Structural Basis for the Conducting Interface between LaAlO$_3$ and SrTiO$_3$

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The complete atomic structure of a five-monolayer film of LaAlO$_3$ on SrTiO$_3$ has been determined for the first time by surface x-ray diffraction in conjunction with the coherent Bragg rod analysis phase-retrieval method and further structural refinement. Cationic mixing at the interface results in dilatory distortions and the formation of metallic La$_{1-x}$Sr$_x$TiO$_3$. By invoking electrostatic potential minimization, the ratio of Ti$^{4+}$/Ti$^{3+}$ across the interface was determined, from which the lattice dilation could be quantitatively explained using ionic radii considerations. The correctness of this model is supported by density functional theory calculations. Thus, the formation of a quasi-two-dimensional electron gas in this system is explained, based on structural considerations.

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The physics responsible for the formation of a high-mobility quasi-two-dimensional electron gas (Q2-DEG) at the interface of two insulators has been the subject of considerable research and controversy since its discovery in the LaAlO$_3$/SrTiO$_3$ (LAO/STO) interface [1]. Although it is generally agreed that this phenomenon is induced by subtle structural changes at the interface, the mechanisms are still hotly contested. In particular, doping with electrons or oxygen vacancies [2–6], interdiffusion [5,7], and the influence of lattice distortions [8–12] have been proposed as possible explanations. A common conclusion is, however, that a comprehensive description of the interface with sub-Angstrom resolution is essential if the responsible mechanisms are to be elucidated. In this Letter, we provide such a structural description and show how it leads to the formation of a Q2-DEG.

The two band insulators STO and LAO have the perovskite structure consisting of a stacking of SrO and TiO$_2$, and LaO and AIO$_2$ atomic layers (ALs), respectively. In the ionic limit, each AL of STO consists of neutral layers, while the nominal charges of LaO and AIO$_2$ in LAO are +1 and −1, respectively. Ohtomo and Hwang demonstrated that the terminations at the interface of nonpolar STO with polar LAO play a crucial role in the formation of a Q2-DEG [1]—the SrO-AIO$_2$ interface is insulating, while the TiO$_2$-LaO interface produces a Q2-DEG.

It was recently shown that a Q2-DEG only occurs for LAO films with thicknesses above 3 monolayers (MLs, whereby a monolayer has a unit cell thickness and consists of two ALs) [4]. This indicates that surface structural effects penetrate to this depth and/or the interface extends over several MLs. It is therefore necessary to solve the structure of the entire film/interface/substrate to fully understand the system. With the high brightness of third-generation synchrotron sources and recent developments in x-ray detector technology [13], surface x-ray diffraction (SRXD) in conjunction with phase-retrieval methods [14] is an ideal tool to achieve this goal [15].

We grew a nominally five-ML LAO thin film by pulsed laser deposition (PLD) [16] under essentially identical conditions to those described in the majority of the literature [1,5,7,11]. The STO(001) substrate was preetched and annealed [17] to produce a TiO$_2$-terminated surface. The nanosecond laser radiation from the fourth harmonic of a Nd:YAG laser (266 nm) had a fluence on the polycrystalline LAO target of 1 J cm$^{-2}$ and a repetition rate of 10 Hz. The oxygen background pressure was $5 \times 10^{-4}$ Pa and the substrate temperature 770 °C. Reflection high-energy electron diffraction images after the deposition showed clear two-dimensional growth, including prominent Kikuchi lines, indicative of high crystal quality. Four-point resistivity measurements of the films as a function of temperature showed them to be metallic, with resistivities that were essentially the same as previously reported [1].

The atomic structure of the LAO/STO sample was investigated at the Materials Science beam line, Swiss Light Source, Paul Scherrer Institut, by SRXD using 16 keV (0.775 Å) synchrotron radiation. 14 inequivalent crystal truncation rods (2400 independent structure factors), plus 9 further symmetry equivalent rods, were recorded up to a scattering vector $Q = 11.3$ Å$^{-1}$ using the PILATUS 100k photon-counting pixel detector [13] and subsequently analyzed using the coherent Bragg rod analysis (COBRA) method [14].

Representative data and the structural information extracted from them using COBRA are shown in Fig. 1. The most important pieces of information are (1) that the LAO-STO interface is not abrupt, but consists of a graded intermixing of Sr with La and Ti with Al over approximately 3 MLs [18], and (2) the lattice constant normal to the surface increases in STO as the nominal interface is approached, after which it drops toward the surface of the film.
The atomic coordinates obtained from COBRA were then used as a starting model for further structural refinement, using the grid-search $\chi^2$-minimization program FIT [19]. It is stressed that, using bulk starting coordinates, FIT failed to converge to a physically reasonable model of this complex system containing 90 fit parameters. Convergence was achieved only by using the parameters extracted by COBRA as the starting point for refinement. The resulting model exhibited an $R$ factor of 8\% and contained no physically unreasonable atomic positions or Debye-Waller factors. Importantly, we were able to further refine the ratios of Sr/La and Ti/Al, and also independently extract their $z$ positions. The transition from more Sr to more La in the interface region occurs not, as might be assumed, 0.5 ML (i.e., 1 AL) deeper into the structure than that for the transition from more Ti to more Al, but 1.5 MLs (3 ALs) deeper [Fig. 2(a)]. This means that MLs 6 to 8 contain significant fractions of LaTiO$_3$ (LTO) [18]. The film surface has a roughness of approximately 2 MLs, probably due to incomplete monolayer coverage, nonperfect layer-for-layer film growth, and/or roughening due to its polar nature [20].

A nonabrupt interface was also seen by Nakagawa et al. using electron energy-loss spectroscopy with scanning transmission electron microscopy, which they attributed to a reduction of the electrostatic energy of the delocalized Ti valence electrons by a compensating dipole emerging from the exchange of Sr and La cations across the interface [7,11]. We can determine in a similar manner how the Ti valence state varies across the interface by requiring that the ratio of Ti$^{4+}$ to Ti$^{3+}$ minimizes the electric field across each ML and that the electric potential be zero at the film boundaries. The result is shown in Fig. 3(a). The dilation in the neighborhood of the interface can therefore be explained by one or both of the following aspects of an interface containing Ti$^{3+}$.

First, the ionic radius of Ti$^{3+}$ is 0.065 Å larger than that for Ti$^{4+}$, which would produce relaxed pseudocubic unit cells in LTO and SrTi$^{3+}$O$_3$ (ST3O) of $a = 3.97$ Å and 4.04 Å, respectively, both larger than the unit cell size of STO of $a_0 = 3.905$ Å [21]. Heteroepitaxial in-plane compressive strain of the film will enhance this effect still further—if we start with the simple assumption that the volume of a unit cell is preserved upon heteroepitaxial compression (i.e., a Poisson ratio of 1/2), it will be dilated in the $z$ direction by about 3$\Delta a$, where $\Delta a$ is the difference in size between the relaxed unit cell size and $a_0$. Using these values and a bulk LAO pseudocubic lattice constant of 3.79 Å, we plot in Fig. 3(b) the cumulative dilation in the $z$ direction, weighted for the different chemical components (see also Table I). The similarity of these data to the experimentally determined values of Fig. 2(b) is striking.
by a structure in which a single ML of LTO separates the STO substrate from the LAO film. We have performed density functional theory (DFT) calculations using the local density approximation [23] on three systems—an abrupt STO/LAO interface with SrO next to AlO$_2$ [Fig. 4(a)]; an abrupt STO/LAO interface with TiO$_2$ next to LaO [Fig. 4(b)]; and an interface in which the TiO$_2$ layer is separated from the LaO layer by a single ML of LTO [i.e., LaO/TiO$_2$; see Fig. 4(c)]. The interface across a TiO$_2$ layer of STO and LaO layer of LAO causes band-bending in the partial density of states, with the $d$-type electrons dipping below the Fermi level, thereby forming a conducting layer. In contrast, and in agreement with the mixed-valence electron transfer model proposed in the literature, no such band-bending is observed for the SrO-AlO$_2$ interface [1,4,7]. When a LTO monolayer is inserted in between the TiO$_2$-LaO interface [compare Figs. 4(b) and 4(c)], the degree of band-bending is enhanced. In addition, and in contrast to the case without the LTO monolayer included, the dilation of the interface with the LTO monolayer is very similar to that found experimentally.

Because Al begins to mix with Ti at shallower depths than does La with Sr, the first ML of the interfacial layer [i.e., the first two ALs at positions 6.0 and 6.5 in Fig. 2(a)] are best described by La$_{1-x}$Sr$_x$TiO$_3$, with $x = 0.86$. The next two MLs have $x = 0.70$ and 0.10, respectively. It has been reported that La$_{1-x}$Sr$_x$TiO$_3$ is conducting between $x = 0.05$ and 0.95 [5,24,25]. The hopping term describing the overlap between the adjacent $d$ orbitals is sensitive to orthorhombic distortions, (which in the bulk causes LTO, with $x = 1$, to be a Mott insulator). In the thin film, however, the interface is forced to be tetragonal—the oxygen octahedra align up, thereby increasing the hopping integral.
in the plane of the interface via O 2p supertransfer [26] and further enhancing the conductivity parallel to the interface in this region.

An important aspect is whether intermixing is induced by the dipole compensation mechanism suggested by Nakagawa et al. [7], or simply by implantation or mixing induced by the energetic deposition flux of the pulsed ablation plume [16]. The fact that mixing of La with Sr becomes evident some 6 Å deeper than that between Al and Ti, and considering that the ionic radii of La and Sr are over twice those of Al and Ti, suggest that simple kinetic disruption caused by the impinging deposition flux cannot be responsible for the mixing, particularly for the modest laser fluences (and, consequently low ablation particle kinetic energies) used here. The transient and local “thermal spike” associated with impingement of energetic deposition particles in techniques like PLD and sputter deposition may, however, assist the cations to overcome kinetic barriers and reach their lowest energy sites.

In conclusion, we have solved the structure of the interface between SrTiO3 and LaAlO3 using SXRD and phase-retrieval methods. Further refinement using fitting procedures have allowed us to determine the layer-by-layer constituent concentrations and the individual atomic positions. The interface is not abrupt—Sr and La intermix at a greater depth than the Ti and Al ions, resulting in the formation of one to two MLs of metallic La1−xSr x TiO3. The concentration profile of Ti3+ ions, calculated by invoking electrostatic energy minimization, showed that their presence quantitatively explains the dilations. DFT calculations of the electronic structure of a system that mimics the experimentally observed structure, composed of STO ending with a TiO2 Al, a single ML of LaTiO3, and a film of LAO starting with a LaO AL, show that near the interface, the Fermi level moves above the bottom of the conduction band, rendering the system electrically conducting. This, and the observed tetragonal distortion, which is expected to enhance the mobility in the plane by increasing the hopping integral of the 3d electrons, provide an explanation of the formation of a Q2-DEG.

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[18] It remains possible that the observed intermixing is not real, but simply a manifestation of nanoscale roughness with characteristic lateral dimensions smaller than the longitudinal coherence length of our focused beam of 40 nm. Although this cannot be completely discounted, the formation of such an interface morphology during or after deposition, starting from an STO surface, which we know from atomic force microscopy to be atomically flat, seems physically improbable.