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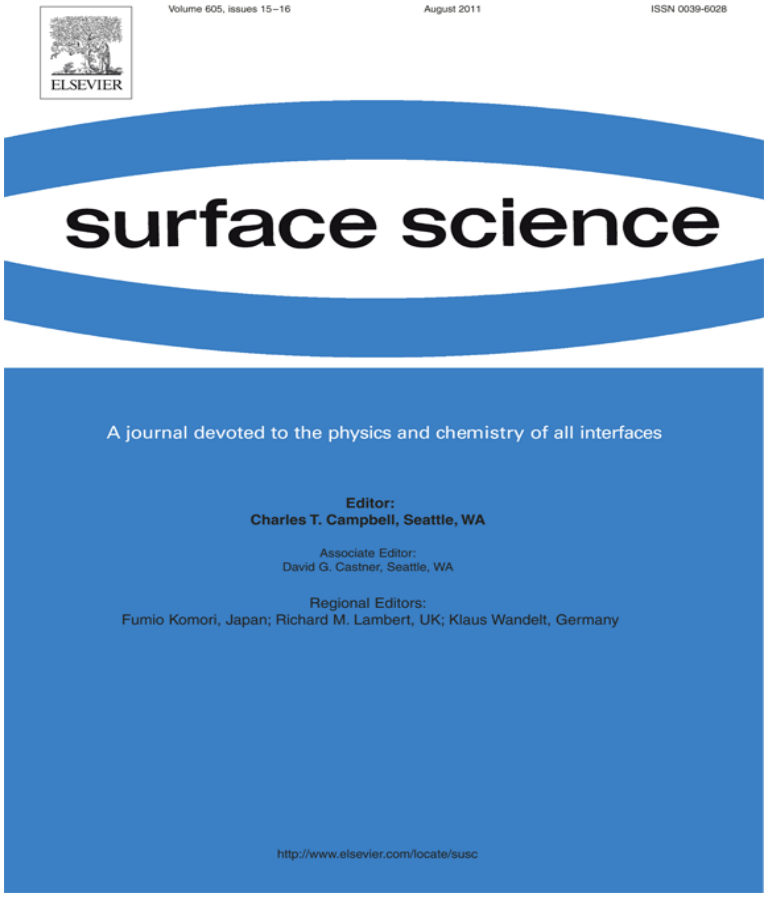

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ABSTRACT

This perspective briefly reviews the recent developments in the study of exotic phenomena at complex oxide heterointerfaces – with special attention to results published by L. Qiao, et al. in this edition – on the $LaAlO_3/SrTiO_3$ heterointerface. The fundamental mechanisms of the observed phenomena are discussed and the results of the current study are placed in context. The importance of rigorous materials characterization and insight into fundamental limitations of modern synthesis techniques are probed.

For nearly 8 years now, researchers working on complex oxide heterointerfaces have been doggedly pursuing one of the most exciting discoveries in this field of late – the development of unexpected phenomena at the interface between seemingly unremarkable insulating oxides. Since the seminal discovery of a conducting interface between the band insulators $LaAlO_3$ and $SrTiO_3$ in 2004 [1], researchers have made a number of exciting findings related to these interfaces including the observation of magnetic ground states [2], superconductivity [3], built-in polarizations [4], and more. Researchers have even incorporated these interfaces on silicon wafers [5] and have demonstrated electric-field writing of insulating and conducting states at the nanometer-scale [6]. Among the more pressing challenges facing researchers in this field is explaining the fundamental origin of these observations – are these exotic phenomena the result of intrinsic electronic effects or do they arise due to defects in the samples? The work of L. Qiao et al. in this issue [7] provides important insight into this fundamental question and sheds light on the complexity of this and many other oxide systems. Through careful study of the chemistry and electronic structure of the surfaces and interfaces of $LaAlO_3/SrTiO_3$ heterostructures, the authors have demonstrated how interdiffusion between materials can dramatically impact the properties at these interfaces.

Metallic conductivity (and a slew of other phenomena) have been observed when $LaAlO_3$ thin films (in excess of 4 unit cells) are grown on TiO_2-terminated $SrTiO_3$ (001) single-crystal substrates. Merely switching the top-layer of the $SrTiO_3$ to be SrO-terminated, however, results in insulating interfaces. Although the subject of great debate, the origin of this interfacial conductivity has been suggested to be electronic reconstruction [8] in which electrons are transferred to the Ti^{4+} in the TiO_2-layer of the $SrTiO_3$ thereby reducing it towards Ti^{3+}. This arises from the fact that the $LaAlO_3$ consists of alternating planes of LaO^+ and AlO_2^- which builds up an electrostatic potential thereby driving motion of the electrons to occupy Ti 3*d* states that form 2-dimensional bands parallel to the interface, prompting some to refer to this as a 2-dimensional electron liquid [9]. Alternative models have also been proposed – including conductivity derived from oxygen vacancies that resulted from particular growth conditions [2, 10]. When it was observed that conductivity was possible even when materials were grown at high growth pressures, however, attention shifted to the idea of how intermixing of cations across these interfaces and the formation of n-type conducting La-doped $SrTiO_3$ could play a role in the exotic phenomena [11]. The work of Qiao et al. in this edition takes this analysis one step further. Through a combination of innovative synthesis techniques and detailed characterization – including angle-resolved X-ray photoelectron spectroscopy (XPS) – the team has determined the extent of cation intermixing in films grown via pulsed laser deposition, how this intermixing is influenced by the (non)stoichiometry of the growing layers, and what the implications are for the electronic structure.

Among the important findings of this and prior work [12] by the authors is that they have brought to light the challenges associated with synthesizing complex oxide materials with different techniques. The advent of modern thin film growth techniques – especially the incorporation of reflection high-energy electron diffraction (RHEED) into the oxide growth process – has spawned unprecedented advances

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in materials synthesis and the ability to control materials down to the atomic-level. As the field of complex oxide thin film growth has developed over the last decade we have seen expanded use of molecular beam epitaxy, pulsed laser deposition, sputtering, metal-organic chemical deposition, and many more techniques for the production of ultra-thin films and multi-layers where interfacial properties and interactions have been shown to be prevalent. Focusing on pulsed laser deposition, the technique used by Qiao et al. in this edition, the field has undergone dramatic changes since the wide-spread adoption of this technique in the 1990s in the expectations and requirements for the growth process and, in turn, the manner in which growth is done on a daily basis. The field now regularly pushes the limits of this technique – in essence asking it to provide sub-unit cell control – and with this comes added complexity. The work of Qiao et al. demonstrates the care and expertise that is required to fully understand the materials that one synthesizes in the modern age. This knowledge base defines the fundamental assumptions that underlie our thinking about these systems and helps place limitations to the conclusions that can be made about these sometimes exotic results. What this work demonstrates to the greater field is the need to revisit some fundamental assumptions that are made about various growth techniques in terms of important issues such as stoichiometry and to develop better understandings of how growth temperatures, adatom energies, materials chemistry, and other factors impact films, surfaces, and interfaces. By incorporating an enhanced characterization regime into the lexicon of common analyzes and leveraging advances in related fields of study and characterization (i.e., synchrotron, electron microscopy, scanning probe, etc.) we will increasingly be given access to the fundamental details and nature of materials at interfaces that will provide us with the insight necessary to fully understand the exciting phenomena we observe.

Prior experimental [4] and theoretical [13,14], studies have suggested the presence of built-in polarizations or electric fields at these interfaces which help explain the origin of the exotic phenomena. The current work by Qiao et al. suggests, as have others, [15,16] that these effects are small and further add that they are consistently small regardless of the La:Al ratio in the $LaAlO_3$ layer. This is an important observation as it suggests that for films grown by pulsed laser deposition under these conditions that the band offsets, band bending, and electric fields appear to be directly driven by the extent of cation intermixing as opposed to the composition in the film itself. This conclusion is further investigated by density functional theory which also suggests that mixed-interfaces could drive the reduction in the band bending observed in this system. This provides an experimental and theoretical framework for continued research into the fundamental nature of these phenomena.

What becomes clear from recapping the developments in this field and placing the current work of Qiao et al. in context, is that these are complex systems. One cannot argue that researchers around the globe have observed similar results in their films and some have even begun to transfer the phenomena into device structures. But despite these advances the fundamental understanding of these systems remains somewhat in question. It is clear that different growth processes and conditions produce different stoichiometry, different interfacial intermixing, and, ultimately, different properties at these interfaces. It should be noted that this field has been developing at an incredible rate since the first observation of these effects in 2004 and with continued advances in synthesis, characterization, and modeling researchers will likely soon make sense of the wide array of data that has been collected. What the work of Qiao et al. and many others in the field demonstrates is that as we investigate our materials closer and closer we may first be met with new challenges, but through rigorous scientific investigation we will soon be given the insight to fully understand even the most complex systems. It is refreshing to see researchers around the world pooling their materials, findings, and ideas to advance the field and working together to expose the bright-lights of scientific discourse to the details of their experiments. Such efforts and attention to detail will, in the end, provide us the insight and understanding we ultimately desire.

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