

Correlated Lattice Instability and Emergent Charged Domain Walls at Oxide Heterointerfaces

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Charged domain walls provide possibilities in effectively manipulating electrons at nanoscales for developing next-generation electronic devices. Here, using the atom-resolved imaging and spectroscopy on $\text{LaAlO}_3/\text{SrTiO}_3//\text{NdGaO}_3$ heterostructures, the evolution of correlated lattice instability and charged domain walls is visualized crossing the conducting $\text{LaAlO}_3/\text{SrTiO}_3$ heterointerface. When increasing the SrTiO_3 layer thickness to 20 unit cells and above, both LaAlO_3 and SrTiO_3 layers begin to exhibit measurable polar displacements to form a tail-to-tail charged domain wall at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, resulting in the charged redistribution within the 2-nm-thick SrTiO_3 layer close to the $\text{LaAlO}_3/\text{SrTiO}_3$ interface. The mobile charges in different heterostructures can be estimated by summing up Ti^{3+} concentrations in the conducting channel, which is sandwiched by SrTiO_3 layers with interdiffusion and/or oxygen octahedral rotations. Those estimated mobile charges are quantitatively consistent with results from Hall measurements. The results not only shed light on complex oxide heterointerfaces, but also pave a new path to nanoscale charge engineering.

conductivity at a head-to-head CDW is 6 orders of magnitude higher than in bulk.^[2] Owing to the narrow domain wall width with only several unit cells (uc), the ferroelectric domain walls can serve as a well-confined conducting channel in the insulating multiferroic BiFeO_3 , leading to the room-temperature electrical conductivity.^[3,4] Furthermore, the conductivity of ErMnO_3 domain walls can be controlled by voltage, indicating the potential for voltage-controllable domain wall-based devices.^[5] Therefore, due to the advantageous properties of CDWs compared to the domains they separate, there is great promise in building novel devices based on CDWs, such as nonvolatile ferroelectric domain wall memory devices.^[6] Sanchez-Santolino et al. reported that the head-to-head CDWs in BTO induce double energy barriers in a single tunnel junction, in which a resonant tunneling phenomenon

1. Introduction

In ferroelectric materials, charged domain walls (CDWs) are particularly interesting. When CDWs break the long-range order of electrical polarization, charge accumulation occurs at nanoscales, leading to a giant change on the local electrical conductivity.^[1] For examples, in BaTiO_3 (BTO), the electrical

was observed.^[7] Furthermore, a recent study showed that nonvolatile switching can be realized by using topologically protected CDWs.^[8] Therefore, it has been said that “the wall is the device.”^[9] To build a CDW-based low power device, the precise control of the CDWs is a prerequisite.


More importantly, CDWs are not exclusive to ferroelectric materials. Some non-ferroelectric oxide layers or heterointerfaces are also capable of exhibiting polar displacement and even CDWs. One example is the so-called polar metal, as explored at the $(\text{La}, \text{Sr})\text{MnO}_3/\text{BTO}$ interface where the induced polar displacement in MnO_6 octahedra is crucial to determine magnetic properties of the $(\text{La}, \text{Sr})\text{MnO}_3$ layer.^[10] Another example is the $\text{LaAlO}_3/\text{SrTiO}_3$ (LAO/STO) interfaces, where the discontinuity of formal polarization drives polar displacement in either LAO or STO.^[11–13] Recently, by changing the LAO layer thickness, Gazquez et al. reported an LAO structural transition from a ferroelectric-like polar mode to an antiferrodistortive rotation mode when the interface becomes conducting.^[14] On the other hand, Lee et al. considered the polar displacement at LAO/STO interfaces as the origin of 2D charge carriers—the head-to-head CDWs are found only at the conducting interface instead of the insulating interface.^[15] Till now, it is generally accepted that CDWs play important roles even in non-ferroelectric oxide heterostructures, but the detailed mechanism is still under debate.

In this study, we focus on the LAO/STO interface that is epitaxially grown on the NdGaO_3 (NGO) substrate. The

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DOI: 10.1002/adfm.201906655

LAO/STO//NGO heterostructures enable us to control carrier confinement by changing the STO layer thickness, and this cannot be achieved at the conventional LAO/STO interface where the LAO layer is grown on the STO bulk substrate. On the other hand, the NGO substrate provides a -1% compressive ($+2\%$ tensile strain) lattice-mismatch-induced strain to the epitaxial STO (LAO) layer, while a $+3\%$ tensile strain is expected at the conventional LAO/STO.^[16] Such an epitaxial strain could modify the bandgap,^[17,18] manipulate the orbital occupancy and bandwidth,^[19] thereby controlling the interfacial transport properties.^[12] By employing the atom-resolved scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS), we demonstrate the STO-thickness-dependent evolution of tail-to-tail CDWs (opposite atomic displacement directions in LAO and STO) that are precisely located at the LAO/STO interfaces. Associated with other factors such as interfacial cation interdiffusion (ID) and oxygen octahedral rotation (OOR), the modulation on carrier densities in a nanometer-thick conducting sheet is realized. Our findings not only highlight the important role of CDWs at the conducting LAO/STO interfaces, but also provide a feasible pathway to nanoscale charge engineering in complex oxide heterostructures.

2. Results

2.1. The Emergence of a Tail-to-Tail Charged Domain Wall

For the LAO/STO//NGO samples, we fix the LAO layer thickness at 15 uc and vary the STO layer thickness t_{STO} from 4 to 30 uc, as sketched in **Figure 1a**. **Figure 1b** compares the inverted annular bright field (ABF) images and corresponding relative displacement (δ_z) maps obtained from samples with $t_{\text{STO}} = 6, 12,$ and 20 uc. The displacement vector δ_z is determined by the relative displacement pointing from negatively charged O plane

(in BO_2 plane, denoted as O_{II} , the oxygen atom in AO plane is denoted as O_I) to the positively charged B-site cations such as Al or Ti. Accordingly, the negative (positive) δ_z in inverted ABF images, as indicated by blue (red) regions in displacement maps, corresponds to the upward (downward) electrical polarization that points from the substrate to sample surface (from the sample surface to substrate). As shown in **Figure 1b**, the $t_{\text{STO}} = 6$ and 12 uc samples show negligible off-center atomic displacements in either LAO or STO. In contrast, when t_{STO} is 20 uc, the LAO layer is characterized by blue color with the upward polarization, while the STO layer shows red color with the downward polarization. The emerging opposite polarization directions in LAO and STO resemble a CDW with a clear tail-to-tail configuration at the LAO/STO interface. Raw ABF images, and additional data on the CDW dependence on STO thickness is included in **Figures S1–S4** in the Supporting Information. From a simple analysis, we find a tail-to-tail domain wall helps to reduce the polar discontinuity between LAO and STO (See **Figure S5** in the Supporting Information and relevant discussions). More specifically, the layer-resolved B-site cation displacement (δ_{B}) and oxygen displacement (δ_{OII}) with respect to the centrosymmetric center of A-site cations are shown in **Figure 1c** for the $t_{\text{STO}} = 20$ uc sample. Both the δ_{B} and δ_{OII} change sign when crossing the LAO/STO interface. Furthermore, the off-center-displacement-induced polarization can be calculated by $p = \frac{\sum_i Z_i \delta_i}{V}$,^[20] where Z_i is the Born effective charge of different ions.^[21–24] δ_i is the ion displacement (δ_{B} , δ_{OII} , and δ_{OI}) relative to centrosymmetric position of A cation position, and V is the unit cell volume. As shown in **Figure 1d**, for the sample with $t_{\text{STO}} = 4–16$ uc, the estimated polarizations ($\approx 5 \mu\text{C cm}^{-2}$) in both LAO and STO layers are comparable with the measurement errors and are far below the typical polarization value observed in conventional ferroelectric materials.^[25,26] When the STO thickness reaches 20 and 30 uc,

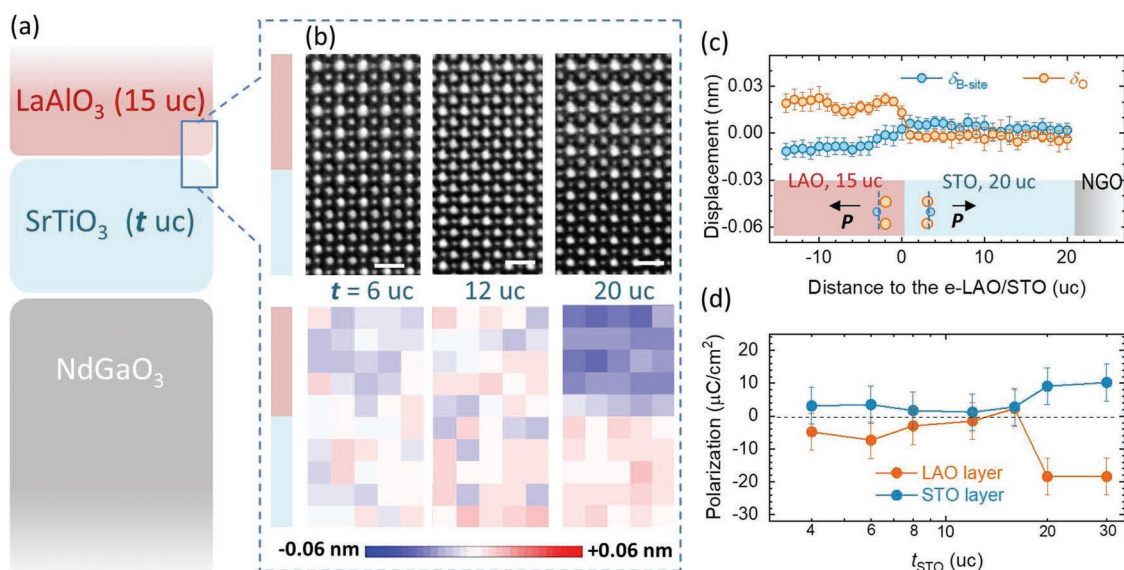


Figure 1. The evolution of atomic off-center displacements and induced polarizations in LAO/STO//NGO heterostructures. a) Schematic diagram of the LAO/STO//NGO heterostructure with 15 uc LAO and t uc STO. b) Inverted ABF images and corresponding relative displacement (δ_z) maps of the LAO/STO interfaces with 6, 12, 20, and 30 uc of STO (scale bars: 0.5 nm). c) The atomic layer-resolved average values of δ_{B} and δ_{O} in the 20 uc sample. d) The atomic displacement-induced polarizations at the LAO/STO interfaces with various STO layer thicknesses.

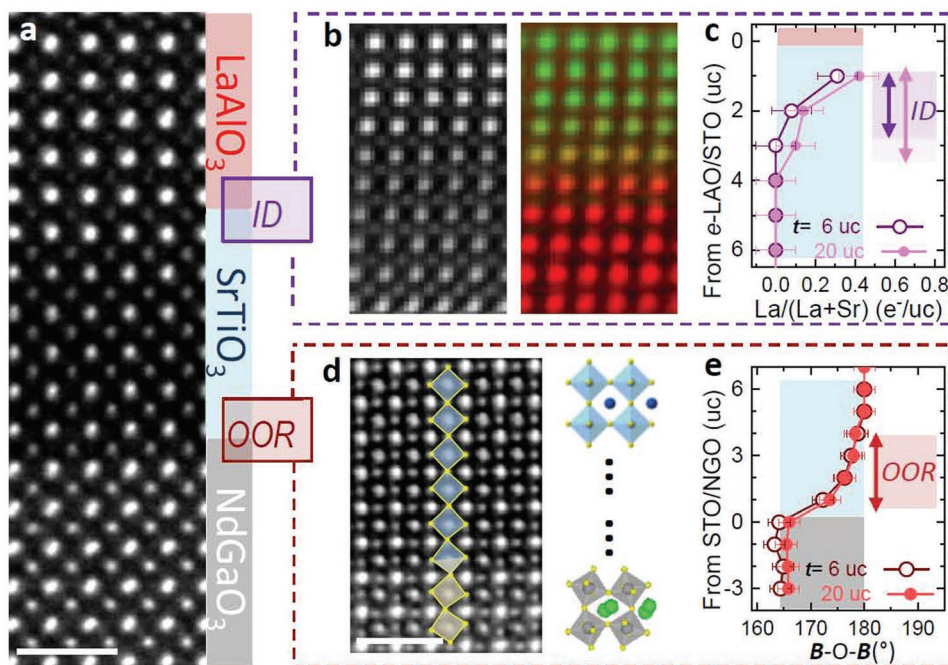


Figure 2. Interdiffusion and oxygen octahedral rotation across the LAO/STO and STO/NGO heterointerfaces. a) ADF image and the corresponding schematic diagram of the $t = 6$ uc sample (scale bar: 1 nm). b) ADF image and La (green) +Sr (red) mapping at the LAO/6-STO interface. c) The cation interdiffusion as a function of distance from the LAO/STO interface in the $t = 6$ and 20 uc samples. d) An inverted ABF image of the 6-STO/NGO interface after radial difference filtering projected along the $[1\bar{1}0]$ direction of NGO (scale bar: 1 nm). e) Calculated bond angle (θ) as a function of distance from the STO/NGO interface in the $t = 6$ and 20 uc samples.

the polarizations in LAO (P_{LAO}) and STO (P_{STO}) increase to around $-17 \pm 5 \mu\text{C cm}^{-2}$ and $11 \pm 5 \mu\text{C cm}^{-2}$, respectively. The emergence of ferroelectricity in STO thin films above a critical thickness was reported by Haeni et al.^[27] In the STO/DyScO₃ heterostructure, the strained STO film becomes ferroelectric at room temperature only when the STO thickness is above 10 nm (≈ 25 uc), close to our values of 20 uc.

2.2. Interdiffusion and Oxygen Octahedral Rotation

Figure 2 demonstrates other interfacial effects, i.e., ID and OOR that also greatly affect interfacial properties in the LAO/STO//NGO heterostructures. Taking the $t_{\text{STO}} = 6$ uc sample for an example, **Figure 2a** illustrates the annular dark field (ADF) image across the entire heterostructure consisting of two interfaces as LAO/STO and STO//NGO. For the LAO/STO interface, the ADF image and EELS elemental map in **Figure 2b** highlight one monolayer of intensive ID with La_{Sr} defects in the STO side, and this observation is also consistent with previous studies on the LAO/STO and LaMnO₃/STO heterostructures.^[15,28] The replacement of one Sr²⁺ ion by La³⁺ in STO forms one localized positive charge, the resultant local lattice distortion and potential fluctuations cause Anderson localization on the transferred two-dimensional electrons.^[29] As a result, La diffused STO region is still insulating despite generally La doped STO in bulk is a good conductor.^[30] In **Figure 2c**, the ID ratio of La/(La+Sr) or La_{Sr} concentration, which is estimated by analyzing EELS data, is compared between the $t_{\text{STO}} = 6$ and 20 uc samples. It can be

seen that ID of La_{Sr} only affects the 2-uc-thick STO layer in the $t_{\text{STO}} = 6$ sample, while the ID layer extends to 3 uc in the $t_{\text{STO}} = 20$ sample. Also, the La_{Sr} concentration is higher than that in the 6 uc sample (more details in **Figure S6** in the Supporting Information). This phenomenon is also observed in the $t_{\text{STO}} = 30$ uc sample, as shown in **Figure S7** in the Supporting Information. Given that the LAO growth conditions are kept the same for all the samples and the change of STO layer thickness is unlikely to affect the interdiffusion between LAO and STO, it is reasonable to link the more intensive ID to the observed tail-to-tail CDWs in the $t_{\text{STO}} \geq 20$ uc samples. In order to stabilize the tail-to-tail CDWs, there must be positive bound charges at the LAO/STO interface.^[31] Therefore, the samples with tail-to-tail CDWs exhibit more intensive La_{Sr} intermixing, which lowers the energy of polar displacements at LAO/STO interface (see **Figures S8–S10** in the Supporting Information and relevant discussions).

For the STO//NGO interface, **Figure 2d,e** show clear OOR-induced deformation in the STO layer adjacent to the NGO substrate. Based on the inverted ABF image in **Figure 2d**, the layer-resolved B–O–B (B represents B-site ions such as Ga and Ti) bond angle θ is measured and plotted in **Figure 2e**. For both $t_{\text{STO}} = 6$ and 20 uc samples, the θ is gradually changed from the NGO-bulk-like 165° to STO-bulk-like 180° when crossing the STO//NGO interface. The thickness of the intermediate STO layer with $165^\circ < \theta < 180^\circ$ is 4 uc in both samples, and it is consistent with previous studies.^[32,33] It is known that the conduction band of STO is formed by Ti 3d t_{2g} orbitals.^[33,34] The hopping amplitude of t_{2g} electrons, or the conduction band width w , is determined by the overlap integral between Ti 3d t_{2g} and O 2p orbitals

in TiO_6 octahedra.^[35] A semiempirical relationship has been built to estimate w in 3d perovskite ABO_3 oxide with $w \approx \cos[(\pi-\theta)/2]/d^{3.5}$, where θ is the B–O–B bond angle and d is the B–O bond length.^[33,36] Therefore, w reaches the largest value with $\theta = 180^\circ$ for the most conducting state, while the reduction on θ lowers the electron hopping amplitude and w to induce the less conducting, or localized states in the perovskite oxides. The reduction of bandwidth can be up to 0.4 eV when the bond angle alters from 180° to 165° .^[37] The decrease of conduction bandwidth will raise the energy position of the conduction band minimum and thus increase the bandgap. Due to the reduction of bandwidth in the OOR region that is adjacent to the STO/NGO interface, the electrons should move to the STO OOR-free region that is close to the LAO/STO interface (evidenced by the fact that no Ti^{3+} is identified at STO/NGO interface). As a consequence, the OOR region near the STO/NGO interface does not contribute any conductivity.

To fully understand the STO-layer-thickness effect in LAO/STO//NGO system, we summarize the ID, OOR, CDW, and mobile charge modulation in Figure 3. In the $t_{\text{STO}} = 4$ uc sample, the 2-uc-thick ID region overlaps the 4-uc-thick OOR-affected region, and a similar phenomenon is also observed in the $t_{\text{STO}} = 6$ uc sample. As described above, both ID and OOR regions cause carrier localization; therefore, there is no conducting channel in the STO layer for transferred electrons in either sample. Increasing the STO thickness to 8–16 uc, the conducting channel is opened, which is sandwiched by the 2-uc-thick ID and 4-uc-thick OOR STO layers. From the quantification from the atomic layer-resolved EELS data (X – Z vertical panels in Figure 3, and 2D plots of these quantitative data shown in Figure S11 in the Supporting Information), the total concentration of Ti^{3+} in the conducting channel can be

estimated. Further increasing the STO thickness to 20 uc and above, the ID region gets extended due to the formation of tail-to-tail CDWs across the LAO/STO interface. Consequently, the conducting channel is 3 uc away from the LAO/STO interface. For the samples with $t_{\text{STO}} = 4$ –30 uc, we compare the estimated Ti^{3+} concentration (spectra and fitting method details seen in Figures S12 and S13 in the Supporting Information) in the conducting channel (blue dot symbols) with the carrier density obtained from room-temperature Hall measurement (red symbols) in the X – Y plane of Figure 3, and they are quantitatively consistent (agreement between blue and red symbols at different thicknesses). For example, in the $t_{\text{STO}} = 20$ uc sample, though the total Ti^{3+} concentration is large (1.13 e^- per uc), most Ti^{3+} ions reside in the extended ID region (0.99 e^- per uc) due to the emergent CDW. The resultant electron concentration from Ti^{3+} in the conducting channel is 0.14 e^- per uc, agreeing with the Hall measurement value of 0.13 e^- per uc. On the other hand, if we take the difference between total Ti^{3+} fraction (1.13 e^- per uc) and the interdiffusion $\text{La}/(\text{La}+\text{Sr})$ contribution (0.66 e^- per uc, read from Figure 2c), it yields 0.47 e^- per uc, which is very close to the idea amount of charge transfer of 0.5 e^- per uc. From this balance, we know Ti^{3+} is only from La diffusion and electronic reconstruction, and oxygen vacancy concentration remains negligible (Figures S14 and S15, Supporting Information). This further validates our model in understanding the LAO/STO//NGO heterostructures.

2.3. Discussion

Now we discuss the origin of the tail-to-tail CDWs, which can be mediated by the STO layer thickness in the LAO/STO//NGO

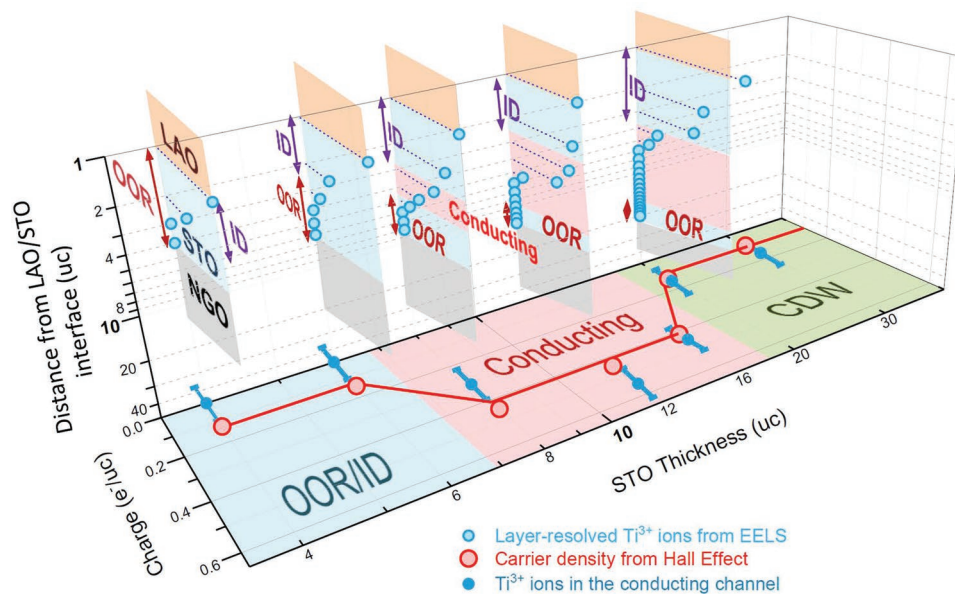


Figure 3. Various effects on the LAO/STO interface depending on the STO layer thickness. The vertical panels describe the evolution of ID, OOR and conducting channels in $t = 4, 6, 8, 12,$ and 20 uc samples. When the STO layer is thin (below 6 uc), interfacial effects such as interdiffusion (ID) and oxygen octahedral rotation (OOR) play dominant roles and result in localized charges (low carrier density). When the STO layer is the range of 8 – 16 uc, the conducting channel in the STO layer is established between ID and OOR regions. When the STO is thicker, tail-to-tail charged domain walls (CDWs) emerge and enhance the interdiffusion with positively charged $\text{La}_{\text{Sr}}^{+}$ which narrow the conducting channel at the LAO/STO interface. In the X – Y panels, the carrier densities (obtained from the Hall effect) show a positive correlation to the Ti^{3+} ions that are located in the conducting channel.

heterostructure. First, we consider the discontinuity of formal polarization at the LAO/STO interface. The alternatively-stacking $\text{LaO}^+/\text{AlO}_2^-$ sublayers give a downward formal polarization of $56 \mu\text{C cm}^{-2}$ in LAO layers, while the formal polarization is 0 in STO.^[38] To compensate such a polar discontinuity, electrons are transferred to interfacial STO layers. When the STO is thin, all those transferred electrons are confined within 2–3 uc STO layers close to the interface, resulting in a complete screening of polar discontinuity. On the other hand, when the STO layer becomes thicker, electrons prefer to propagate much deeper in STO to lower the energy raised by quantum confinement. However, when electrons are transferred to STO, the STO layer becomes charged with energy being increased. Accordingly, the energy of a charged sheet at the LAO/STO interface can be written as $E_{2\text{DEG}} \approx n\hbar^2/2mt_{2\text{DEG}}^2 + \sigma^2 t_{2\text{DEG}}/24\epsilon_0\epsilon$, where n is the electron density per unit area, m is the electron mass, σ is the sheet charge density, and ϵ is the dielectric constant of SrTiO_3 .^[16] By using the parameters as $n = 3.3 \times 10^{14} \text{ cm}^{-2}$, $\sigma = 50 \mu\text{C cm}^{-2}$, and $\epsilon = 100\text{--}300$ (considering the smaller ϵ for STO thin films), the value of $t_{2\text{DEG}}$ for minimizing the total energy is 4–6 uc. This is consistent with our EELS data, where the Ti^{3+} ions can be found only in the first five STO ucs which are closest to the LAO/STO interface with $t_{\text{STO}} \geq 8$ uc. By contrast, when t_{STO} is thinner than 8 uc, the transferred electrons are well confined in a 2–3 uc thick channel. Given that the screening length in charged STO is only 1–2 uc,^[39] this propagation of transferred electrons to 5 uc weakens the screening effect. Therefore, another mechanism, which is related to lattice-instability-induced polar displacements, is brought in to compensate the polar discontinuity. Our experiments reveal that when t_{STO} is 20 uc and above, the lattice-instability-induced polarization reaches around $-17 \mu\text{C cm}^{-2}$ (upward) in LAO and $11 \mu\text{C cm}^{-2}$ (downward) in STO to compensate 50% of the polar discontinuity at the LAO/STO interface.

The second possible explanation of the emergence of the tail-to-tail CDW focuses on strain engineering. The compressively strained STO thin film can exhibit ferroelectricity in the out-of-plane direction.^[27,40] In our case, with the increasing thickness of the compressively strained STO thin film, the possibility of the paraelectric-to-ferroelectric phase transition also increases. When the atomic displacement-induced polarization appears in the STO side, the emergence of the polarization in LAO with the opposite direction, more specifically, a tail-to-tail wall can stabilize the 2DEG at the LAO/STO interface.^[41] To maintain the charge neutrality, the presence of the tail-to-tail domain wall needs positive charge accumulation at the LAO/STO interface,^[42] thus leading to another localization mechanism to reduce the carrier concentration.^[31,43,44] As a result, the Ti^{3+} concentration in conducting channel of the 20 and 30 uc samples are 0.14 and 0.15 e^- per uc, which are very close to Hall effect measured carrier concentrations, 0.13 and 0.12 e^- per uc, respectively. Overall, the change of the Ti^{3+} concentration within the conducting channel as a function of STO thickness correlates accurately with transport measurements (Figure 3, X–Y plane blue and red symbols). We hence introduce a microscopic visualization of such correlation via atomic-resolution spectrum imaging and polarization analysis.

3. Conclusion

In summary, by the combination of aberration-corrected STEM imaging and EELS analysis, we discover the emergence of tail-to-tail CDWs at the LAO/STO interface on the NGO substrate when the STO layer thickness is above 20 uc. To stabilize the CDW, La/Sr interdiffusion is enhanced when STO thickness is 20 uc or above. The interdiffusion region, charged domain walls (at the LAO/STO interface) and oxygen octahedral rotation at the STO/NGO interface, induce a 2D confined conducting system, where the conducting channel is tunable by epitaxial STO layer thickness. It offers additional freedom to tune the conducting interface compared to conventional LAO/STO interfaces. The emergent CDWs in the LAO/STO/NGO heterostructures, as clearly demonstrated in our results, may provide possible non-volatile functionality that links to the ferroelastic domain walls in STO for next-generation electronic devices.

4. Experimental Section

Sample Fabrication: LAO/STO heterointerfaces were epitaxially grown on (110) oriented NGO substrates. The films were deposited by pulsed laser deposition (PLD) under an oxygen pressure of 2×10^{-4} Torr. The deposition temperature was 760 °C. In this experiment, LAO/STO heterostructures retain a fixed thickness of 15 uc for the LAO layers and with various STO thickness of 4, 6, 8, 12, 16, 20, and 30 uc, respectively.

STEM Imaging and EELS Analysis: The cross-sectional lamellas were prepared by a focused ion beam (FIB) machine (FEI Versa 3D), operated at 30 kV and cleaned at 2 kV. The STEM characterization was conducted on a JEM-ARM200F (JEOL) equipped with a cold field emission gun, an ASCOR aberration corrector and a Gatan Quantum ER spectrometer, operated at 200 kV. The HAADF and ABF images were acquired using the respective collection semiangles of 90–370 and 9–21 mrad, with a convergence angle of 24 mrad. The processed images were filtered by a radial difference filter, and raw images are provided in the Figure S1 in the Supporting Information. To determine the accurate location of atom columns, an iterative center-of-mass peak finding method is used.^[45] EELS results were recorded using an EELS collection angle of 100 mrad with 0.1 and 1 eV per channel, for energy loss near edge structure (ELNES) acquisition and EELS elemental mapping, respectively. The EELS chemical maps were subject to noise reductions by a principal component analysis (PCA) filter.

Transport Properties: Electrical contacts onto $5 \times 5 \text{ mm}^2$ samples were made with Al wires using wire bonding, and electrical measurements were performed by a Quantum Design physical property measurement system. While the Hall effect of all LAO/STO heterostructures was measured in the van der Pauw geometry.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors acknowledge the financial support from the Singapore National Research Foundation (NRF) under the Competitive Research Programs (CRP Awards No. NRF-CRP15-2015-01). C.L. acknowledges the financial support from the Lee Kuan Yew Postdoctoral Fellowship through the Singapore Ministry of Education Academic Research Fund Tier 1 (R-284-000-158-114). A.A. would like to thank the Agency for Science, Technology and Research (A*STAR) under its Advanced Manufacturing

and Engineering (AME) Individual Research Grant (IRG) (A1983c0034) and the National University of Singapore (NUS) Academic Research Fund (AcRF Tier 1 Grant No. R-144-000-403-114) for the financial support. S.J.P would like to acknowledge the financial support by the Ministry of Education, Singapore under its Tier 2 Grant (Grant No. MOE2017-T2-1-129).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

charged domain walls, correlated systems, nanoscale charge engineering, oxygen octahedral rotation, STEM-EELS

Received: August 13, 2019

Revised: September 10, 2019

Published online: September 26, 2019

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