Localized and delocalized Ti 3d carriers in LaAlO₃/SrTiO₃ superlattices revealed by resonant inelastic x-ray scattering

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The important source of interface conductivity in LaAlO₃/SrTiO₃ heterostructures, the Ti 3d carriers, is probed with resonant inelastic x-ray scattering at the Ti 2p_{3/2} edge of epitaxially grown superlattices. We reveal unambiguously the generation of both localized and delocalized Ti 3d carriers as a result of the built-up heterointerface. Furthermore, we determine that the interface Ti³⁺O₆ octahedra are orthorhombically distorted and quantify the crystal-field splitting energies. We argue that for as-grown superlattices, both types of Ti 3d carriers originate mainly from oxygen vacancies, whereas for fully oxidized samples they result from electronic reconstruction.

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Artificially tailored oxide-based heterostructures display exotic phenomena not existing in the individual constituents. The interface between simple band insulators, LaAlO₃ (LAO) and SrTiO₃ (STO), exhibits metallicity, magnetism, and two-dimensional superconductivity.^{1–5} In spite of intense efforts in the development of devices based on such oxide heterostructures, an ongoing controversy exists with regard to the origin of its interface conductivity. Electronic reconstruction, i.e., partial change of Ti ions from the 4+ to the 3+ oxidation state by transferring half an electron from LAO to STO, was proposed to occur to avoid the divergence of the electric potential at the interface.^{6,7} This scenario amounts to a theoretical sheet carrier density $\sim 3.3 \times 10^{14} \text{ cm}^{-2}$.⁷ However, the real mechanism seems to be more complex than this ideal picture. Extremely high sheet carrier densities, e.g., $\sim 10^{16}–10^{17} \text{ cm}^{-2}$, are widely present in samples grown under low oxygen pressures ($< 10^{-6}$ mbar), which highlights the dominance of growth-induced oxygen vacancies (OV) in obtaining the interface carrier density.^{8–10} It has been identified by hard x-ray photoelectron spectroscopy (HAXPES) that doping of OV in LAO/STO bilayers contributes to Ti³⁺ states.¹¹ On the other hand, transport measurements on well-oxidized LAO/STO bilayers showed conductivity appearing when the thickness of LAO exceeds four unit cells (uc),¹² indicating that electronic reconstruction is an essential part of the real mechanism. The sheet carrier density experimentally found for such samples is $\sim 2 \times 10^{13} \text{ cm}^{-2}$,¹² almost one order of magnitude lower than the theoretical value. This strongly suggests that a complicated mechanism of several processes may be at play.^{6–10,13,14}

To understand the intrinsic origin of the interface conductivity, considerable efforts have been made using several spectroscopic techniques.^{7,11,15,16} However, detecting the interface Ti³⁺ signal is extremely difficult in such studies, as both bulk Ti⁴⁺ and interface Ti³⁺ states are simultaneously probed and the spectral weight of the Ti³⁺ states constitutes only a small fraction of the total signal.

A recent resonant inelastic x-ray scattering (RIXS) study of the interface Ti³⁺ states in LAO/STO bilayers made it possible to give an upper bound of 500 meV for the intra-*t*_{2g} (and -*e*_g)

Ti 3d crystal-field splitting.¹⁷ A discrepancy of carrier density has been claimed between those spectroscopic data and previous transport measurements,¹¹ which might be connected to the coexistence of localized and delocalized carriers at the interface.^{3,18–20}

In this Rapid Communication, we reveal direct spectroscopic signatures from localized as well as delocalized Ti 3d carriers in LAO/STO superlattices using RIXS at the Ti 2p_{3/2} edge.²¹ With RIXS we are sensitive to extremely small amounts of Ti³⁺ states despite the majority of Ti⁴⁺ states in this system. For Ti⁴⁺ (3d⁰ configuration) states, only an elastic emission signal arises, when the excited 2p_{3/2} core electrons recombine with the core hole. The single existing 3d electron for Ti³⁺ states opens additional decay channels yielding inelastic emission (*dd* excitations), which gives a distinct signature for Ti³⁺ (3d¹ configuration) [see the scheme in Fig. 1(a)].²² In our present high-resolution study, we quantify the energy separation between all Ti 3d crystal-field levels. This allows us to determine that the interface Ti³⁺O₆ octahedra experience compressed orthorhombic distortion in contrast to the tetragonally compressed interface Ti⁴⁺O₆ octahedra. We further studied the carrier density evolution as a function of LAO thickness for both as-grown and oxidized LAO/STO superlattices. From this, we ascribe the basic driving force for the appearance of these two types of 3d carriers to oxygen vacancies and electronic reconstruction for as-grown and oxidized samples, respectively. Our studies strongly suggest that the presence of the two types of Ti 3d carriers and the distinct interface structural distortion are responsible for the discrepancy between the experimentally observed and theoretically predicted sheet carrier density in LAO/STO heterostructures.

A series of LAO/STO superlattices (SL's) was grown with the pulsed laser deposition setup at the SIS beamline of the Swiss Light Source (SLS) at the Paul Scherrer Institut (PSI). All SL's contain 10 LAO/STO stacking periods, in which the thickness of LAO layers is increased from 3 to 6, 8, and 10 uc, while STO layers are fixed to 10 uc. In the following, SL's are denoted as LAO_{*m*}, where *m* stands for the thickness of LAO layers in uc. Growth and annealing procedures are described elsewhere.²³ The RIXS experiments [see the setup in Fig. 1(b)]

FIG. 1. (Color online) (a) Sketch of the Ti 2*p*-RIXS process. Ω and ω are incident and emitted x-ray energies, respectively. The left panel describes the RIXS process for Ti^{4+} states, in which $\omega = \Omega$ and only elastic emission is allowed. The right panel describes 2*p*-RIXS for Ti^{3+} states, where an extra emission channel is opened ($\omega \neq \Omega$) in addition to the elastic peak. (b) A schematic view of the XAS and RIXS experimental setup. Samples are aligned with the surface normal (001) in the scattering plane. The incident x-ray beam ($h\nu_{\text{in}}$) is linearly polarized [π (σ) means in-plane (out-of-plane) polarization] and impinges on the sample surface with a grazing angle of 20° . The emitted x rays ($h\nu_{\text{out}}$) are detected at an angle of 90° with respect to the incoming beam.

with a total energy resolution of 150 meV were performed with the SAXES spectrometer at the ADDRESS beamline of the SLS at PSI.²⁴ All measurements were carried out at 15 K. X-ray-absorption spectroscopy (XAS) spectra were collected in total electron yield (TEY) mode. RIXS spectra are normalized to the integrated high-energy fluorescence originating from the predominant Ti^{4+} states in STO. Due to the photon attenuation length of ~ 80 nm at the Ti 2*p*_{3/2} edge,²⁵ we probe the total sample volume of the SL's in our RIXS experiment.

Figure 2(a) displays TEY Ti 2*p*-XAS spectra from the LAO3 SL with light polarization vector **E** aligned along both in-plane (**E**||*ab*) and out-of-plane (**E**||*c*) directions. In general, our SL's show very similar spectral profiles²³ to those from a recent XAS study on LAO/STO bilayers.¹⁶ The first two peaks in Ti 2*p*-XAS are due to Ti^{4+} 2*p*_{3/2}-3*d* *t*_{2*g*} and 2*p*_{3/2}-3*d* *e*_g transitions, respectively. Since only a small amount of Ti^{3+} is expected in LAO/STO heterostructures, Ti^{3+} 2*p*_{3/2}-3*d* *e*_g transitions in XAS are very difficult to detect between the dominating Ti^{4+} peaks. Therefore, we employ the direct signature of *dd* excitations in Ti^{3+} RIXS. In Fig. 2(b), we show RIXS spectra excited at incident energies Ω [indicated with arrows in Fig. 2(a)] across the Ti^{3+} 2*p*_{3/2}-3*d* *e*_g resonance. Pronounced double-peak excitations show up in all spectra for an energy loss of -2.6 and -3.0 eV, respectively. In addition, low-energy excitations ~ -0.3 eV are seen as a shoulder of the elastic peak. The double peak is known from LaTiO_3 (3*d*¹ configuration) to be caused by *dd* excitations between the on-site *t*_{2*g*} and *e*_g orbitals, while the shoulder stems from intra-*t*_{2*g*} excitations.²² As described above, *dd* excitations at constant energy loss are a clear signature for localized Ti 3*d* electrons, and we can therefore conclude that such electrons are created in LAO3. Very interestingly, an additional remarkable excitation not showing a constant energy loss emerges between ~ -1 and -2 eV in all spectra. Excitations of nonconstant energy loss in RIXS are the well-known response of delocalized electrons, for which photon

FIG. 2. (Color online) (a) Total electron yield (TEY) mode Ti 2*p*-XAS spectra of the LAO3 SL for both in-plane (black line) and out-of-plane (red line) polarization. The first two peaks are the Ti^{4+} 2*p*_{3/2}-3*d* *t*_{2*g*} and 2*p*_{3/2}-3*d* *e*_g resonances, respectively. Arrows label the incident energies used for RIXS. (b) Series of RIXS spectra of LAO3 SL excited across the Ti^{3+} 2*p*_{3/2}-3*d* *e*_g threshold with out-of-plane polarization. RIXS spectra from STO substrate (solid black line) and STO film (dotted gray line) references are also displayed.

absorption and emission are decoupled.²¹ Therefore, we assign this additional peak in our RIXS experiments to originate from delocalized Ti 3*d* electrons. RIXS spectra from other as-grown SL's with increasing thickness of LAO layers show the same localized and delocalized excitations (see Fig. 4) as displayed by LAO3. As a reference, we performed RIXS on a pure TiO_2 -terminated STO substrate treated in the same way as the SL's. This reference measurement delivers a negligible background signal, which shows that Ti 3*d* carriers must be generated during the SL growth. In addition, RIXS measured on a 100-uc-thick homoepitaxial STO film (equal STO volume as in the SL's) grown under exactly the same conditions as the SL's reveals only delocalized excitations with much lower intensity compared to LAO3. From the difference between the STO substrate and film on the one hand and our superlattices on the other, it is clear that the occurrence of delocalized and localized Ti 3*d* electrons in SL's must be induced by the building of LAO upon STO. This is in strong contrast to RIXS spectra of the Mott insulator LaTiO_3 , which are only characterized by localized *dd* excitations.²² We thus conclude that two types of electrons are created in the build-up

of LAO/STO heterointerfaces: ones localized and bound to Ti^{4+} forming Ti^{3+} states, and others in the vicinity of the Ti^{4+} -producing delocalized carriers.

To explain the discrepancy of sheet carrier density between transport measurements and the pure electronic reconstruction scenario, Popović *et al.* suggested that in addition to delocalized carriers, localized ones occur, with the latter not contributing to interface conductivity.¹⁸ Interestingly, recent HAXPES¹¹ and RIXS¹⁷ studies have detected a finite spectral weight of Ti^{3+} in LAO/STO bilayers. A difference in carrier density from those spectroscopic data and from Hall measurements has been claimed by the authors of Ref. 17. They connect this, in agreement with other experiments,^{3,20} to the theory prediction of localized and delocalized carriers at the interface.^{18,19} However, the study by Berner *et al.*¹⁷ could not give direct spectroscopic evidence of such delocalized carriers. Instead, our present investigation directly reveals localized and delocalized electrons employing the different RIXS spectral response of these carriers. Our results, therefore, give unambiguous experimental proof of the coexistence of localized and delocalized types of carriers, with the latter having higher mobility.^{18–20}

DFT theory calculations predict d_{xy} orbitals to have the lowest energy at the interface.^{18,19} Berner *et al.*¹⁷ implied that the crystal-field splitting of the t_{2g} manifold is considerably smaller than their instrumental broadening of 500 meV. In this way, they could only give an upper limit for the local distortion of the TiO_6 octahedra at the interface. With our present high-resolution RIXS study, on the other hand, we accurately determine the crystal-field splittings and the local structural distortion at the interface layer.

In Fig. 3(a), one of the RIXS spectra from LAO3 ($\Omega = 459.2$ eV) shows localized intra- t_{2g} and t_{2g} - e_g excitations resolved in four distinct spectral peaks. Because the single d electron in the occupied $3d$ orbital can be excited to all other unoccupied $3d$ orbitals for the Ti^{3+} oxidation state, this clearly indicates that the $3d$ state degeneracy is fully lifted. Using the crystal-field multiplet calculations²⁶ shown in Fig. 3(b), we reveal that Ti^{3+}O_6 octahedra face compressed orthorhombic distortion, with d_{xy} being the lowest occupied orbital.²³ This

FIG. 3. (Color online) (a) RIXS spectrum ($\Omega = 459.2$ eV) (red dotted line) of LAO3 SL after subtracting the elastic peak and the result from the multiplet calculations (solid line). (b) Scheme of the crystal-field splitting for Ti^{4+} and Ti^{3+} states in our LAO/STO SL's.

FIG. 4. (Color online) (a) Elastic peak subtracted RIXS spectra of LAO3, LAO6, LAO8, and LAO10 ($\Omega = 459.2$ eV). Thin and thick lines represent experimental and fitted data, respectively. Spectra are stacked vertically for clarity; annealed spectra are shown in the upper part and as-grown ones in the lower part. (b) Integrated spectral weight of RIXS excitations ($\Omega = 459.2$ eV) between -4.2 and 0 eV. Error bars are the first standard deviation from fitting.

differs from Ti^{4+} states for which a tetragonal distortion was revealed near the interface.¹⁶ The four localized excitations at -0.25 , -0.35 , -2.65 , and -3.05 eV can be assigned to electronic transitions from the d_{xy} to d_{xz}/d_{yz} , d_{yz}/d_{xz} , $d_{x^2-y^2}$, and d_{z^2} orbitals, respectively [Fig. 3(b)]. We thus determine the values for the intra- t_{2g} and intra- e_g crystal-field splitting of the Ti^{3+}O_6 octahedra to 300 and 400 meV, respectively. These are nearly four times larger than for interface Ti^{4+}O_6 octahedra. Such an increase of crystal-field strength is connected with enhanced Coulomb repulsion and covalency between Ti 3d and oxygen 2p states due to the extra occupation of Ti 3d electrons. Our results are consistent with the Jahn-Teller distortion suggested by surface x-ray diffraction studies, indicating that TiO_6 octahedra are strongly compressed along the surface normal of LAO/STO.²⁷ Additionally, Pentcheva *et al.*¹³ calculated that the structural distortion can partially compensate for the electric potential at the interface. According to this structural distortion mechanism, the valence-band discontinuity can be partially reduced.

In Fig. 4(a), we show that the creation of both types of Ti 3d electrons depends strongly on the thickness of LAO layers (m). The intensities of both localized and delocalized excitations increase considerably with m , while their energy positions are unchanged. This proves that the orthorhombic structural distortion of the Ti^{3+}O_6 octahedra does not vary with an increasing number of LAO uc, and it suggests that additional LAO uc simply add Ti 3d electrons. However, the origin of these Ti 3d electrons is unclear, since transferred electrons from both OV and electronic reconstruction can be electron donors.

To clarify the origin of the observed carriers, all samples were annealed in oxygen to remove OV. RIXS spectra from annealed SL's are also displayed in Fig. 4(a). Annealing reduces significantly the intensities of both types of excitations due to the reduction of Ti^{3+} to Ti^{4+} ,²⁸ while the energy positions of localized and delocalized excitations are not altered. This proves that robust orthorhombic distorted Ti^{3+}O_6 octahedra are established at the interfaces independent of LAO thickness and oxygen annealing. To gain a quantitative understanding,

the spectral weight of localized and delocalized excitations of all as-grown and annealed samples was integrated. The resultant spectral weights shown in Fig. 4(b) are proportional to the carrier density because of unchanged structural distortion for all SL's. In general, the density of both types of carriers of as-grown SL's increases monotonically with the thickness of the LAO layers. The strong decrease of the carrier density in the SL's upon oxygen annealing is characteristic of carrier density reduction.^{8,11} The spectral weight of delocalized excitations in the reference STO film does not change at all with annealing, suggesting that these are connected with intrinsic defects generated during the growth.²⁹ Based on these observations, we conclude that the Ti 3d carriers in as-grown SL's are mostly caused by OV, which are created during the growth of LAO layers and then migrate into the LAO/STO interface region.

The evolution of the RIXS spectral weight with LAO thickness variation after annealing provides further insight into the origin of Ti 3d electrons. From Fig. 4(b), one can learn that upon annealing, the delocalized spectral weight of LAO3 and LAO6 is reduced to the defect level of the STO film. Larger localized intensity is, however, present for LAO3 and LAO6. Above LAO6, both localized and delocalized spectral weights increase and reach a plateau. This LAO thickness dependence also exists in RIXS spectra recorded at other incident energies. Such a development resembles the behavior of the electrical conductivity in LAO/STO bilayers showing a sharp rise beyond a critical thickness of LAO, as explained by the electronic reconstruction scenario.¹² Since OV are refilled after annealing, the sudden increase of the spectral weight must be connected with electronic reconstruction for fully oxidized films. Our observation of the critical thickness is in good agreement with a DFT calculation predicting that 8 uc of LAO are needed to avoid electrical potential divergence in

LAO/STO SL's.³⁰ This compares well with the conductivity of STO/LAO/STO trilayers saturating above 6 uc of LAO.² We therefore propose that during the growth of SL's, oxygen vacancies play a major role in the creation of Ti 3d carriers, while after annealing the electronic reconstruction is essential for the presence of carriers in samples exceeding the critical thickness.

In conclusion, we reveal the coexistence of both localized and delocalized types of Ti 3d carriers in LAO/STO superlattices using RIXS at the Ti 2p_{3/2} edge. The generation of these two types of carriers results from the built-up heterointerfaces, while the thickness of LAO layers and post-growth annealing affect the carrier density. We observe orthorhombic structural distortion for interfacial Ti³⁺O₆ octahedra in our superlattices not depending on the LAO layer thickness. Both characteristics—the existence of two types of carriers and the occurring structural distortion—may explain the reported discrepancy between theoretically calculated and experimentally measured carrier density values in LAO/STO heterostructures. Our investigation demonstrates how studies of the electronic properties of oxide heterostructure interfaces with RIXS can increase the general understanding of these systems.

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²³See supplemental material at [<http://link.aps.org/supplemental/10.1103/PhysRevB.83.201402>] for the growth and annealing procedures and the crystal field multiplet calculations.

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