Spectroscopic evidence of in-gap states at the $SrTiO_3/LaAlO_3$ ultrathin interfaces

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Experimental evidence of differences in the electronic properties of an insulating and a conducting $SrTiO_3/LaAlO_3$ interface is provided by soft x-ray spectroscopies. While core level photoemission measurements show that only at the conducting interface Ti ions with 3+ ionization state are present, by using resonant photoemission and x-ray absorption spectroscopies, it is shown that in both samples in-gap states with a Ti 3*d* character are present, but their density is higher at the conducting interface. © *2011 American Institute of Physics*. [doi:10.1063/1.3549177]

Evidence of a conducting interface between the band insulators $SrTiO_3$ (STO) and $LaAlO_3$ (LAO)[1] has opened up the possibility of using complex oxide materials in two-dimensional electron gas applications. The initially reported large carrier mobility[1] turned out to be caused by oxygen vacancies effectively donating charge to the STO, not being related to the interface *per se*.[2–4] Still, when taking care to avoid oxygen vacancies, the metallic conductivity remains and, from a number of experiments, it has become clear that the conductivity is really confined at the interface. Strong evidence for the latter is provided by the substrate termination dependence of the conductivity,[1] the interlayer spacing dependence of coupled interfaces,[5] the abrupt onset of conductivity above a critical LAO thickness of 4 unit cells,[6] and conducting atomic force microscopy across cleaved samples.[7] The mechanism causing the interface conductivity is believed to be charge transfer from the LAO surface to the STO side of the interface to prevent the electrical potential from diverging due to the polar nature of LAO.[8] This electronic reconstruction picture is supported by *ab initio* calculations.[9–12] Recent theoretical investigations have also explored the possibility that the incorporation of oxygen vacancies at the LAO surface can be driven by the polar nature of the underlying LAO.[13]

So far, the electronic structure of LAO/STO heterointerface has been mainly probed by hard x-ray photoemission spectroscopy[14,15] and x-ray absorption spectroscopy.[16] Ti^{3+} states have been detected in core level hard x-ray photoemission by Sing *et al.*[14] and a Ti $3d_{xy}$ orbital occupation was observed by x-ray absorption linear dichroism.[16] However, the soft x-ray photoemission measurements reported by Yoshimatsu *et al.*[15] have not revealed any Ti^{3+}. Furthermore, no spectroscopic evidence of in-gap states or conduction electrons at the LAO/STO interface has been so far reported, preventing any investigation on the nature of the charge carries confined at the heterojunction.

In this letter, by matching the results of x-ray core level photoemission and resonant photoemission spectroscopies, we show that Ti^{3+} is present in a conducting sample of 5 unit cells LAO on STO, at a larger extent than in the insulating sample of 3 unit cells LAO on STO. Furthermore, we provide an experimental evidence of in-gap states at the LAO/STO interface and, from the analysis of constant initial state (CIS) photoemission profiles, a Ti 3*d* character is ascribed to these in-gap states.

The present samples have been grown, respectively, by depositing 3 and 5 unit cells (u.c.) of LAO on TiO_2 terminated STO substrates. The growth by pulsed laser deposition has been performed at 850 °C. Attention has been paid to grow the two samples at the same oxygen partial pressure (1.2×10^{-3} mbar) to exclude differences in the extrinsic inclusion of oxygen vacancies. The sample with 3 u.c. of LAO is found to be insulating, the two-point resistance at room temperature being larger than 100 MΩ. The sample with 5 u.c. of LAO is found to be metallic with a four-point resistance at room temperature of the order of a few kilo-Ohms over a distance of a few millimeters. Unlike previous synchrotron radiation studies,[15] no additional doping was introduced to increase the conductivity and quench possible charging effects due to the high photon fluxes. Furthermore, by engineering the samples so as to have very shallow insulating interfaces (3 u.c.) and a shallow metallic interface (5 u.c.), we have been able to use conventional x-ray sources and soft x rays to probe the interface layers. The estimated photoelectron escape depth $\sim\lambda_e$ in the present experiment is comparable to the thickness of the LAO layer for both samples (as is shown in Ref. 17).

X-ray photoemission (XPS) spectra were collected at a base pressure of 2×10^{-10} mbar by using a twin anode (Al $K\alpha$ and Mg $K\alpha$) x-ray source and a VG-Scienta R3000 spectrometer, Box 15120, 750 15 Uppsala, Sweden. Resonant photoemission (RESPES) and x-ray absorption spectra (XAS) across the Ti L-edge have been collected at the BACH beamline of the Elettra synchrotron in Trieste (Italy).

In Fig. 1 (left panel), the Ti 2*p* XPS core lines of the 5 u.c. sample (dots) and the 3 u.c. sample (line) are shown

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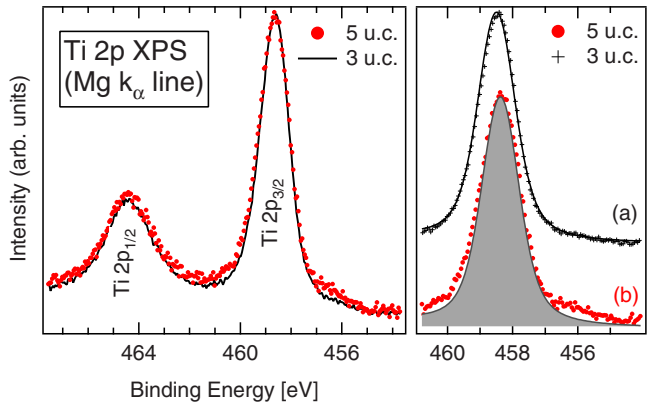

FIG. 1. (Color online) Left panel: Ti 2*p* XPS core level spectra of the 5 u.c. sample (dots) and the 3 u.c. sample (line). Right panel: detailed view of the Ti $2p_{3/2}$ main line region. The spectrum of the 3 u.c. sample [(a) crosses] has been fit with a Voigt function [(a) line]. The Voigt profile is reported below the data from the 5 u.c. sample [(b) filled circles].

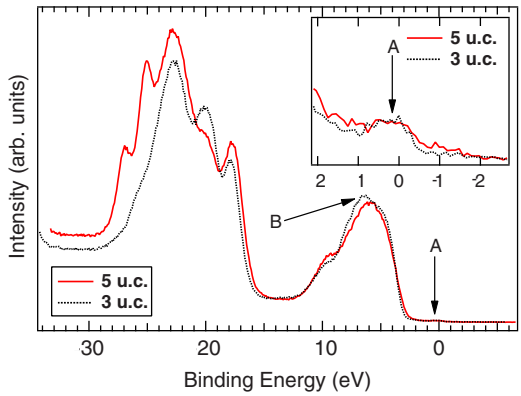

FIG. 3. (Color online) Valence band spectra of the 3 (dashed line) and 5 u.c. (line) samples collected at a photon energy of 457 eV. The inset show the in-gap states for both samples.

together to single out differences between the Ti 2*p* spectral weight of these interfaces. The 5 u.c. sample spectrum is normalized to match the Ti $2p_{3/2}$ intensity of the 3 u.c. XPS spectrum. In both spectra, two peaks are detectable, which are ascribed to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ spin-orbit split components. The Ti $2p_{3/2}$ core lines have the same full width at half maximum linewidth on both samples (1.4 eV). Such narrow linewidths are comparable to those measured on rutile single crystals, indicating a highly stoichiometric environment for the Ti ion. These peaks are indicative of Ti in a +4 ionization state. A shoulder on the low binding energy side of the Ti 2*p* peaks is present in the 5 u.c. sample (consistent with Ref. 14), while it is missing on the 3 u.c. one, as is shown in detail in the right panel of Fig. 1. When contaminations are excluded, as in the present case for the buried interface capped by the LAO overlayer, this shoulder is usually ascribed to Ti^{3+} ions and is also present in oxygen deficient TiO_2 rutile layers, where oxygen vacancies are known to reduce Ti ions.[18] The Ti valence reduction could both be related to oxygen defects, as well as to electronic reconstruction. However, because of the similar deposition conditions and the fact that no Ti 3+ signature is detected in the case of the insulating three-layer sample, *extrinsic* oxygen defects seem to be an unlikely cause.

The occupied electronic states in the valence band have been studied by RESPES with photon energies across the Ti L_3-edge, as recently done in the case of TiO_2 rutile.[19] The RESPES spectra (Fig. 2) show a resonant behavior of the peak at BE=6 eV (marked as B in both RESPES set of data), which is usually ascribed to Ti states hybridizing with O-states in the valence band.[20] The resonance is largest for the 3 u.c. sample [Fig. 2(b)], where the Ti is closer to the surface than for the 5 u.c. sample.

The RESPES also reveals in-gap electronic states (marked as A in Fig. 3). The analysis of these states is accomplished by examining two spectra collected with a photon energy of 457 eV, as shown in Fig. 3. Apparently, the in-gap states have the same weight in both samples. How-

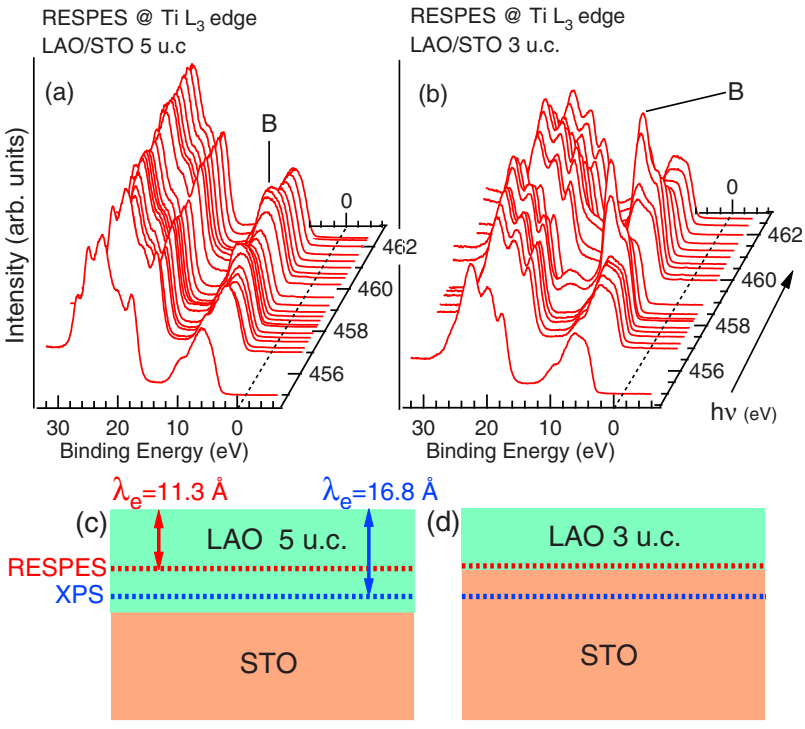

FIG. 2. (Color online) Top panel: RESPES spectra collected at the Ti L_3 edge from the (a) 5 u.c. sample and from the (b) 3 u.c. sample. Bottom panel: schematic representation of the calculated electron escape depth λ_e (Ref. 17) for electrons photoemitted from the Ti $2p_{3/2}$ core level (dashed line, XPS, $h\nu$=1256.6 eV, λ_e =16.8 Å) and from the valence band (dashed line, RESPES, $h\nu$=457 eV, λ_e=11.3 Å); (c) and (d) refer to 5 and 3 u.c. samples, respectively.

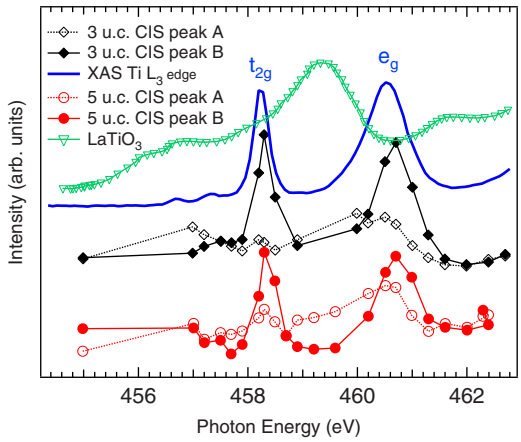

FIG. 4. (Color online) XAS of the 5 u.c. sample (thick line) and of $LaTiO_3$ (adapted form Ref. 16, triangles). CIS profile of the A and B features for the 3 u.c. sample (empty and filled diamonds, respectively). CIS profile of the A and B features for the 5 u.c. sample (empty and filled circles, respectively).

ever, because of the thicker LAO overlayer in the 5 u.c. sample, the effective density of the in-gap states is largest for the conducting 5 u.c. sample. The excess of in-gap electronic states is consistent with the Ti^{3+} states found in XPS Ti 2*p* core level data of the 5 u.c. sample (Fig. 1). If we assume that the only difference between the two samples is the thickness of the LAO overlayer, the attenuation of the signal based on the estimated λ_e for electrons with 457 eV kinetic energy would give an $I(A)_{3u.c.}/I(A)_{5u.c.}=1.97$ ratio between the intensities *I* of the A peaks of the two samples. Thus, as the measured intensities appear to be the same, the density of in-gap states for the 5 u.c. sample results to be 1.97 times that of the 3 u.c. sample.

Finally, in Fig. 4, we analyze the CIS spectra for the in-gap states (A feature), as well as for the most resonating feature at BE=6 eV (B feature). The Ti L_3-edge XAS spectrum (Fig. 4, thick line) is in agreement to those already reported for a set of LAO/STO interfaces.[16] The peak at 458.2 eV is ascribed to t_{2g} states arising from crystal field splitting, while the broad peak at 460.6 eV is ascribed to e_g states. As can be observed for both samples, the CIS spectra of the B feature follow the intensity of the Ti L_3-edge XAS (only the XAS for the 5 u.c. sample is shown, the other being quite similar) in agreement with their origin from Ti^{4+} electronic states in the valence band. In turn, the CIS spectrum of the A band shows a different behavior, with a quenching of the intensity below the t_{2g} peak and a shift toward lower photon energies of the e_g band. In spite of the weaker signal with respect to the CIS spectrum extracted form peak B, the CIS profiles of peak A show a higher intensity where the most intense XAS bands of a Ti^{+3} ion are found [see, e.g., the Ti L_3 edge of $LaTiO_3$ (Fig. 4, triangles; adapted from Ref. 16)]. This adds further evidence that a $3d^1$ character can be ascribed to the in-gap states.

In conclusion, a clear signature of in-gap states in the photoemission spectra collected from LAO/STO heterojunctions is provided. An effect of titanium reduction to Ti^{3+} is detected in the core level data of the conducting 5 u.c. sample alone, but in-gap states are detected in both samples through RESPES experiments. Both samples have been grown under the same conditions, ruling out differences in the extrinsic oxygen vacancy concentration between the insulating and the conducting samples. This should give the same density of in-gap states related to the oxygen vacancies. However, when the signal attenuation through the two different LAO overlayers is accounted for, an excess of in-gap states is found in the metallic 5 u.c. sample with respect to the insulating 3 u.c. sample (about 2:1 ratio). We rationalize our findings in terms of excess conducting electrons in the 5 u.c. sample, consistent with electronic reconstruction models.[8]

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