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Surface Science Prospectives

Understanding the mechanism of conductivity at the $LaAlO_3/SrTiO_3(001)$ interface

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ABSTRACT

The observation of conductivity at (001)-oriented interfaces of the 2 band insulators $LaAlO_3$ and $SrTiO_3$ is both fascinating and potentially useful for next-generation electronics. The paradigm commonly used to explain this phenomenon is an electronic reconstruction resulting from the instability created by forming an interface of polar and nonpolar perovskites, leading to the formation of a two-dimensional electron gas. This explanation has typically been conceptualized within the framework of an atomically abrupt interface. However, a significant and growing body of data now exists which reveals that the interface is not abrupt, and that all four cations diffuse across the interface. Yet, the potential roles of the resulting defects and dopants in alleviating the polar catastrophe and promoting conductivity are rarely considered. The purpose of this prospective is to take an overview of the field from outside the reigning paradigm and consider ways in which dopants and defects might affect the electronic structure.

1. Context

The role of oxide materials in electronics and photonics has shifted from passive, in which oxides are used as "support" materials such as gate insulators, to active, in which the oxide is at the heart of the device. Examples include the use of indium tin oxide in liquid crystal displays, flat panel displays, plasma displays, organic light-emitting diodes and solar cells, as well as zinc oxide in thin-film transistors and light-emitting diodes. At the level of fundamental electronic materials research, oxides containing transition metal cations are of particular interest because electron correlation effects accompanying cations with partially occupied *d* orbitals exhibit physical phenomena not found in conventional semiconductors. These phenomena can in principle be used to introduce new functionality at the device level, and exploration of such phenomena is a very active field in materials physics [1].

Interfaces are integral to this endeavor because it is here that the diversity of physical properties exhibited by oxides can most readily be exploited. A recent example is the achievement of very high electron mobility (up to 180,000 $cm^2\,V^{-1}\,s^{-1}$) at very low temperature (0.06 K) and the observation of the fractional quantum Hall effect at $Mg_xZn_{1-x}O/ZnO$ heterojunctions grown by molecular beam epitaxy (MBE) [2]. Here electrons originating from Zn interstitial and/or oxygen vacancy donors accompanying growth at low oxygen partial pressure are confined in a two-dimensional electron gas (2DEG) structure created by band bending and the conduction band discontinuity. The physics of this II–VI-based 2DEG structure is similar to that of III–V based 2DEGs studied previously [3].

Another example of intense current interest is the observation of conductivity at the interface of 2 band insulators — $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) — when LAO is grown on a TiO_2-terminated STO(001) substrate [4–6]. The effect is in general not observed when the LAO is deposited on SrO-terminated STO. Unlike $Mg_xZn_{1-x}O/ZnO$, for which the 2DEG originates from a well understood cause, at least two distinct physical effects could be causing conductivity at the LAO/STO heterojunction. One is an electronic reconstruction resulting from the formation of an abrupt interface between polar LAO(001) and nonpolar STO(001) [7–9]. Here the diverging electrostatic potential associated with this structure increases with LAO film thickness until the LAO valence band maximum (VBM) crosses the Fermi level of the STO and charge tunnels from the LAO surface to the interface. The transferred charge removes the surface and interface dipoles as well as the diverging potential and stabilizes the system. The amount of transferred charge required to mitigate the 'polar catastrophe' in this model amounts to 0.5 electrons or holes per unit cell (u.c.), or ~$3.3\times10^{14}\,e^-$ or h^+ per cm^2. Electron transfer is required when LAO is grown on TiO_2-terminated STO (resulting in the descriptor 'n-type interface'), and hole transfer is required for growth on SrO-terminated STO (the 'p-type interface').

Another candidate cause for alleviation of the polar catastrophe and formation of a conductive layer is doping and/or defect formation in the underlying STO. Cation exchange can eliminate the interface

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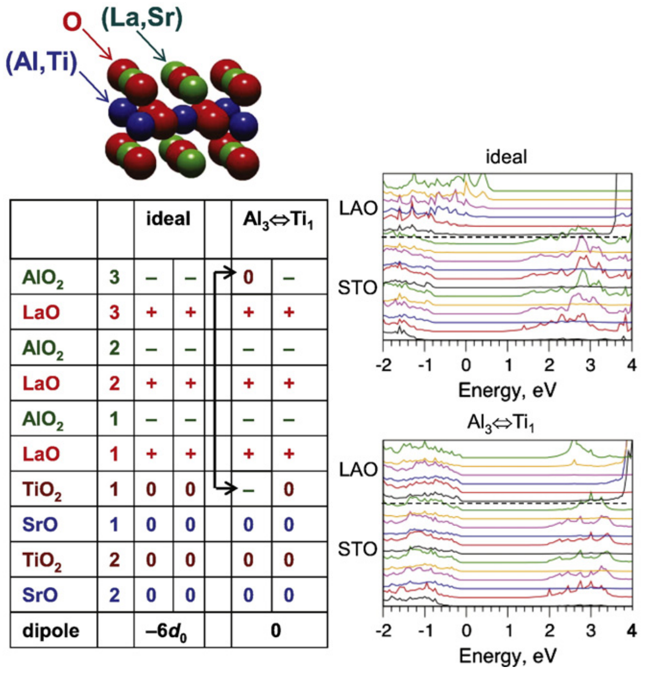
dipole, as illustrated in Fig. 1. Here exchange of a Ti(IV) cation from the interface layer of STO with an Al(III) cation from the surface layer of LAO eliminates the dipole. The densities of states calculated by density functional theory (DFT) and projected onto each layer in these two configurations for a 3 u.c LAO/6 u.c. STO(001) √2a × √2a supercell are shown to the right [10]. Notice that the electric fields present near the idealized abrupt interface are largely removed by this particular intermixed configuration. Many other intermixed configurations also alleviate the polar catastrophe. A set of calculations based on classical potentials for over 65,000 intermixed configurations revealed that ~49% of these are energetically more stable than the idealized abrupt interface. The dipole is zero in ~8% of all configurations, and among the most stable 10% of these 65,000, 29% have no dipole [10]. Moreover, depending on which cations undergo site exchange and their relative proportions, intermixing can also promote conductivity via doping. The large band gap of LAO (>5.5 eV) makes doping and defect creation leading to conductivity in LAO unlikely. However, both oxygen vacancies (O_v) and La at Sr sites (La_{Sr}) are *known* donors in STO (band gap = 3.2 eV). It is by now more generally accepted that intermixing occurs to some extent at this interface, and that the interface is not as atomically perfect as is often assumed, particularly in theory papers [11,12]. Indeed, to the best of the author's knowledge, every group which has done the measurements required to detect intermixing has found it, and an atomically abrupt LAO/STO interface has not been demonstrated in material grown by any method. Moreover, many papers focus on novel transport properties and interpret data in light of an (assumed) abrupt and atomically perfect interface, but do not verify that the interface is as it is assumed to be.

2. Defects at the interface

The vast majority of groups who observe conductivity use pulsed laser deposition (PLD) and a rather low O_2 partial pressure to deposit LAO. Moreover, many groups anneal in a higher O_2 pressure after growth to eliminate O_v, if indeed such defects form during growth. It is commonly assumed that this step is adequate to eliminate O_v altogether, in part because the sheet carrier concentrations measured in many laboratories (low 10^{13} cm^{-2} range) are below what was observed early on when inadequately oxidizing conditions were used and O_v creation was strongly suspected to occur [7,13]. The importance of employing adequately oxidizing growth and processing conditions cannot be overstated in light of a recent secondary ion mass spectrometry (SIMS) investigation which conclusively shows that LAO films grown on ^{18}O-labeled STO can extract O from the substrate when grown under low oxygen partial pressure, and the extent of O migration depends on the substrate temperature [14].



		ideal		$Al_3 \Leftrightarrow Ti_1$	
AlO_2	3	–	–	0	–
LaO	3	+	+	+	+
AlO_2	2	–	–	–	–
LaO	2	+	+	+	+
AlO_2	1	–	–	–	–
LaO	1	+	+	+	+
TiO_2	1	0	0	–	0
SrO	1	0	0	0	0
TiO_2	2	0	0	0	0
SrO	2	0	0	0	0
dipole		$-6d_0$		0	

Fig. 1. Illustration of how a single Al-Ti exchange in the LAO/STO system can eliminate the dipole ($-6d_o$, where d_o is the dipole moment per u.c.). The layer-projected densities of states for the abrupt and mixed configurations in a 3 u.c. LAO / 6 u.c. STO(001) supercell with a lateral size of √2a x√2a are shown to the right. Taken from ref. [10].

In order for cation intermixing to result in n-type conductivity in STO, the relative amounts of indiffused La and Al atoms, and which cation site the Al occupies, are important. When La substitutes for Sr in STO (La_{Sr}), it subsequently exhibits a +3 formal charge, and one additional electron per La atom is added to the conduction band (CB). Likewise, an Al atom substituting for Ti (Al_{Ti}) and subsequently exhibiting a charge of +3 would result in a net reduction of one in the electron count, giving rise (in principle) to an itinerant hole or, more likely, a deep-level electron trap [15]. Alternatively, Al could substitute for Sr (Al_{Sr}), resulting in donor formation. DFT calculations predict that Al preferentially occupies Ti sites in STO under more oxygen rich conditions, resulting in hole formation [16]. These holes would exactly compensate itinerant electrons from La_{Sr} donors if Al_{Ti} and La_{Sr} were present in equal concentrations. However, the calculations in Ref. [16] predict that Al will be amphoteric (forming both Al_{Ti} and Al_{Sr}) under more oxygen poor conditions, resulting in Al self compensation. In this case, La would dope the STO n-type whether or not Al_{Ti} and La_{Sr} were present in equal proportions.

Analysis of surface X-ray scattering data is consistent with more extensive intermixing at the A sites (Sr and La) than at the B sites (Al and Ti), suggesting that the observed conductivity could be caused by La doping [17]. We corroborate this finding with some of the results obtained in a multi-technique investigation of interface composition at conductive LAO/STO heterojunctions grown by off-axis PLD at the Universities of Tokyo and Augsburg [10]. As an example, we show in Fig. 2 La 4d and Al 2p X-ray photoelectron spectra (XPS) for 4 and 25 u.c. films from both laboratories measured at normal emission (take-off angle = 90°), along with schematic diagrams to illustrate the significance of the results. Inasmuch as the thickness of the 25 u.c. films (~9.5 nm) exceeds the XPS probe depth (~3λ, where λ is the electron attenuation length), which is ~5 nm when AlKα X-rays are used, the detected La 4d and Al 2p photoelectrons originate within the top half of the film, well away from the interface. However, since the thickness of the 4 u.c. films (~1.5 nm) is substantially less than the probe depth, La 4d and Al 2p photoelectrons in these spectra probe not only the entire film, but also the interfacial region and the top few nm of the STO. We can thus test for preferential La diffusion into the STO by comparing the La 4d/Al 2p peak area ratios for the 4 and 25 u.c. films; this ratio is independent of thickness for uniform composition in all layers (i.e. no preferential indiffusion near the interface). Doing so reveals an interesting result. In the case of the Tokyo films (Fig. 2a), which were not annealed in O_2 after growth, the La 4d/Al 2p peak area ratio is 10.4(1) and 10.3(1) for the 25 and 4 u.c. films, respectively. These two numbers are within experimental error, and thus preferential La indiffusion is not detected. However, in the case of the Augsburg films (Fig. 2b), which were annealed after growth in O_2, this ratio is 10.5(1) and 9.9(1) for the 25 and 4 u.c. films, respectively, giving clear evidence for preferential La indiffusion in this 4 u.c. film.

Moreover, scanning transmission electron microscopy/electron energy loss spectroscopy (STEM/EELS) results show that La diffuses further into the STO than Al in a 25 u.c. film from Augsburg, as seen in Fig. 3. After taking beam broadening into account, the extent of La diffusion (4 u.c. into the STO) exceeds that of Al (2 u.c. into the STO) by an amount which exceeds experimental uncertainty. Additionally, both Rutherford backscattering spectrometry (RBS) and medium