sup>4,8</sup> already indicated that this insulating state differs from that found in either bulk  $\text{LaMnO}_3$  or  $\text{SrMnO}_3$ , the electronic structure measurements obtained by ARPES now reveal the origin of the metal–insulator transition. Monkman and colleagues find that as the distance between the  $\text{LaMnO}_3/\text{SrMnO}_3$  interfaces increases with larger  $n$ ,

the low-energy electronic structure near the Fermi level that originates from the interfaces between the two oxides becomes more two-dimensional. Simultaneously, a substantial redistribution of energy states occurs as  $n$  goes from 2 to 3: the states near the Fermi level are largely suppressed and a broad incoherent feature grows below the Fermi energy suggestive of enhanced many-body interactions. The result being that for  $n = 3$  the superlattice has a Fermi surface that vanishes despite the metallic band structure persisting. In other words, a pseudogap state is induced by the dimensionality enhanced correlations.

The present work provides unique insight into the metal–insulator transition in manganite superlattices, but more broadly, it illustrates the critical role that an integrated synthesis–ARPES approach (Fig. 1) can play in revealing interface-specific electronic structures. Combined with recent advances in atomically resolved electron spectroscopies<sup>9</sup> and synchrotron-based photoemission spectroscopy<sup>10,11</sup>, the experimental capabilities that are now available in the discovery and understanding of novel interfacial electronic phases have expanded the materials explorers' arsenal. The ability to measure the intrinsic electronic structure is essential to building electronic–atomic structure property relationships necessary

to engineer the phases of complex oxides superlattices with correlated electrons. We anticipate rapid actions will be taken in laboratories throughout the world to replicate the unique capabilities of the techniques applied here. The rate at which new electronic phases are discovered will accelerate and the newly acquired data will provide important tests for the theoretical understanding of correlation effects in atomic-scale oxide superlattices. The integration of oxide MBE and ARPES represents a great stride forward in explaining Sir Eddington's 'and'.

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## METAL/MOLECULE INTERFACES

# Dispersion forces unveiled

The role of dispersion forces in molecule–metal bonding has often been underestimated or ignored. Two groups now report independent single-molecule experiments that illustrate and quantify the effect of such interactions on bonding strength.

Jan van Ruitenbeek

Research in molecular electronics traditionally relies on cartoons to interpret and communicate experimental results. Typical experiments are aimed at applying two electrical contacts to individual organic molecules and at characterizing electronic transport through the molecular bridges formed. The fact that the molecules are ten times smaller than any structure that can currently be nanofabricated implies that some form of self-assembly needs to be used in the process. This strategy seems to be very effective in that it has

led to a lot of successful experiments, but the inherent difficulty remains that the structures formed can neither be controlled nor imaged. Almost without exception, experimental papers therefore contain some artistic representation of the molecular structure, the bonding configuration and the atomic-scale metal electrodes. Usually these pictures show the molecule suspended straight, bound through its anchoring groups to nicely ordered pyramidal gold electrode tips. Only recently have deviations from this ideal geometry been appreciated<sup>1,2</sup>.

Writing in *Nature Materials*, Sriharsha Aradhya and colleagues at Columbia University and Brookhaven National Laboratory, USA, now describe experiments and calculations that call for another revision of our simplified model of molecular junctions<sup>3</sup>. The researchers study two types of molecules between gold electrodes: bipyridine and a longer variant based on the same bonding concept. Their experiment is relatively simple: it makes use of an atomic force microscope with a conductive tip that is periodically driven in and out of contact with a molecule–