Switchable Induced Polarization in LaAlO$_3$/SrTiO$_3$ Heterostructures

C. W. Bark,† P. Sharma,‡ Y. Wang,‡ S. H. Baek,† S. Lee,† S. Ryu,† C. M. Folkman,† T. R. Paudel,‡ A. Kumar,∥ S. V. Kalinin,∥ A. Sokolov,‡ E. Y. Tsymbal,‡ M. S. Rzchowski,§ A. Gruverman,‡ and C. B. Eom*†

†Department of Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin 53706, United States
‡Department of Physics and Astronomy, Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, Nebraska 68588, United States
§Department of Physics, University of Wisconsin, Madison, Wisconsin 53706, United States
∥Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

Supporting Information

ABSTRACT: Demonstration of a tunable conductivity of the LaAlO$_3$/SrTiO$_3$ interfaces drew significant attention to the development of oxide electronic structures where electronic confinement can be reduced to the nanometer range. While the mechanisms for the conductivity modulation are quite different and include metal–insulator phase transition and surface charge writing, generally it is implied that this effect is a result of electrical modification of the LaAlO$_3$ surface (either due to electrochemical dissociation of surface adsorbates or free charge deposition) leading to the change in the two-dimensional electron gas (2DEG) density at the LaAlO$_3$/SrTiO$_3$ (LAO/STO) interface. In this paper, using piezoresponse force microscopy we demonstrate a switchable electromechanical response of the LAO overlayer, which we attribute to the motion of oxygen vacancies through the LAO layer thickness. These electrically induced reversible changes in bulk stoichiometry of the LAO layer are a signature of a possible additional mechanism for nanoscale oxide 2DEG control on LAO/STO interfaces.

KEYWORDS: Heterointerfaces, complex oxides, oxygen vacancies, piezoresponse force microscopy

Since the discovery of a conducting two-dimensional electron gas (2DEG) at the interface between the insulating oxide materials LaAlO$_3$ (LAO) and SrTiO$_3$ (STO), significant advances in altering and controlling its properties are positioning 2DEG-based heterostructures as viable electronic devices. These control mechanisms include field effect from a back or front gate, epitaxial strain, atomic substitution at the 2DEG, and local heterostructure modification with scanning probe microscopy (SPM) techniques. In comparison to other methods, SPM has proved to be extremely flexible, allowing nanoscale rewritable modulation and control of the 2DEG conductivity.

An important aspect of the scanning probe modification of the 2DEG is a deposition of electric charge on the LAO$_3$ surface, and its subsequent electrostatic modulation of the 2DEG carrier concentration. In its most basic form, the capacitor structure formed by the LAO dielectric causes positive LAO surface charge to induce negative charge at the opposing capacitor plate formed by the 2DEG, thereby enhancing the 2DEG conductance. Electrostatic force microscopy (EFM) measurements indicate that a probing tip positively biased with respect to the 2DEG deposits positive charge on the LAO surface, and negatively biased tip deposits negative LAO surface charge.

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heterostructures, we propose that under an applied bias the oxygen vacancy structure distribution throughout the LAO thickness is reversibly modified, leading to the switchable electromechanical response, and to a corresponding change in 2DEG carrier concentration.

Epitaxial LaAlO$_3$/SrTiO$_3$ thin film heterostructures were grown on various single crystal substrates using pulsed-laser deposition (PLD) with in situ high-pressure reflection high-energy electron diffraction (RHEED). Here we focus on two sets of samples, one in which the LAO thickness was varied, and the other set with varying biaxial strain set by the substrate. The first set of samples had an epitaxial top LaAlO$_3$ layers of various thickness in the range from 5 to 80 unit cells (u.c.), grown on 50 u.c. thick (001) STO films on (001) (LaAlO$_3$)$_{0.3}$−(Sr$_2$AlTaO$_3$)$_{0.7}$ (LSAT) substrates. In addition, to perform comparative analysis epitaxial LAO films were grown on conducting oxide Sr$_0.2$Ca$_0.8$RuO$_3$ (SCRO) thin films on LSAT substrates.

The second set of samples had varying degrees of biaxial tensile strain in the LAO layer obtained by growing LAO(20uc)/STO(50uc)/LSAT surface with the SPM probe under a dc bias with an alternatingly changing polarity ($V_{\text{write}} = \pm 8$ V). The EFM image was acquired with a dc read voltage of +2 V. (d) PFM phase and amplitude hysteresis loops acquired in the same heterostructure. (e) PFM phase and amplitude hysteresis loops acquired in the Pt/LAO/STO/LSAT heterostructure through the top Pt electrode.

Our basic results are indicated in Figure 1, where combined EFM and PFM analysis of the LAO/STO/LSAT heterostructures subjected to poling by positive and negative bias are shown. Note that EFM is sensitive to the presence of the surface charge, while PFM tests the electromechanical response and, as such, is sensitive to the bulk properties of the sample. In this experiment, a set of concentric frames has been written by scanning the LAO surface with the SPM probe under a dc bias with polarity alternatingly changing from frame to frame ($V_{\text{write}} = \pm 8$ V). The EFM image of the produced pattern obtained with a dc read voltage of +2 V is shown in Figure 1a. In EFM, dark areas, which appear under the application of the positive bias, correspond to a positive surface charge. Bright areas (written by negative bias) correspond to negative surface charge. On the other hand, analysis of the PFM phase image of the same pattern (Figure 1b) reveals that in the positively written area (appearing as bright areas in Figure 1b) a differential positive bias increases the sample thickness. Interpreting this as a response to an electric field in the same direction as an LAO ferroelectric polarization, this would correspond to negative bound polarization surface charge, that is, opposite to the sign of the surface charge detected by EFM. Similarly, PFM analysis assigns a positive sign to the bound polarization charge in the areas subjected to the negative writing bias (dark regions in the PFM phase image in Figure 1b). This suggests that the surface charge detected in EFM is a deposited “free” charge not associated with any LAO polarization and is not related to the PFM signal.

PFM spectroscopic measurements performed by monitoring the electromechanical response at a fixed tip position on the LAO surface as a function of the writing voltage swept in a cyclic manner reveal a clear hysteresis behavior (Figure 1d), very similar to that observed in ferroelectrics. Surface charge writing observed by EFM is consistent with results reported by Xie et al. However, our PFM data suggest that in addition to surface charge deposition, there is a change in the bulk properties, which produce a PFM response resembling that from an LAO ferroelectric polarization.
In PFM imaging of ultrathin oxide heterostructures, there is always a concern that an electromechanical signal could be affected by electrostatic tip−sample interaction effects. However, in our measurements the PFM signal arises mainly from the true electromechanical response and not from the electrostatic effect. Evidence for this includes a strongly nonlinear bias-dependent behavior of the PFM amplitude signal, PFM phase change range of almost 180°, as well as an essentially different appearance of the PFM amplitude and phase images with much sharper features than in the EFM image. This conclusion is further supported by the fact that both EFM and PFM images of the written patterns exhibit quite different relaxation rates (EFM signal decaying much slower than the PFM signal, i.e., 2−3 h for EFM and tens of minutes for PFM). Most importantly, we have also observed a switchable electromechanical response and hysteresis behavior in the LAO/STO/LSAT samples with top Pt electrodes (Figure 1e). In this geometry, electrostatic forces are typically too small to affect the PFM signal19−21 and the contribution of purely electrostatic interactions to the PFM hysteresis behavior can be largely excluded.

The next question we addressed was the source of the switchable PFM behavior: does it stem from the STO or LAO layer, or is it a result of the interplay between responses from both layers and an interaction with the 2DEG? To answer this question we grew a 20 u.c. thick LAO layer on top of the lattice-matched conducting oxide Sr_{0.2}Ca_{0.8}RuO_{3} (SCRO), on an LSAT substrate (Figure 2a). Remarkably, poling and subsequent PFM imaging as well as PFM spectroscopic measurements revealed pattern maps and hysteresis behavior (Figure 2b,c) closely resembling the corresponding data obtained on LAO/STO/LSAT heterostructure (Figure 1c,d). For an LAO substrate with no conducting bottom electrode, we find (by EFM measurements) that surface charge is deposited under electrical bias, but no PFM response is observed. For a 50 u.c. thick STO layer deposited on the SrRuO_{3}/SrTiO_{3} substrate, only EFM and no PFM contrast has been recorded (Figure 2d−f). We conclude, therefore, that the switchable electromechanical response in LAO/STO stems from the LAO layer with the conducting bottom interface playing a role.

Switchable piezoresponse and hysteretic PFM behavior makes it very tempting to interpret the observed features as a manifestation of a spontaneous electric polarization directly switchable with external electric field. However, attributing the switchable electromechanical response to a switchable polarization seems to be in contradiction with the known polar behavior of LAO/STO heterostructures. In undistorted LAO, positively charged (LaO)^+ atomic layers and negatively charged...
structural distortions in the SrTiO₃ layer leading to further LAO overlayer to strained STO results in ferroelectric-like experimental work²³,²⁴ indicates that an epitaxial interface with voltage have been written on the LAO surface using a dc writing STO(50uc)/LSAT heterostructure. Square-shaped patterns electromechanical response has been obtained by studying ization as a dominant mechanism can be excluded. data suggests that the presence of stable ferroelectric polar-ization as a dominant mechanism can be excluded. However, in conjunction consistent with the field-induced ionic migration process or and PFM response is nonlinear on thickness in principle is increase with LAO layer thickness before saturating at large thickness. The fact that nucleation bias is thickness dependent (Figure 3b). From the hysteresis loops analysis, it can be seen that the initial (before poling) piezoresponse amplitude signal decreases with thickness (Figure 3c), consistent with increased electric field spreading in the LAO layers with larger thickness. In addition, the nucleation bias $V_n$ (determined as the bias voltage of the PFM amplitude minimum) exhibits an increase with LAO layer thickness before saturating at large thickness. The fact that nucleation bias is thickness dependent and PFM response is nonlinear on thickness in principle is consistent with the field-induced ionic migration process or ferroelectric polarization switching. However, in conjunction with the observed decay of the written domain patterns, this data suggests that the presence of stable ferroelectric polarization as a dominant mechanism can be excluded.

Further information related to the mechanism of the electromechanical response has been obtained by studying the relaxation behavior of the written states of a LAO(20uc)/ STO(50uc)/LSAT heterostructure. Square-shaped patterns have been written on the LAO surface using a dc writing voltage $V_{\text{write}} = \pm 6$ V. PFM images were obtained at various time intervals with the decrease in PFM amplitude signal being an indicator of the relaxation behavior. Figure 4 shows a time dependence of the PFM amplitude signal in a region poled with $-6$ V (corresponds to unstable state). The PFM amplitude $P(t)$ is consistent with a logarithmic law decay $PR(t) = P_0 - \alpha \ln(t/t_0)$. We have found that the relaxation rate of the PFM amplitude signal depends on LAO lattice strain. The inset to Figure 4 shows composite PFM amplitude images with the left parts showing maps taken immediately after poling and right parts acquired at a later time. It can be seen that larger tensile strain leads to a significant increase in the relaxation rate: LAO with 2% tensile strain on a STO/LSAT template shows a retention of 10⁻⁵ s in comparison with only 10⁻² s in the LAO/STO/DSO with 4% tensile strain.

Hysteresis in the PFM response can be considered in terms of hysteretic switching of an electric polarization in the LAO layer. As ferroelectricity is not a plausible mechanism, we propose an alternative mechanism that could produce a switchable PFM response that is related to oxygen vacancy migration under the influence of an applied electric field. Indeed, the molar volume of materials generally increases with oxygen vacancies (since cation effective radii in lower oxidation states are higher), so that injection and removal of oxygen

Figure 3. (a) Schematic diagram of the LAO/STO/LSAT heterostructure. Thickness of LaAlO₃ layer was varied from 5 to 80 unit cells. (b) PFM phase and amplitude hysteresis loops of the LAO/STO/LSAT heterostructures for various LAO thicknesses. (c) Thickness dependence of the nucleation bias $V_n$ and zero-bias piezoresponse signal PRS.

Figure 4. Relaxation behavior of the LAO(20uc)/STO(50uc) heterostructures. Insets show composite PFM amplitude images of the LAO layers on the different substrates imposing various degrees of tensile strain. Left parts of the composite images illustrate patterns immediately after poling and right parts show patterns at a later time. A solid line represents a logarithmic function $PR(t) = P_0 - \alpha \ln(t/t_0)$. A solid line represents a logarithmic function $PR(t) = P_0 - \alpha \ln(t/t_0)$. A solid line represents a logarithmic function $PR(t) = P_0 - \alpha \ln(t/t_0)$.
vacancies can cause the strain modulation leading to switchable electromechanical response. More fundamentally, a switchable internal electric field or induced electric polarization would bias the intrinsic electrostriction and produce a switchable PFM response. The required electric field could arise from a bistable surface charge or a bistable distribution of oxygen vacancies, driven by the tip bias. Recent theoretical calculations\(^{31}\) show that oxygen vacancies have a small local energy minimum at the LaO–TiO\(_2\) interface. The LAO surface is also expected to be a local energy minimum for oxygen vacancies, which provides a mechanism for two stable oxygen vacancy configurations at the LAO surface and the LAO–STO interface. Note that previously demonstrated surface charge deposition that control 2DEG conductivity\(^2\) would not be present in our samples with Pt top electrodes.

The electrically induced oxygen vacancy migration mechanism is consistent with our measurements of PFM relaxation in LAO/STO heterostructures on substrates with different lattice constants (Figure 4). Biaxial tensile strain leads to a unit cell volume increase, which likely leads to an increase in the density of oxygen vacancies. The higher oxygen vacancy concentration would lead to faster diffusivity, and faster relaxation of the PFM signal, consistent with the experimental results described above.

The above considerations are supported by a simple model for oxygen vacancy formation based on the electrostatic energy of the system. The model assumes that a uniform electric field is developed in the polar LAO layer and in STO due to the free-electron charge distributed within confinement width \(\lambda\) near the interface.\(^{32}\) Oxygen vacancies are formed within a plane located at distance \(d\) away from the interface. Two uncompensated electrons move to the interface leaving positively charged holes at the vacancy site.\(^{31,33}\) The hole–electron pair creates an electric field. If oxygen vacancies are created in LAO this electric field is opposite to the intrinsic field in the LAO and thus the energy is reduced. The reduction in the electrostatic energy increases when moving to the LAO surface. This creates a minimum for the oxygen vacancy formation energy at the LAO surface (Figure 5). If oxygen vacancies are created in STO the field due to electron–hole pairs partly compensates the electric field due the free-electron charge penetrating into STO which reduces the electrostatic energy. However, this reduction is limited to the confinement width \(\lambda\) because at larger distances oxygen vacancies create an uncompensated electric field, which enhances the electrostatic energy (Figure 5). Thus, the model predicts the existence of two minima in the oxygen formation energy that may be responsible for the hysteretic behavior observed in our experiment.

It is also possible that oxygen vacancies are not concentrated at the LAO surface or at the LAO/STO interface but are distributed nonuniformly throughout the LAO thickness. In this case, an electric polarization could be induced by the resulting strain gradient through the flexoelectric effect.\(^{34}\) This polarization would be switchable by an electric field along with the oxygen vacancy strain gradient and would bias the electrostriction in the same way as an electric field arising from external sources.

These mechanisms produce a PFM response consistent with our observations. Recent experimental and theoretical study\(^{35}\) has demonstrated a large electrostrictive response of the LAO layer in LAO/STO heterostructures, finding an electric-field dependent \(c\)-axis strain of \(\varepsilon = -(0.2 \ A^2/V^2)E\), with \(E\) the electric field in the LAO layer. Here \(E\) is made up of a switchable static field and the ac field from the PFM tip. Taking a switchable field on the order of half the 0.24 V/Å intrinsic LAO electric field arising from interlayer charge transfer gives an ac strain of \(\varepsilon \approx -(0.4 \ A^2/V^2)E_{dc}E_{ac} \approx -(20 \ pm/V)E_{ac}\). The relative phase between the PFM response and \(E_{ac}\) would then shift by 180° when \(E_{dc}\) is reversed, which is consistent with the experimental data. Such a switchable electric field in principle could also arise from hysteretic behavior of electric charge deposited on the bare LAO surface by the PFM tip. However, as was mentioned above, the effect of the surface charge can be ruled out based on the fact that the switchable PFM response is present even in the LAO/STO heterostructures with the Pt top electrode (Figure 1e) when the electrostatic contribution to the measured response is negligibly small.

Finally, as the strained LAO layers on the Ti-terminated (001) STO exhibit not only a switchable polarization but also two-dimensional electron gas (2DEG)\(^{6,36}\) and it has been predicted that polarization can be used to control 2DEG properties at oxide heterointerfaces,\(^{37,38}\) we have investigated correlations between these two effects. Specifically, we have found that the conductivity of the 2DEG can be modulated significantly via LAO poling. A 40 \(\times\) 20 \(\mu\)m\(^2\) LAO/STO bridge structure has been fabricated on the LSAT substrate by ion milling to make it suitable for 4-point probe transport and PFM measurements (Figure 6a). The 20 \(\times\) 20 \(\mu\)m\(^2\) area across the bridge has been poled first by +9 V and then by −9 V by a PFM tip as is schematically shown in Figure 6a. Resulting change in the interface resistance upon poling by almost a factor of 2 is illustrated in Figure 6b. Note the apparent bias dependence of resistance for the −9 V poled state, which is actually resistance relaxation during the measurement cycle consistent with relaxation of the piezoresistive signal shown in Figure 4.

To summarize, we have observed switchable, hysteretic PFM response from the LAO layer in the LAO/STO/LSAT and LAO/SCRO/LSAT heterostructures. We propose that oxygen vacancies mobile under the influence of an applied electric field have a bistable configuration and that this is responsible for switchable hysteretic PFM response and contributes to switchable 2DEG conductance in LAO/STO heterostructures.

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**Figure 5.** Oxygen vacancy formation energy calculated using the electrostatic model. Parameters used in the calculation are as follows: the free electron density at the interface \(\sigma = 0.1 \ e/u.c.,\) the electron density due to oxygen vacancies \(\sigma_v = 0.5 \ e/u.c.\) (red line) and \(\sigma_v = 0.25 \ e/u.c.\) (blue line), and the dielectric constant of LAO \(\varepsilon_L = 24\) and that of STO \(\varepsilon_S = 36.\)
This represents an additional control mechanism for modification of the electrical properties of heterointerfaces. The proposed mechanism of switchable electromechanical response should be active in many other oxide heterosystems, but its detailed manifestation likely depends on a number of subtleties, such as oxygen octahedra rotations and distortions, strain, and lattice couplings at the nanoscale. Control of this phenomenon will enable new structures and devices that exploit nanoscale electromechanical coupling. A more complete understanding of the proposed mechanism is necessary to provide this control, which would be facilitated by advances in the nanoscale measurement of vacancy concentrations and their dynamics.39

ASSOCIATED CONTENT

Supporting Information
This section provides detailed information on materials and methods used to fabricate and characterize devices the LAO/STO heterostructures. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: eom@engr.wisc.edu.

Notes
The authors declare no competing financial interest.

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Figure 6. Tuning resistivity of 2DEG via poling in the LAO(20 uc)/STO(50 uc)/LSAT heterostructure. (a) An upper panel shows an optical image of the structure fabricated on the LSAT substrate for 2DEG resistivity measurements. A lower panel shows a schematic view of the part of the structure marked by a yellow block on the upper panel. A dashed-line block indicates the area that has been poled by a biased probe. (b) Bias dependence of the interface resistance after poling by $V_{\text{poling}} = -9 \text{ V}$ and $V_{\text{poling}} = +9 \text{ V}$. Note the 2DEG resistance change during measurements for the $-9 \text{ V}$ poled state is in agreement with the relaxation behavior illustrated in Figure 4. The inset schematically shows the changes in 2DEG upon poling.