Hidden lattice instabilities as origin of the conductive interface between insulating LaAlO$_3$ and SrTiO$_3$

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The metallic interface between insulating LaAlO$_3$ and SrTiO$_3$ opens up the field of oxide electronics. With more than a decade of researches on this heterostructure, the origin of the interfacial conductivity, however, remains unsettled. Here we resolve this long-standing puzzle by atomic-scale observation of electron-gas formation for screening hidden lattice instabilities, rejuvenated near the interface by epitaxial strain. Using atomic-resolution imaging and electron spectroscopy, the generally accepted notions of polar catastrophe andcation intermixing for the metallic interface are discounted. Instead, the conductivity onset at the critical thickness of 4-unit cell LaAlO$_3$ on SrTiO$_3$ substrate is accompanied with head-to-head ferroelectric-like polarizations across the interface due to strain-rejuvenated ferroelectric-like instabilities in the materials. The divergent depolarization fields of the head-to-head polarizations cast the interface into an electron reservoir, forming screening electron gas in SrTiO$_3$ with LaAlO$_3$ hosting complementary localized holes. The ferroelectric-like polarizations and electron-hole juxtaposition reveal the cooperative nature of metallic LaAlO$_3$/SrTiO$_3$.

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The metallic LaAlO$_3$(LAO)/SrTiO$_3$(STO) interface fuels the modern quest of electronics based on correlated electrons in oxides and the collective characteristics of superconductivity, ferromagnetism and electromechanical sensitivity typical to insulating ferroelectrics (FEs). This two-dimensional (2D) electron system manifests the manifold possibilities of oxide electronics. The conductive LAO/STO, therefore, forms the model system of emergent phenomena at oxide interfaces. However, why this LAO/STO system can display so versatile physical properties remains an open question, with the origin of the 2D metallicity constituting the most basic problem in the context.

Electrostatically, the bulk ABO$_3$ perovskite, LAO, is non-polar. The layer-by-layer thin-film growth of LAO with repeated AO and BO$_2$ units can nonetheless turn the film polar by the charged essence of (LaO)$_n$ and (AlO)$_n$ planes. The STO substrate with Sr$^{2+}$ and Ti$^{4+}$ in LAO/STO heterostructures is conversely non-polar. To obtain conductive LAO/STO, a polar-catastrophe (TiO$_2$)$_0$-(LaO)$_{1.5}$ interface is an indispensable prerequisite, with the LAO surface being readily (AlO)$_{1.5}$-terminated. This electrostatic boundary condition implies an electric field (E = 236 meV Å$^{-1}$) in LAO and the corresponding potential would diverge with increasing LAO thickness. With 4 unit cells (uc) of LAO (lattice parameter, 3.79 Å) on STO and more, this diverging potential enables the LAO valence-band maximum to overcome the STO conduction-band minimum (offset, 3.2–3.3 eV). Charge transfer from LAO to STO readily becomes possible, diminishing the built-in field and resulting in conductive LAO/STO. Below 4-uc LAO, the interface shall be otherwise insulating. This critical thickness of 4-uc LAO for the 2D electron gas (2DEG) formation in STO was indeed verified, providing the evidence of polar catastrophe for the interfacial metallicity. The possible existence of an interfacial metallic (La,Sr)TiO$_3$ phase by cation intermixing addresses the 4-uc dependence of the metallicity (Fig. 1h). The increasing 2DEG density with increasing LAO thickness, expected within the framework of the diverging polar-catastrophe potential, is also discounted by the nearly constant 2DEG in insulating and conductive LAO/STO in Fig. 1c.

The plane-specific charge deduced from Fig. 1e is shown in Fig. 1f for clarity, 10 uc only and leads to the plane-by-plane potential variations in Fig. 1g according to the Gauss law in Maxwell’s equations. Figure 1h displays the intermixing counterparts (charge-neutral uc without interfacial charges) of the potential variations. Notably, cation intermixing (Fig. 1b) reduces the diverging potential of polar catastrophe (grey), like the graded electrostatic divergence in polar semiconductor heterojunctions by intermixing. Polar catastrophe no longer addresses the 4-uc dependence of the metallicity (Fig. 1h). The increasing 2DEG density with increasing LAO thickness, expected within the framework of the diverging polar-catastrophe potential, is also discounted by the nearly constant 2DEG in metallic LAO/STO (Fig. 1e). The ubiquitous intermixing in both insulating and conductive LAO/STO in Fig. 1c is evidently for grading polar catastrophe and this intermixing tendency, characteristic to heterostructural growths, is indeed general in the different STEM–EELS and SXRD characterizations of various LAO/STO specimens (Fig. 1c).

Nevertheless, not every oxide interface with polar catastrophe is conductive and the observation of an inherent field in LAO of metallic heterostructures is inconsistent with polar catastrophe. It becomes compelling that one should also consider the less-emphasized lattice degree of freedom, for unravelling the origin of the metallic interface. A quantitative tackling of the structural and intervening chemical and electronic parameters with atomic accuracy will, therefore, be most critical.

Here we report the investigation of this kind using scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS), establishing why the notions of polar catastrophe and cation intermixing are inconsistent with the whole picture and how the interfacial metallicity is originated from the structural aspect of hidden FE-like instabilities in LAO and STO.

### Results

#### Quantitative unveiling of chemical and electronic features

STEM and EELS were performed on insulating 3-uc and metallic 4-, 5- and 10-uc LAO/STO, all of which were optimally post-annealed to restore oxygen vacancies (Methods). Figure 1a shows the high-angle annular dark-field (HAADF) imaging of 10-uc LAO/STO, which is the sum over three images for ensuring good representativeness. The coloured panel in Fig. 1a is an individual STEM–EELS chemical map. Figure 1b exhibits the HAADF blowup, unravelling Al-site displacements towards the interface and tetragonality in STO. Figure 1c is the averaged chemical profiles over five STEM–EELS maps, acquired on different regions of each LAO/STO with small deviation among the five corresponding data sets (Supplementary Fig. 1), and thus-statistically derived results suggest AO- (La and Sr) and BO$_2$-plane (Al and Ti) cation concentrations. The diffusive cation distribution at the interface (Fig. 1c) indicates intermixing and appears not only in insulating 3-uc, but all conductive LAO/STO (grey, known intermixing in insulating 3-uc and metallic 5-uc heterostructures by surface X-ray diffraction (SRXD)). Figure 1d shows the STEM–EELS electronic probing of Ti (the only mixed-valence element rendering its charge-accommodation role), averaged over five data sets. Summing up Fig. 1c,d leads to the unprecedented uc-by-uc charge distributions in LAO/STO (Fig. 1e; Methods), with 2DEG in the STO of metallic heterostructures and, surprisingly, holes in the LAO (ref. 22). The insulating 3-uc LAO/STO is free from interfacial charge.

The plane-specific charge deduced from Fig. 1e is shown in Fig. 1f for clarity, 10 uc only and leads to the plane-by-plane potential variations in Fig. 1g according to the Gauss law in Maxwell’s equations. Figure 1h displays the intermixing counterparts (charge-neutral uc without interfacial charges) of the potential variations. Notably, cation intermixing (Fig. 1b) reduces the diverging potential of polar catastrophe (grey), like the graded electrostatic divergence in polar semiconductor heterojunctions by intermixing. Polar catastrophe no longer addresses the 4-uc dependence of the metallicity (Fig. 1h). The increasing 2DEG density with increasing LAO thickness, expected within the framework of the diverging polar-catastrophe potential, is also discounted by the nearly constant 2DEG in metallic LAO/STO (Fig. 1e). The ubiquitous intermixing in both insulating and conductive LAO/STO in Fig. 1c is evidently for grading polar catastrophe and this intermixing tendency, characteristic to heterostructural growths, is indeed general in the different STEM–EELS and SXRD characterizations of various LAO/STO specimens (Fig. 1c).

### Picometre-scale characterization of FE-like distortions

We now turn to the structural distortions in Fig. 1b. The lattice degree of freedom was scrutinized by peak-pair analysis (PPA) of summed HAADF images, like Fig. 1a. This image-summation method can improve the statistics of observed atomic features, and the subsequent statistical PPA characterization at sub-pixel level led to a structural-evaluation precision of ~2 pm (Fig. 2a,b, Supplementary Fig. 3 and Supplementary Note 1). Figure 2a shows the uc-dependent variations in $c$ axis (dotted line, 3.905 Å of bulk STO), and Fig. 2b exhibits the corresponding atomic displacements along $c$-direction, with solid (empty) symbols for the A-site (B-) Sr and La (Ti and Al). Figure 2c,d depict the PPA-determined strain maps of insulating 3-uc and metallic 4-uc LAO/STO for respective $\varepsilon_{xx}$ and $\varepsilon_{zz}$, which reveal the strain characteristics basically along $c$ and $a$ axes. Figure 2e displays a colour-coded annular bright-field exemplification of the cross-interface rotation of oxygen cages in 10-uc LAO/STO (Supplementary Fig. 4a for the original grey-scale image; Supplementary Notes 2 and 3).

In Fig. 2d, the similar contrast level in LAO to that in STO reveals the clamping of $ab$-plane in LAO to that in STO (2.9% tensile strain to LAO), signifying conventional pseudomorphic-strained LAO (refs 8,25). The $c$ axis should be readily contracted to 3.762 Å (dotted–dashed line, Fig. 2a;...
Poison’s ratio $^{8,16}$, 0.24). Surprisingly, we observe gradually c-elongated LAO in metallic LAO/STO towards the interface (Fig. 2a), with the same tendency for the STO uc on the interfacial conductivity onset$^{11,19}$ (Fig. 2c). Similar c-elongation characteristics were observed in otherwise SRXD (refs 8,10,11), TEM (ref. 26) and STEM–HAADF (refs 27,28) investigations. The metallic heterostructures have then to be described by c-elongated, volume-expanded interfacial LAO and STO uc. By contrast, the insulating 3-uc LAO/STO consists of bulk-like STO and c-elongated LAO (Fig. 2a). This structural difference between insulating and conductive LAO/STO is further elaborated in Fig. 2b, where the positive sign points to the LAO surface. The Sr- and Ti-site displacements in Fig. 2b were determined by the displacements from the respective reference planes in undistorted, parent cubic interfacial uc$^{10,11,16}$. The La cage in each LAO uc, instead, defines the lattice frame (thus null, Fig. 2b) for the precise determination of the Al-site off-centre displacement (like Supplementary Fig. 3), which is the central structural character of the LAO (ref. 16). The high-precision, statistical determination of atomic displacements in LAO/STO (Fig. 2b) was not reported in the previous TEM and STEM–HAADF studies$^{26–28}$. All displacements in conductive LAO/STO point to FE-like symmetry breaking, whereas the insulating 3-uc counterpart preserves the cubic essence with negligible off-centre atomic displacements.

The metallic heterostructures are firmly addressed by FE-like symmetry breaking, while the insulating LAO/STO shows c-elongated, symmetry-preserved LAO. All these structural features are unexpected considering a typical pseudomorphic epitaxy under the tensile strain should lead to uniformly c-contraction LAO without symmetry breaking$^{8,13,25}$. It naturally raises the question: what if the epitaxial strain is accommodated by FE-like distortions?

We readily evaluate the corresponding epitaxial-strain and FE-like distortion energies$^{16,29}$ (Supplementary Note 5), with the
STO LAO

LAO/STO. The SXRD results of the heterostructures with various LAO Fe-like distortions is cancelled out by the anti-phase oxygen-cage (Supplementary Note 5)\textsuperscript{16}. Note that the oxygen contribution to the characteristic anti-phase oxygen-cage rotation (guiding white cages) in reference to a STO area far from the interface (out of the displayed range, metallic heterostructure (c in interfacial STO uc shows an abrupt onset on the interfacial metallicity, 4 uc strain maps of insulating 3-uc and conductive 4-uc LAO/STO, showing the similarity of elastic properties of LAO (ref. 31) and STO (ref. 32) and corresponding electrostatic energies, which are the functions of A- and B-site atomic displacements from the equilibrium positions in high-symmetry reference lattices (d_{A,B}; Supplementary Note 5)\textsuperscript{15}. Note that the oxygen contribution to FE-like distortions is cancelled out by the anti-phase oxygen-cage rotation\textsuperscript{30} (Fig. 2e and Supplementary Fig. 4) and Fig. 2b signifies \(d_{A,B}\). In Fig. 3, we show the associated epitaxial-strain (grey histograms) and FE-like distortion energies (black curves). The red dotted–dashed curve (Fig. 3) specifically indicates the FE-like distortion energies in respective 4-, 5- and 10-uc LAO/STO due to the maximal off-centre Al-site (Ti- and Sr-site) displacements of \(\sim 0.1\) (both \(\sim 0.1\)), \(\sim 0.15\) (\(\sim 0.1\)) and \(\sim 0.25\) (\(\sim 0.15\)) Å in the interfacial LAO (STO) uc in Fig. 2b. The insulating 3-uc counterpart is free from FE-like distortion, thus null in Fig. 3 (red dotted–dashed).

Notably, the evolution of the epitaxial-strain and FE-like distortion energies above 3-uc LAO closely mimics each other (Fig. 3), implying comparable costs between the pseudomorphically c-contrasted LAO and the FE-like distorted LAO and STO, and establishing the energetics footing of the FE-like distortions as a strain-accommodation alternative. The close similarity of elastic properties of LAO (ref. 31) and STO (ref. 32) should be critical, since the misfit-strain field would readily distort both the materials rather than, in principle, the film\textsuperscript{25}

This requirement of simultaneously strained LAO and STO finds a viable solution in the hidden FE-like instabilities of the materials, which are resurrected by stretching the uc (Fig. 2a,b) as also microscopically suggested in our ab initio calculations (Supplementary Figs 5 and 6 and Supplementary Notes 2 and 3). This elongated LAO in insulating 3-uc LAO/STO, therefore, indicates a tendency towards this FE-like state and the corresponding accumulated epitaxial-strain energy should be close to that required for resurrecting the hidden FE-like instabilities in LAO/STO.

**Head-to-head polarizations across the metallic interface.**

Figure 4a shows the FE-like polarizations in all interfacial uc, \(P = q_A \mu_{A,B}/V\) (P, polarization; \(q_A,B\), the cation valence in Fig. 1e; \(d_{A,B}\), Fig. 2b; V, uc volume in Fig. 2a) in the point-charge approximation\textsuperscript{29,33}. While the insulating LAO/STO is free from polarization, the metallic heterostructures show head-to-head polarizations across the interface (Fig. 4b), strikingly similar to the head-to-head, charged domain walls (DWs) in insulating FE\textsuperscript{33}.

Within the framework of Maxwell’s equations, the divergent Coulomb repulsion of the head-to-head polarizations set-ups a pair of depolarization fields, which symmetrically point away from the DWs (for example, Fig. 4b), and the corresponding diverging-potential pair (analogous to polar catastrophe) renders the DWs as electron reservoirs. The thus-accumulated electron gas screens the polarizations and turns the DWs charged and conductive, with the electron-gas density (\(n\)) of \(n = 2P/eW\) (\(W\), DW width)\textsuperscript{29,33}. Maxwell’s equations are universal and the head-to-head polarizations in the 4-, 5- and 10-uc LAO/STO (Fig. 4a) should dictate the 2DEG formation, with \(n = (P_{LAO} + P_{STO})/eW\) (\(w\), the contributing LAO and STO uc).

In 10-uc LAO/STO (Fig. 4a and Table 1), the respective polarizations of contributing LAO and STO are \(P_{LAO} \sim 16.5\) and \(P_{STO} \sim 11.6\) μC⋅cm\(^{-2}\) in average, referring to \(n \sim 2.7 \times 10^{20}\) cm\(^{-2} \sim 4.2 \times 10^{13}\) cm\(^{-2}\) that is in remarkable agreement with the average 2DEG in STO (~4.4 × 10\(^{13}\) cm\(^{-2}\); Fig. 1e) and the corresponding Hall measurement (~4.6 × 10\(^{13}\) cm\(^{-2}\); Table 1). The average density of holes in the LAO, ~4.6 × 10\(^{13}\) cm\(^{-2}\) (Fig. 1e), is surprisingly close to that of 2DEG in the STO, directing to an overall charge balance in the context of classical electroteics\textsuperscript{20,22}. The metallic 4- and 5-uc LAO/STO show comparable quantitative agreements (Table 1). The interfacial conductivity in LAO/STO is firmly mandated by the strain-resurrected head-to-head polarizations. A subtle difference in the maximum-\(P_{STO}\) location (~1–1 UC uc for...
The electronic and structural characteristics of conductive LAO/STO.

| Characteristics | 4 uc | 5 uc | 10 uc |
|-----------------|------|------|-------|
| 2DEG (cm⁻²) *  | 4.3 x 10¹³ | 4.8 x 10¹³ | 4.4 x 10¹³ |
| 2D holes (cm⁻²) * | 4.1 x 10¹³ | 4.6 x 10¹³ | 4.6 x 10¹³ |
| \( P_{\text{LAO}} \) (µC cm⁻²) | 8.7 | 10.2 | 16.5 |
| \( P_{\text{STO}} \) (µC cm⁻²) | 6.0 | 8.4 | 11.6 |
| \( n \) (cm⁻²) | 4.0 x 10¹³ | 4.1 x 10¹³ | 4.2 x 10¹³ |
| \( w \) (uc) | 9 (6, STO; 3, LAO) | 11 (6, STO; 5, LAO) | 16 (8, STO; 8, LAO) |
| \( E_{\text{2DEG}} \) (meVÅ⁻²) | 4.4 | 4.9 | 4.5 |
| \( E_{\text{LAO}} \) (meVÅ⁻²) | 41.0 | 48.1 | 77.8 |
| \( E_{\text{STO}} \) (meVÅ⁻²) | 2.0 | 2.9 | 4.0 |
| Hall measurement (cm²) | 6.3 x 10¹³ | 3.5 x 10¹³ | 4.6 x 10¹³ |
| \( \Delta E \) (meV) | 49 | 50 | 50 |

*The experimental results in Figs 1e and 4a.
†The estimated 2DEG through \( n = (P_{\text{LAO}} + P_{\text{STO}})/eC_0 \), where \( w \) is the total length scale of contributing LAO and STO uc.
‡\( E_{\text{2DEG}} = e\Delta n/C_0 \), with \( e\Delta n = (e\sigma_{\text{LAO}} + e\sigma_{\text{STO}})/2 \) in the first approximations, \( n \) basically the average of 2DEG and 2D holes, and \( C_0 \) the vacuum permittivity.
§\( \sigma_{\text{LAO}} = P_{\text{LAO}}/C_0 \) and \( \sigma_{\text{STO}} = P_{\text{STO}}/C_0 \).
|| uc, band bending below the Fermi level due to the 2DEG in STO (Supplementary Note 4).

Discussion

The 2DEG-hole juxtaposition in the LAO/STO is similar to a plate capacitor with \( E_{\text{2DEG}} \approx 4.5 \text{meV Å}^{-1} \) (Fig. 4b, 10 uc) and the otherwise FE-like depolarization fields of \( P_{\text{LAO}} \) and \( P_{\text{STO}} \) are \( E_{\text{LAO}} \sim 77.8 \) and \( E_{\text{STO}} \sim 4.0 \text{meV Å}^{-1} \) (Table 1), respectively. Indeed, 2DEG perfectly screens \( P_{\text{STO}} \) (Figs 1e and 4a) and, therefore, \( E_{\text{STO}} \) is diminished, consistent with the vanishing potential in Fig. 1g. The anti-parallel \( E_{\text{2DEG}} \) to \( E_{\text{LAO}} \) is nonetheless like poling \( P_{\text{LAO}} \) (Fig. 4b), mediating robust \( E_{\text{LAO}} \) that could account for the observed field in the LAO of metallic LAO/STO (Fig. 1g; 80.1 for 20 uc, ref. 14; \( \sim 30 \text{meV Å}^{-1} \) for 5 uc, ref. 18). Moreover, the LAO in conductive heterostructures tends to restore to the \( \varepsilon \)-contracted, symmetry-preserved limit (grey dotted–dashed in Fig. 2a; and Fig. 2b) from the eighth uc, with the same observation in heterojunctions thicker than 8-uc LAO (ref. 8). Our investigations thus propose an upper bound of eight respective LAO and STO (ref. 19) uc, which display the strain-rejuvenated head-to-head polarizations, and the LAO (STO) uc atop (beneath) are bulk-like, centrosymmetric, corroborating the finite length scale of an interfacial strain field.

Indeed, there have been attempts to address the polarization distortions in LAO/STO using SXRD (refs 11,16) and HAADF (ref. 27), and these experimental reports are basically related to the theoretical prediction of a FE-like dipole in the LAO of insulating LAO/STO, pointing to the LAO surface to compensate for the corresponding polar-catastrophe electric field. While the LAO/STO, the otherwise vanishing field in the LAO is accompanied with diminishing FE-like distortions. In metallic LAO/STO, the structural degree of freedom at play...
should rather reside in the STO. The HAADF study\textsuperscript{27} proposed a separate pattern, with the FE-like polarization in LAO (STO) pointing to (away from) the metallic interface. These experimental contributions\textsuperscript{11,16,27} show conflicting structural conclusions, and the theoretical report\textsuperscript{20} has not taken into account the relevance of structural distortions in STO, which were nonetheless established in Fig. 2a and various reports\textsuperscript{10,11,19,26–28,39}. A close examination of refs 11,16,27 reveals that the characteristic anti-phase oxygen-octahedral rotations in LAO/STO (\(a^\prime\)\(-\)\(a^\prime\)\(-\)\(a^\prime\)) type in Glazer’s notation\textsuperscript{30}, Fig. 2e and Supplementary Fig. 4) have not been noticed therein. The improper reference-LAO lattice used in the SXRD deduction of atomic displacements\textsuperscript{11,16}, and the compromised electron-optics condition used in the HAADF imaging\textsuperscript{27} lead to further inconsistencies on the characterized structural details\textsuperscript{11,16,27}. These dissatisfactory factors in the experimental\textsuperscript{11,16,27} and theoretical\textsuperscript{20} studies may account for why our unambiguous observation of head-to-head FE-like polarizations (Fig. 4) was not found therein.

There exists another theoretical report concerned with polarizations in LAO/STO (ref. 40) in addition to ref. 20, while neither works predicted head-to-head polarizations in conductive heterostructures. Indeed, both reports could not have been aware of the three experimentally observed structural factors hereby, simultaneously strained interfacial LAO and STO uc due to the similar elastic constants of the materials, hidden FE-like instabilities of the strained LAO and STO, and accompanied octahedral rotations. The lack of considerations on these lattice degrees of freedom\textsuperscript{20,40} may explain why there is no existing theoretical prediction on our experimentally resolved polarization configuration. It is nonetheless noted that head-to-head polarizations are customarily found in \(n^\prime\)-type FEs, such as \(\text{BaTiO}_3\) (ref. 41) and \((\text{Ca,Sr})_3\text{Ti}_2\text{O}_7\) (ref. 42), whereas the tail-to-tail counterparts prefer \(p^\prime\)-type FE materials, for example, \(\text{HoMnO}_3\) (ref. 43) and \(\text{YMnO}_3\) (ref. 44). This intriguing correlation is addressed by the conventional electrostatic argument that head-to-head (tail-to-tail) polarizations are to be screened by electrons (holes)\textsuperscript{29}. Concerning LAO/STO, STO is known to be \(n^\prime\)-type, while LAO features the Fermi level at mid-gap\textsuperscript{14}. Electrons readily constitute the most apparent carriers in LAO/STO and head-to-head polarizations may thus be favoured in the heterostructures. This proposed electrostatic motif for the polarization geometry would, however, need to be scrutinized by future first-principles and phenomenological mean-field calculations that can incorporate the three structural ingredients.

Our exploration of the interfacial conductivity in LAO/STO due to strain-rejuvenated FE-like instabilities yields broad implications to the metallic interfaces in \(\text{ZnO/ZnMgO}\) (ref. 45)
and AlGaN/GaN (ref. 46), where residual piezoelectric moments appear across the interfaces of these wide-band-gap materials. What in common in these oxide and semiconductor heterojunctions is readily the presence of free charge carriers to screen the interfacial dipoles, which is an elementary concept in Maxwell’s equations. This prevailing cause of interfacial conductivity in accordance with Maxwell’s equations provides a con genital picture for future integration of oxide- and semiconductor-heterostructure physics. We believe that the FE-like sensitivity of conductive LAO/STO to electromechanical stimuli can find a structural basis herein, since the suggested contribution by electron–donor oxygen vacancies in the LAO (refs 5,6) is inconsistent with the holes found in the film (Fig. 1e). The current discovery also provides new structural hints for future experimental, theoretical investigations of the origin of superconductivity and ferromagnetism in metallic LAO/STO at low temperatures. Our quantitative atomistic-scale investigations advance the understanding in LAO/STO and would stimulate explorations of exotic strained 2D states like strain-resurrected magnetic, topological order parameters at crystallite boundaries.

Methods

The growth of LAO/STO heterostructures. The pulsed-laser depositions of (001)-oriented LAO/STO heterostructures were performed on TiO₂-terminated substrates at 850 °C under the oxygen pressure of 2 × 10⁻⁵ torr, with the post annealing at 700 °C for 20 min under 500 torr oxygen. These growth and oxygen post-annealing conditions are compatible with the suggested parameters for optimally reducing oxygen vacancy contributions to the interfacial metallicity (Supplementary Note 6). The STEM and EELS studies were performed on thus-grown LAO/STO with 3-, 4-, 5- and 10-uc LAO. The 4-, 5- and 10-uc (3-uc) LAO/STO are metallic (insulating) as expected, and the Hall measurements revealed the carrier density, 3 × 10¹⁵ cm⁻² Table 1, characteristic of conventional high-mobility electron gases at the LAO/STO interface. The 2DEG density has been known to show little variation as a function of temperature and only gently rises below 30 K, with the low-temperature upturn in electron density to be associated with increased electrostatic screening by the large dielectric constant of STO at low temperature. While STO is subject to a tetragonal phase transition at ~105 K, this low-temperature phase is centrosymmetric (space group, I4/mcm) and constitutes the ground state of STO (refs 51,52), with noticeably small tetragonal distortion of c/a₀ = 1.001 (p, primitive cell) and free from polarization displacement. Two latter structural ingredients of STO at low temperature would, therefore, only marginally affect the head-to-head polarizations formed at room temperature, and the effect of increased dielectric constant of STO at low temperature is basically on the screening characteristics of 2DEG (refs 50,53). The 2DEG densities in Table 1 represent the characteristic values at 80 K.

The STEM imaging and STEM-EELS chemical mapping. The STEM investigations were conducted on a JEOL-2100F microscope, operated at 200 keV and equipped with a CEDOS spherical-aberration corrector and a Gatan-Efina EELS spectrometer. The cross-sectional samples were prepared by conventional mechanical polishing, followed by Ar-ion milling and a gentle Ar⁺-beam cleaning before STEM study. The thickness of the specimens along the incidence is systematically 0.3–0.4 μm, and a probe current of ~78 pA was exploited. The HAADF and annular bright-field imaging experiments were subject to the respective collection angles of 72–72.2 and 19.2–21.2 mrad, with the frame time of ~8 s (32 μs per pixel; 512 × 512 pixels; 0.36 Å per pixel). The STEM and EELS investigations were performed with a defocus of 150 ms and the line-scan targeting of Ti L₃-edges (Supplementary Fig. 7a) and O K-edge spectra (Supplementary Fig. 8a) was conducted with an exposure time of 600 ms per pixel and a dispersion of 0.2 eV per pixel (corresponding energy resolution, ~1.0 eV). All STEM-EELS results were acquired on an EELS collection angle of 30 mrad and constitute the characteristic values at 80 K.

Data availability

The data that support the findings of this study are available from the corresponding author M.-W. C. on request.

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