



Structural Basis for the Conducting Interface between LaAlO₃ and SrTiO₃

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(Received 6 June 2007; published 9 October 2007)

The complete atomic structure of a five-monolayer film of LaAlO₃ on SrTiO₃ 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_xTiO₃. By invoking electrostatic potential minimization, the ratio of Ti⁴⁺/Ti³⁺ 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.

DOI: 10.1103/PhysRevLett.99.155502

PACS numbers: 68.35.Ct, 61.10.Nz, 71.15.Mb, 72.20.-i

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 LaAlO₃/SrTiO₃ (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 TiO₂, and LaO and AlO₂ atomic layers (ALs), respectively. In the ionic limit, each AL of STO consists of neutral layers, while the nominal charges of LaO and AlO₂ 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-AlO₂ interface is insulating, while the TiO₂-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

(SXR) 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 TiO₂-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 × 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 SXR 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 $Q = 11.3 \text{ \AA}^{-1}$ 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 dips toward the surface of the film.

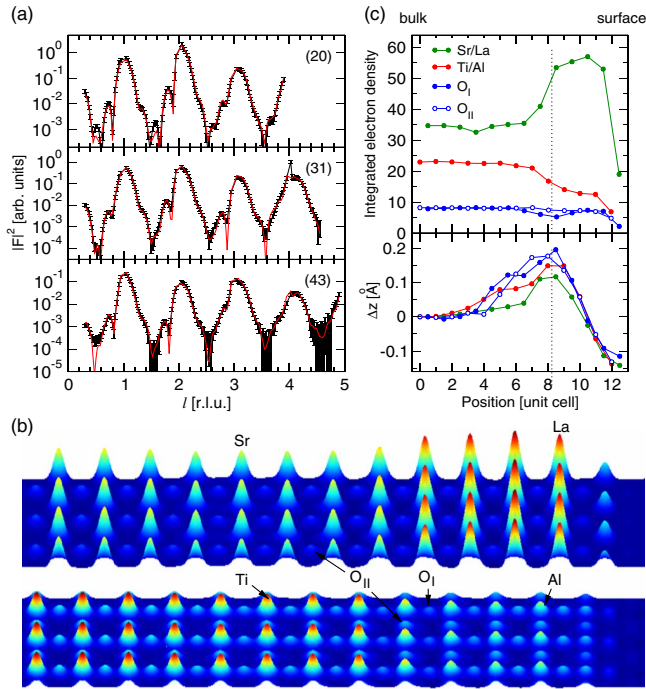


FIG. 1 (color online). (a) Representative SXR D data (black) of the LAO/STO system, plus the structurally refined model (gray, red online) obtained by FIT. (b) The electron density maps emerging from COBRA, showing the plane normal to the surface containing the La, Sr, and O_{II} atoms and the plane containing the Al, Ti, O_I, and O_{II} atoms. (c) Top: the integrated electron densities of the Gaussian-like features in the electron density maps in (b). Bottom: the cumulative displacement Δz of the atoms from the reference frame of the positions for bulk STO. The dotted line represents the nominal interface.

The atomic coordinates obtained from COBRA were then used as a starting model for further structural refinement, using the grid-search χ^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 LaTiO₃ (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

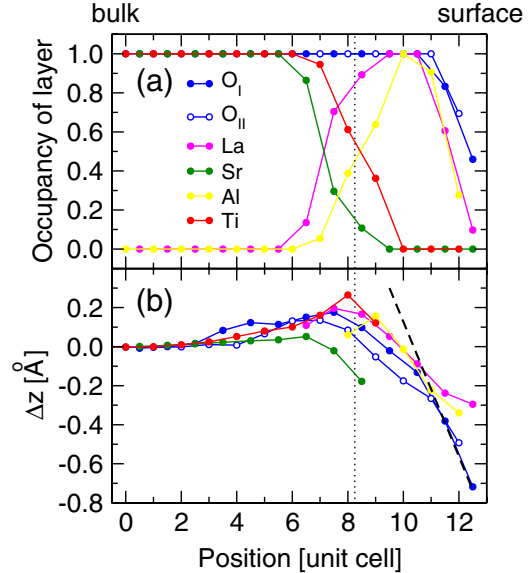


FIG. 2 (color online). Summary of the structural refinement results. The occupancies (a), and cumulative displacements Δz (b) of each atom. Error bars are small compared to the data-point circles, except for the 5% Al point at 7 ML—the positioning of the integrated electron density of only 0.65 electrons had little or no effect on the quality of the fit and was therefore removed. The dashed line has a gradient of $3.56\text{--}3.905 = -0.345$ Å per unit cell, the change in Δz predicted by the simple model in the text explaining the dilation.

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-charge state varies across the interface by requiring that the ratio of Ti⁴⁺ to Ti³⁺ 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 Ti³⁺.

First, the ionic radius of Ti³⁺ is 0.065 Å larger than that for Ti⁴⁺, which would produce relaxed pseudocubic unit cells in LTO and SrTi³⁺O₃ (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 Δa 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.

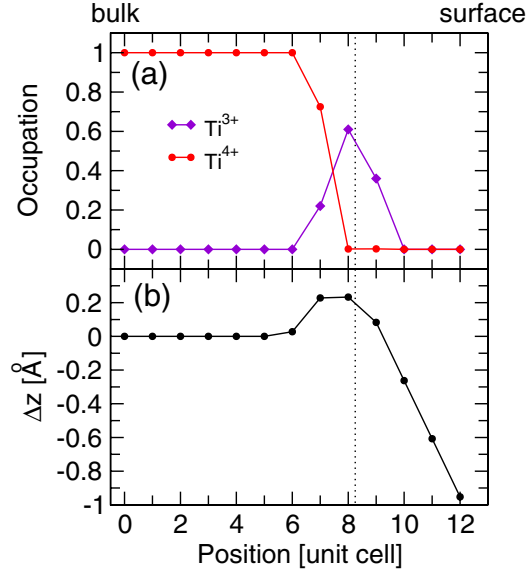


FIG. 3 (color online). (a) The concentration of Ti^{3+} was determined by invoking a minimization of the electrostatic potential. The sum of these two curves is equal to the Ti concentration shown in Fig. 2(a). (b) The predicted cumulative unit cell displacements from bulk STO positions, based on the component ionic radii.

Second, experimental [11,22] and theoretical studies [3] indicate that Jahn-Teller distortions elongate the oxygen octahedra at the interface along the z direction. Furthermore, calculations of the Ti $3d$ charge densities at the STO/LTO interface by Okamoto *et al.* [12] predict that screening provided by ferroelectric relaxations produces a long “tail” of $3d$ -electron charge distribution extending far away from the interface. These two predictions should therefore result in a gradual increase of the c -axis lattice constant in STO as the interface is approached, and indeed we observe this [Fig. 2(b)].

To a first approximation, the differing depths of intermixing between Sr and La, and Ti and Al, can be modeled

TABLE I. Concentrations of the component unit cell types (columns 2–5) in MLs 5 (the last bulklike STO ML) to 12. Column 6 gives the deviation of the epitaxially strained c -axis length (calculated from the weighted average lattice constants of the component unit cell types) from bulk STO, while column 7 shows the cumulative deviation, i.e., the deviation from the bulk STO positions.

ML	STO	ST3O	LTO	LAO	Δc [Å]	$\sum(\Delta c)$ [Å]
5	1	0	0	0	0	0
6	0.86	0	0.14	0	0.027	0.0273
7	0.075	0.225	0.65	0.05	0.201	0.2279
8	0	0.10	0.51	0.39	0.005	0.2333
9	0	0	0.36	0.64	-0.151	0.0827
10	0	0	0	1	-0.345	-0.2623
11	0	0	0	0.61	-0.345	-0.6073
12	0	0	0	0.10	-0.345	-0.9523

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 $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$, with $x \approx 0.86$. The next two MLs have $x = 0.70$ and 0.10 , respectively. It has been reported that $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ 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

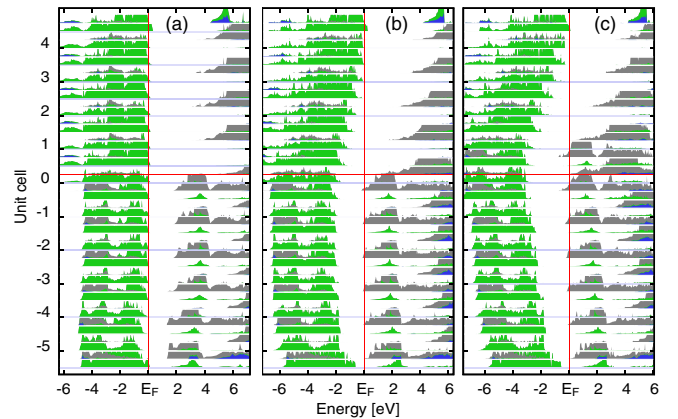


FIG. 4 (color online). Band structure calculations of an LAO/STO interface by DFT. Each ML contains four partial densities of state of s -like electrons (given in lighter gray above the Fermi edge, blue online), two p -like electrons (darker gray below the Fermi edge, green online) and d -like electrons (gray). The interface is at $x = 0$. (a) An abrupt interface across SrO and AlO_2 ALs. (b) An abrupt interface across TiO_2 and LaO ALs. (c) An interface including the insertion of a single LTO monolayer between TiO_2 and LaO.

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, consequentially 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 La_{1-x}Sr_xTiO₃. The concentration profile of Ti³⁺ ions, calculated by invoking electrostatic energy minimization, showed that their presence quantitatively explains the dilation. 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.

We thank O. Bunk for assistance with the FIT program. Support of this work by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung and the staff of the Swiss Light Source is gratefully acknowledged. This work was partly performed at the Swiss Light Source, Paul Scherrer Institut, and was supported in part by US Department of Energy Grant No. DE-FG02-06ER46273 and by US National Science Foundation Physics Frontier Center Grant No. PHY-0114336.

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