Orientational tuning of the Fermi sea of confined electrons at the SrTiO$_3$ (110) and (111) surfaces

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We report the existence of confined electronic states at the (110) and (111) surfaces of SrTiO$_3$. Using angle-resolved photoemission spectroscopy, we find that the corresponding Fermi surfaces, subband masses, and orbital ordering are different from the ones at the (001) surface of SrTiO$_3$. This occurs because the crystallographic symmetries of the surface and sub-surface planes, and the electronic effective masses along the confinement direction, influence the symmetry of the electronic structure and the orbital ordering of the $t_{2g}$ manifold. Remarkably, our analysis of the data also reveals that the carrier concentration and thickness are similar for all three surface orientations, despite their different polarities. The orientational tuning of the microscopic properties of two-dimensional electron states at the surface of SrTiO$_3$ echoes the tailoring of macroscopic (e.g. transport) properties reported recently in LaAlO$_3$/SrTiO$_3$ (110) and (111) interfaces, and is promising for searching new types of 2D electronic states in correlated-electron oxides.

Two-dimensional electron gases (2DEGs) in transition-metal oxides (TMOs) present remarkable phenomena that make them unique from a fundamental viewpoint and promising for applications. For instance, heterostructures grown on the (001) surface of SrTiO$_3$, a TMO insulator with a large band-gap of $\sim 3.5$ eV, can develop 2DEGs showing metal-to-insulator transitions, superconductivity, or magnetism. Recently, 2DEGs at the (111) and (110) interfaces of LaAlO$_3$/SrTiO$_3$ were also reported. The latter showed a highly anisotropic conductivity and a superconducting state spatially more extended than the one at the (001) interface. Interestingly, theoretical works have also predicted that exotic, possibly topological, electronic states might occur at interfaces composed of (111) bilayers of cubic TMOs, as two (111) planes of transition-metal ions form a honeycomb lattice, similar to the one found in graphene. In this context, the discovery that 2DEGs can also be created at the bare (001) surfaces of SrTiO$_3$ and KTaO$_3$, and more recently at the (111) surface of KTaO$_3$, opened new roads in the fabrication and study of different types of 2DEGs in TMOs—in particular using surface-sensitive spectroscopic techniques, which give direct information about the Fermi surface and subband structure of the confined states. The origin of the confinement is attributed to a local doping of the surface region due to oxygen vacancies and/or lattice distortions.

Here we show that new types of 2DEGs can be directly tailored at the bare (110) and (111) surfaces of SrTiO$_3$. Imaging their electronic structure via angle-resolved photoemission spectroscopy (ARPES), we find that their Fermi surfaces, subband masses, and orbital ordering are different from the ones of the 2DEG at the SrTiO$_3$ (001) surface and the ones predicted for the bulk, being thus uniquely sensitive to the confining crystallographic direction. This occurs because the crystallographic symmetries of the 2DEG plane, and the electronic effective masses along the confinement direction, influence the symmetry of the electronic structure and the orbital ordering of the $t_{2g}$ orbitals. Furthermore, the observed carrier concentrations and 2DEG thicknesses for different surfaces allow us to showcase the impact of oxygen vacancies and of the polar discontinuity on distinctive features of the confined conducting sheet.

The confined states were either created by fracturing the samples in vacuum or by chemically and thermally preparing the surfaces in situ, and studied through ARPES at the Synchrotron Radiation Center (SRC, University of Wisconsin, Madison) and the Synchrotron Soleil (France). The sample preparation, similar to the one in references 20, 21, is detailed in the Supplemental Material 22. All through this paper, we describe the crystal structure in a cubic basis of unit-cell vectors, and note as $[hkl]$ the crystallographic directions in real space, $(hkl)$ the corresponding directions in reciprocal space, and as $(hkl)$ the planes orthogonal to those directions.

The major difference between the confined states at various surface orientations of SrTiO$_3$ originates from the different symmetries of the corresponding crystal planes: 4-fold for the (001) plane, 2-fold for the (110) surface, and 6-fold for the (111) surface. Another difference is the polar character of the surface. Thus, while the (001) termi-
nations, namely SrO or TiO₂, are nominally non-polar, the (110) terminations are alternatively (SrTiO)⁴⁺ and (O₂)⁴⁻, and the (111) terminations are either Ti⁴⁺ or (SrO₂)⁴⁻. These different surface symmetries and their polarity are illustrated in figures 1(a-d). Note in particular, from figure 1(d), that a (111)-type bilayer of Ti⁴⁺ cations forms a honeycomb lattice, as noted in Ref. [10].

For our discussion later, it will be instructive to contrast the observations at the (110) and (111) SrTiO₃ surfaces with both the 2DEG at the (001) surface and a model bulk electronic structure. Figure 1(e) shows the bulk Fermi surface from a simplified tight-binding (TB) model where the electron hopping amplitudes between the three t₂g orbitals of neighboring Ti⁴⁺ are tₓ = 0.236 eV and tᵧ = 0.035 eV, and we neglect spin-orbit coupling and tetragonal distortions. Near the Γ point, this gives effective masses listed in the first row of table I for various directions. Figures 1(f, g) show cross sections of the bulk Fermi surface along the (110) and (111) planes through the Γ point, illustrating their respective 2-fold and 6-fold symmetries. The experimental spectra at the SrTiO₃ (001) surface [14], on the other hand, fit well to a TB form where the hopping amplitudes are tₓ = 0.36 eV and tᵧ = 0.025 eV, leading to values of the effective masses near the Γ point shown in the second rows of table I. Note that all these masses differ by about 30% from the bulk theoretical ones.

We now present our experimental results. Figure 2(a) shows the Fermi surface measured at the fractured (110) surface of an undoped insulating SrTiO₃ sample. As we will see, our observations are similar to another recent study of the 2DEG at the SrTiO₃(110) surface in a Nb-doped sample prepared in situ by Wang et al. [24]. The metallic states we observe present the same 2-fold symmetry of the unreconstructed (110) surface Brillouin

![Fig. 1](image-url)
masses along a parabolic approximation, we obtain the effective band particularly, from the band bottom and Fermi momenta, using states associated to such a high charge carrier density.

From the data above, we model the Fermi surface of the 2DEG at the SrTiO$_3$ (110) surface as two orthogonal ellipses, one along (001) with semi-axes of 0.3 Å$^{-1}$ and 0.1 Å$^{-1}$, the other along (110) with semi-axes 0.25 Å$^{-1}$ and 0.13 Å$^{-1}$. From the area $A_F$ enclosed by the Fermi surfaces, we obtain a carrier density $n_{2D}^{(110)} = A_F/2\pi^2 \approx 1 \times 10^{14}$ cm$^{-2}$. The electronic states associated to such a high charge carrier density must be confined to the region near the surface—otherwise the bulk would be highly conductive, in contradiction with the insulating nature of the samples studied. Similarly, from the band bottom and Fermi momenta, using a parabolic approximation, we obtain the effective band masses along (001) and (110) (and equivalent directions), listed in the third row of Table I. These effective masses are similar to the ones determined in the aforementioned study of the 2DEG at the SrTiO$_3$(110) surface. In our study, the band bottom of the heavy band, c.f. Figure 2(b), and the carrier density of the 2DEG are slightly lower, probably due to the different surface preparation techniques.

Henceforth, we focus on new experimental results at the (111) surface of SrTiO$_3$, which as we will see presents the hexagonal symmetry of the unreconstructed surface, and could thus be an interesting platform for the quest of new electronic states and macroscopic properties at oxide surfaces.

Figure 3(a) shows the Fermi surface measured at the SrTiO$_3$(111) surface prepared in-situ, as described in the Supplemental Material. It consists of three ellipses forming a six-pointed star, thus strongly differing from the Fermi surface at the SrTiO$_3$ (110) surface, shown in Figure 2(a), or the one at the SrTiO$_3$(001) surface, discussed in previous works. Additional experiments show that for surfaces prepared in-situ with either (1×1) or (3×3) reconstructions, the band structure and periodicity of the confined states are identical, and correspond to the one expected from an unreconstructed surface.

This indicates that the 2DEG at the SrTiO$_3$(111) surface is also located in the sub-surface layers, and is at best weakly affected by the surface reconstructions at the po-
lar (111) surface.

The 2D-like character of the electronic states is strictly demonstrated from the Fermi surface map in the (111) – (1¯12) plane, shown in figure 3(b). Here, one sees that the bands do not disperse along \( k_{(111)} \) over more than half a bulk Brillouin zone, thereby confirming the confined (i.e., localized) character of the electrons along the [111] direction in real space. The modulation of the intensity in the Fermi surface map, a typical feature of quantum well states, is discussed in the Supplemental Material. Interestingly, note that the red rectangles in figures 2(a) and 3(b) represent the Brillouin zone in the (110) (or equivalent) plane. Yet, as seen from those figures, the shapes of the corresponding Fermi surfaces are completely different. This directly shows the orientational tuning of the Fermi surface due to different confinement directions.

Figure 3(c) shows the energy-momentum map at the \( \Gamma \) point along the (112) direction, corresponding to the major axis of the ellipsoids forming the 6-pointed-star Fermi surface. The dispersions of one light band and one heavy band are clearly visible. These constitute the ground state of the 2DEG. Additional subbands are not observed, implying that the band bending at the surface is too low to populate the upper quantum-well states. Within our resolution, the heavy and light bands are degenerate at \( \Gamma \), with their band bottom located at about \(-57 \text{ meV}\). We fit simultaneously these dispersions and the whole Fermi surface of figure 3(a) using a simple tight-binding model. The fit, shown by the continuous blue lines, yields Fermi momenta of about \( 0.07 \text{ Å}^{-1} \) and \( 0.36 \text{ Å}^{-1} \) for, respectively, the light and heavy bands along (112). This gives an electron concentration \( n_{e}^{(111)} \approx 1.0 \times 10^{14} \text{ cm}^{-2} \) and effective masses listed in the third row of table IV.

We now draw some comparisons between the effective masses and thicknesses of the 2DEGs at the \( \text{SrTiO}_3 \) (001), (110) and (111) surfaces. Table IV shows that, while the masses along the “natural” electron-hopping directions in the bulk ([001] and equivalent) are comparable between the 2DEGs at the \( \text{SrTiO}_3 \) (001) and (110) surfaces, the masses along [110] at the (110) surface, and all the masses of the 2DEG at the (111) surface, are very different from the ones expected from the tight-binding parameters describing the bulk or the 2DEG at the (001) surface. In this respect, note that if the confinement direction is [110] or [111], then the electrons moving in the 2DEG plane along a direction other than [001] will experience the confining potential gradient and the modified crystal field outside the surface, as they will hop in staircase patterns between first neighbors along [001] (or equivalent) directions – see figures 1(a-d) and Ref. 8, 12. The understanding of these mass differences, also reported in quantum well states at thin films of simple-metals or strongly-correlated oxides, should be the subject of further theoretical works.

The maximal spatial extension \( d_{\text{max}} \) of the 2DEGs at the \( \text{SrTiO}_3 \) (110) and (111) surfaces can be estimated using a triangular potential well model. We obtain \( d_{\text{max}}^{110} \approx 1.7 \text{ nm} \), which amounts to 6 2D-layers or 3 bulk unit cells along [110], and \( d_{\text{max}}^{111} \approx 1.9 \text{ nm} \), corresponding to \(~9\) layers of Ti (111), or again about 3 bulk unit cells along [111].

Finally, we note that the orbital ordering of the electronic states at the (110) and (111) surfaces of \( \text{SrTiO}_3 \) is different from the one at the (001) surface. In the first two cases, the bands are degenerate within our experimental resolution, whereas at the (001) surface the smallest observed splitting between bands of different orbital character is of 50 meV. As the confinement energy of each band is inversely proportional to its effective mass along the confinement direction, different surface orientations result in different orbital ordering. But along the [111] direction the effective masses of the three \( t_{2g} \) bands are identical, and so their degeneracy at the \( \Gamma \) point is not lifted by the confinement. Similarly, the effective masses of bands of different orbital character along [110] are quite similar (see table II). Hence, the degeneracy lift is rather small, and cannot be observed in our data. This demonstrates the influence of the confinement direction on the orbital ordering.

Several scenarios have been proposed to explain the origin of the 2DEG at the \( \text{LaAlO}_3/\text{SrTiO}_3 \) (001) interface. According to one of these, the formation of a conducting sheet prevents the occurrence of a polar catastrophe in the material. Yet, the discovery of a confined 2DEG at the (001) surface of \( \text{SrTiO}_3 \), with characteristics similar to those of the above heterostructure, suggests that the driving mechanism may not be unique, as in the bare \( \text{SrTiO}_3 \) all the layers are electrically neutral. Instead, in the latter case, surface oxygen vacancies are believed to cause and to confine the gas. Additionally, for the (110) and (111) \( \text{SrTiO}_3 \) surfaces, of nominal polar charge \( 4e \), one would expect a much larger carrier concentration in the 2DEG, and a very strong electric field confining the electrons in a narrow sheet at the surface. However, we observe that the carrier concentrations and thicknesses of the 2DEGs are quite comparable for all three orientations (this work and Ref. 14): \( n_{2D} \approx 10^{14} \text{ cm}^{-2} \), \( d_{\text{max}} \sim 2 \text{ nm} \). In fact, in the polar \( \text{SrTiO}_3 \) surfaces studied here, the polar catastrophe does not seem to be compensated by the electrons of the 2DEG but by surface reconstructions or relaxations, while the 2DEG lies in the subsurface layers. Thus, although the 2D electronic structure (effective masses, orbital ordering) depends on the surface orientation, the thickness and carrier concentration of the 2DEG might be controlled by another factor, probably oxygen vacancies and/or lattice distortions induced by the synchrotron light irradiation, as discussed in the Supplemental Material.
fined states at the surface of TMOs can be tailored by 
confining the electrons along different directions in the 
same material. Such orientational tuning echoes the 
differences of transport properties reported recently in 
LaAlO$_3$/SrTiO$_3$ (110) and (111) interfaces [2,3]. In 
particular, from our data, the highly anisotropic transport 
behavior observed in the (110) interfaces [8] can be di-
rectly related to the 2-fold symmetry of the Fermi surface 
measured by ARPES. More generally, our results provide 
an exciting route for obtaining new types of 2D electronic 
states in correlated-electron oxides.

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SUPPLEMENTAL MATERIAL

ARPES Experiments

The ARPES measurements were conducted at the 
Synchrotron Radiation Center (SRC, University of Wis-
consin, Madison) and the Synchrotron Soleil (France). 
We used linearly polarized photons in the energy range 
20 – 120 eV, and Scienta R4000 electron detectors with 
vertical slits. The angle and energy resolutions were 0.25° 
and 25 meV at SRC, and 0.25° and 15 meV at Soleil. The 
mean diameter of the incident photon beam was smaller 
than 100 µm. The samples were cooled down to 10-30 K 
before fracturing or measuring, in pressure lower than 
6 × 10$^{-11}$ mbar. The confined states were either created 
by fracturing the samples in vacuum or by chemically 
and thermally preparing the surfaces in situ, as detailed 
in the next section. The results were reproduced for at 
least five different samples for each surface orientation.

Surface preparation

The non-doped, polished crystals of SrTiO$_3$ were sup-
plied by CrystTec GmbH and Aldrich. To prepare the 
surface, the samples were ultrasonically agitated in deion-
ized water, subsequently etched in buffered HF and an-
nealed at 950°C for several hours in oxygen flow. De-
pending on the annealing time, this treatment yields a 
Ti-rich, single-terminated or mixed-terminated step-and-
terrace structured surface of SrTiO$_3$ (111) [20]. Fig-
ure 3(a) shows the atomic-force microscopy (AFM) im-
age of the single-terminated (111) surface of a sample 
annealed for 3h. This treatment produces a (1 × 1) un-
reconstructed surface, shown by RHEED image in fig-
ure 4(b). Longer annealing (10h) results in a mixed-
terminated surface [21], as shown in the AFM friction 
image in figure 3(c), measured in contact mode. The 
surface prepared in such a way is (3 × 3) reconstructed, 
as displayed in the RHEED image in figure 4(d). The 
surface state of the cleaved samples was not determined 
by imaging or diffraction techniques.

To perform the surface-sensitive ARPES measurements, 
one needs pristine and crystalline surfaces. To 
clean the surface of contaminations, the samples prepared 
as described above were further annealed in-situ in vac-
uum at a pressure of approximately $p = 3 \times 10^{-9}$ mbar 
at a temperature of $T = 550$°C for about 2 hours. This 
annealing step cleans the surface, does not change the 
surface reconstruction, and also introduces oxygen va-
cancies in the bulk of the SrTiO$_3$ samples. Note that the 
introduced bulk charge carrier density is at least three 
orders of magnitude lower than the one observed for the 
confined states in the ARPES measurements, as detailed 
in the main text. Moreover, Plumb et al. demonstrated 
that various in-situ sample preparations, including an-
nealing in an O$_2$-rich atmosphere which results in a non-
doped bulk, create identical confined states at the (001) 
surface of TiO$_2$-terminated SrTiO$_3$ [19]. Recall also, 
from figure 3(b), that the states observed in our exper-
iments do not disperse along the confinement direction, 
which demonstrates their quasi-2D character.

For the confined states at the (111) surface, the qual-
ity of the obtained ARPES data is better for the surface 
prepared in-situ. This might be due to the strong polar 
nature of the (111) surface of SrTiO$_3$. Hence, fractur-
ing a sample along a (111) plane might yield a partly 
disordered surface.

The electronic structure of the 2DEG at the 
SrTiO$_3$ (111) surface is similar for the cleaved and the 
two differently prepared surfaces (unreconstructed and 
(3 × 3) reconstructed). In fact, for all three types of sur-
faces the periodicity of the electronic structure in recip-
ocal space, shown in figure 5(a) for the prepared, (3 × 3) 
reconstructed surface, corresponds to the one expected 
of an unreconstructed surface. By Bloch theorem, the 
very existence of dispersive bands and well-defined Fermi 
surfaces implies the existence of a periodic in-plane po-
tential acting on the confined electrons, hence of crys-
talline order at the layer(s) where the 2DEG is located. 
As the electronic structure has the periodicity of the un-
reconstructed surface, the 2DEG seems to stabilize in a 
sub-surface region, where it is not affected by any sur-
face reconstructions or superstructures related to vicinal 
surfaces or terraces. A possible explanation for this ob-
ervation would be that the electrons of the Ti cations in 
the topmost layer are localized, while the itinerant elec-
trons exist in the subsurface layers. For the (110) surface, a surface preparation similar to the one described above for the (111) surface was conducted. The data quality of fractured and prepared samples are quite similar as the chemical etching step is not perfectly adapted to the (110) surface. Sr and Ti are both situated in one of the alternating (110) layers of (SrTiO)$_4^+$ and O$_{2}^-$ building up the crystal lattice. Thus, the selective etching of Sr-related species might result in a rather rough surface.

**Photon energy dependence**

The photon energy dependence of the electronic states at the SrTiO$_3$ (111) surface is displayed in the main text in figure 3. Although the states do not disperse, confirming their confined nature, the intensity of the states drops rather quickly moving away from $\Gamma_{222}$. This observation is similar to the intensity modulation as a function of the photon energy reported previously at the (001) surface of SrTiO$_3$ [14] and KTaO$_3$ [15], as well as in quantum well states of metals [25, 26]. This modulation is due to photoemission dipole selection rules: the optical excitation of the electrons occurs from initial states in the near surface region that do not disperse along the confinement direction (the confined electrons) to dispersing bulk final states. Moreover, if the wave function of the confined states is not exactly localized in a 2D layer, but exists over several unit cells, the dispersion along the confinement direction will be affected. This can be intuitively understood from Heisenberg uncertainty principle: only a strict 2D confinement in real space yields a complete indetermination of the electron momentum along the confinement direction, hence an exactly cylindrical Fermi surface. Some delocalization along the confinement direction, as in quantum-well states, implies a small dispersion of the Fermi surface along that direction.

Bearing these effects (selection rules in quantum wells, finite delocalization) in mind, one can comprehend the data in figure 4(a), which shows a superposition of Fermi surface maps measured at different photon energies, for a (111) surface prepared in-situ. The black hexagons are the Brillouin zones assuming an unreconstructed surface. Thus, due to selection rules, the intensity of the photoemission peak from the confined states is highest close to positions corresponding to $\Gamma$ points of the bulk, where final states at the same $k_{(111)}$ momentum are available for the optical transition. But this intensity will decrease rapidly by moving along $k_{(111)}$, away from the bulk $\Gamma$ points [23]. Experimentally, this is done by changing the photon energy. This results in the necessity to measure in-plane Fermi surface maps at different photon energies,
FIG. 5. (Color online) (a) Superposition of Fermi surface maps measured for the chemically and thermally prepared SrTiO$_3$ (111) sample ((3 × 3) reconstructed surface) at photon energies of $h\nu$ = 47 eV and $h\nu$ = 96 eV. (b) Reciprocal 2D space in the (111) plane. Inside each Brillouin zone the projections of the different bulk $\Gamma$ points corresponding to available final states during the photoemission process at the specified photon energy are indicated. This diagram helps understanding the Fermi-surface intensities shown in panel (a). The color (red, blue, green) of the hexagons indicates which $\Gamma$ points are located in the same (111) plane in reciprocal space.

and then superpose them to retrieve the complete periodicity of the electronic states, as illustrated in figure 5(b). This figure shows the positions of the experimentally observed $\Gamma$ points projected in the (111) plane. The photon energy inside each Brillouin zone corresponds to the $k_\perp$ value of the $\Gamma$ points assuming a work function of $W = 4.25$ eV and an inner potential of $V_0 = 12$ eV.

Fermi surface of SrTiO$_3$(110)

As stated in the main text, the Fermi surface map shown in figure 2 is a superposition of intensities measured in the bulk $\Gamma_{130}$ and $\Gamma_{131}$ Brillouin zones. Figure 5 shows the intensities measured in those Brillouin zones. Due to photoemission matrix elements, only the vertical ellipsoidal Fermi surface is observed around the $\Gamma_{130}$ point, while both the vertical and the smaller horizontal ellipsoidal Fermi surfaces are observed around the $\Gamma_{131}$ point.

Estimate of the spatial extensions of the 2DEGs at the SrTiO$_3$ (110) and (111) surfaces.

In our data, figures 2 and 3 of the main text, only the lowest-energy subbands are observed. To estimate the maximal extension $d_{\text{max}}$ of the corresponding confined states, we follow the same strategy of Ref. 19. We assume that the second subbands are slightly above the Fermi level, hence unoccupied and not detectable by ARPES. We then use a triangular potential well model, and take as effective masses along the [110] and [111] confinement directions, respectively, $m_{110} \approx 1.6m_e$ (the lightest of the masses gives the largest 2DEG thickness) and $m_{111} = 1.0m_e$ (given by extrapolating the experimental masses at the (001) surface to the bulk [111] direction) – see table I of the main text. This gives $d_{\text{max}}^{110} \approx 1.7$ nm, amounting to 6 2D-layers or 3 bulk unit cells along [110], and $d_{\text{max}}^{111} \approx 1.9$ nm, corresponding to
FIG. 7. (Color online) (a) Angle-integrated spectra of an SrTiO$_3$ sample prepared in-situ, measured at a photon energy of $h\nu = 110$ eV, with a step size of 50 meV, showing the density of states for binding energies between $-45$ eV and 2 eV. The black curve was measured shortly after the first exposure of the sample to the UV light, and the red curve at the end of the measurements (about 36 hours later). The spectra are normalized to the intensity of the Sr 4p-peak at lower binding energies, indicating electron transfer from Ti$^{4+}$ to a lower valency state. Second, the decrease in intensity of the valence band in its low binding energy region. Third, the increase in intensity of the in-gap states and of the peak corresponding to the confined states. All these observations could be explained by both scenarios: the creation of oxygen vacancies and the ferroelectric lattice distortions.

In contrast to samples prepared in-situ, cleaved samples show a different behavior regarding the UV light exposure. The subbands of the 2DEG in all the cleaved SrTiO$_3$ surfaces we have studied so far, i.e. (001), (110) and (111), are all observed essentially immediately after cleaving, with no or little time delay after the first exposure to UV light. A more detailed study on the UV induced effects is beyond the scope of this paper.

UV dose dependence: enhancement of Ti$^{3+}$ signal

Understanding the influence of the UV synchrotron illumination on the observed confined states is important to determine the origin of such states. Recent photoemission studies on the 2DEGs at the (001) or (110) surface of SrTiO$_3$ proposed that the UV light creates oxygen vacancies $\text{O}^{2-}$, and/or ferroelectric lattice distortions $\text{Ti}^{3+}$ in the surface region. The two effects are difficult to disentangle using photoemission, as in both cases charge is transferred from O to Ti. Figure 7(a) shows the angle-integrated spectra, measured at $h\nu = 110$ eV, of a SrTiO$_3$ sample prepared in-situ for binding energies between $-45$ eV and 2 eV. The black curve was measured shortly after the first exposure of the sample to the UV light, while the red curve was recorded at the end of the measurements (36 hours later). The spectra are normalized to the intensity of the Sr 4p-peak, which should be rather independent of the concentration of oxygen vacancies and/or ferroelectric lattice distortions. Figure 7(b) is a zoom over the valence band region, while figures 7(c, d) show the in-gap states and the confined states at the Fermi level. The change of various features under UV irradiation is obvious: first, the formation of a shoulder in the Ti-3p peak at lower binding energies, indicating electron transfer from Ti$^{4+}$ to a lower valency state. Second, the decrease in intensity of the valence band in its low binding energy region. Third, the increase in intensity of the in-gap states and of the peak corresponding to the confined states. All these observations could be explained by both scenarios: the creation of oxygen vacancies and the ferroelectric lattice distortions.

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Tight-binding calculations of the 2DEG at the SrTiO$_3$(111) surface

The band dispersions shown in the main text correspond to the bottom of the conduction band of SrTiO$_3$, which is formed by Ti-3d orbitals hybridized with O-2p orbitals. The interaction between the oxygen anions forming an octahedron and the Sr cation generates a large crystal field which splits the d states in a lower $t_{2g}$ triplet and an higher $e_g$ doublet. Hence, only the $t_{2g}$ orbitals are considered in our tight-binding model, which is based on the calculations of reference 10. Our model for the SrTiO$_3$(111) surface is limited to a bilayer of Ti atoms. This approach is sufficient to fit the experimental data as shown in the main text, but does not necessarily imply the confinement of the electrons to a bilayer.

The Hamiltonian $H$ of the system in the basis $\{d_{I,n}\}$, where $I = (X,Y,Z)$ correspond to the orbital character $(yz, zx, xy)$ of the $t_{2g}$ orbitals and $n = 1, 2$ indicates the number of the layer of Ti cations, is given by:

$$H = \begin{pmatrix}
    d_{X,1} & \hat{\epsilon}_X & \epsilon_X \\
    d_{Y,1} & \hat{\epsilon}_Y & \epsilon_Y \\
    d_{Z,1} & \hat{\epsilon}_Z & \epsilon_Z \\
    d_{X,2} & \epsilon_X^* & \hat{\epsilon}_X \\
    d_{Y,2} & \epsilon_Y^* & \hat{\epsilon}_Y \\
    d_{Z,2} & \epsilon_Z^* & \hat{\epsilon}_Z
\end{pmatrix}\begin{pmatrix}
    d_{X,1} \\
    d_{Y,1} \\
    d_{Z,1} \\
    d_{X,2} \\
    d_{Y,2} \\
    d_{Z,2}
\end{pmatrix}$$

Here, $\hat{\epsilon}_I$ describes the hopping of electrons between next nearest neighbors of Ti cations (intra-layer hopping), characterized by the hopping amplitude $t_{\sigma''}$, whereas $\epsilon_I$ describes the hopping between nearest neighbors (inter-layer hopping) with hopping amplitudes $t_\pi$ and $t_\delta'$.
\[\hat{\varepsilon}_X = -2t_{\sigma''} \cos(-\frac{\sqrt{3}}{2} \tilde{a} k_x + \frac{3}{2} b k_y)\]
\[\hat{\varepsilon}_Y = -2t_{\sigma''} \cos(\frac{\sqrt{3}}{2} \tilde{a} k_x + \frac{3}{2} b k_y)\]
\[\hat{\varepsilon}_Z = -2t_{\sigma''} \cos(\sqrt{3} \tilde{a} k_x)\]
\[\epsilon_X = -t_{\pi} e^{-i\alpha} k_y \left[ 1 + e^{i\frac{1}{2}(-\sqrt{3} k_y + 3k_y)} \right] - t_{\delta'} e^{i\frac{1}{2}(-\sqrt{3} k_y + k_y)}\]
\[\epsilon_Y = -t_{\pi} e^{-i\alpha} k_y \left[ 1 + e^{i\frac{1}{2}(\sqrt{3} k_y + 3k_y)} \right] - t_{\delta'} e^{i\frac{1}{2}(\sqrt{3} k_y + k_y)}\]
\[\epsilon_Z = -2t_{\pi} e^{\frac{i}{2} k_y} \cos(\frac{3}{2} \tilde{a} k_x) - t_{\delta'} e^{-i\alpha} k_y.\]

In the above expressions, \(k_x\) corresponds to \(k_{(110)}\), \(k_y\) to \(k_{\bar{1}12}\), and \(\tilde{a}\) to the cubic lattice constant \(a\) projected in the (111) plane \(a = \sqrt{2/3}a\). Compared to the calculations of reference 14, our data can be fitted rather well using a simplified model. We neglect in our model the spin-orbit coupling, the trigonal crystal field, the layer potential difference, crystal distortions at low temperature, and the hopping \((t_{\sigma''})\) between next nearest neighbors of different orbital symmetry. The fits shown in figures 3(a) and 3(c) of the main text are based on such a simplified model using fitting parameters of \(t_{\pi} = 1.6\) eV, \(t_{\delta'} = 0.07\) eV and \(t_{\sigma''} = 0.05\) eV.

Note that such value of \(t_{\pi}\), which quantifies the hopping energy between nearest neighbors along the [100] (and equivalent) directions, is here over 4 times larger than the same parameter inferred from the 2DEG at the SrTiO\(_3\) (001) surface (namely, \(t = 0.36\) eV, see the main text). This shows again that the effective masses of the 2DEG at the SrTiO\(_3\) (111) surface strongly differ from what would be expected from a model based on the 2DEG at the (001) surface. As discussed in the main text, the electrons moving along any direction in the (111) plane will actually hop in zig-zag patterns between first neighbors along [001] (or equivalent) directions, and thus will experience the confining potential gradient and the modified crystal field outside the surface. These effects are not accounted by our minimalist TB model. Additionally, our TB model only considers one bilayer of Ti atoms. However, it is known that in quantum well states the effective masses of the confined electrons depend on the width of the quantum well or, equivalently, the number of layers. All these effects should be taken into account in future theoretical works addressing the 2DEGs at the different surfaces of SrTiO\(_3\). On the other hand, while distortions of the crystal lattice, and thereby of the overlap between the different \(t_{\delta'}\) orbitals, might exist at the surface and be slightly different depending on the surface orientations, they should bear a negligible effect on the 2DEGs reported here, as we have seen that their electronic structure is essentially insensitive to surface polarity or reconstructions.

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