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Tunable conductivity at LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$ (0 $\leq$ x $\leq$ 1) heterointerfaces

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The two-dimensional electron gas formed at LaAlO$_3$/SrTiO$_3$ heterointerfaces exhibits a variety of interesting physical properties. Herein, we report on tunable conductivity at LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$ heterostructures. By changing the Sr content in the Sr$_x$Ca$_{1-x}$TiO$_3$ (0 $\leq$ x $\leq$ 1) layers, the orthorhombicity of the films, which inevitably accompanies TiO$_6$ octahedral distortions in the unit cells, could be varied. As a result, the interfacial conductivity can be tuned over 6 orders of magnitude. We suggest that the use of pseudosubstrates with chemical substitution or alloying is a promising route to finely tune conductivity at oxide heterointerfaces.

Heterointerfaces play a crucial role in observing unexpected and astonishing properties of oxide-based complex material systems. One of the most prominent examples is the formation of two-dimensional electron gas (2DEG) at the interface between two insulating oxides LaAlO$_3$ and SrTiO$_3$,$^2$ where 2DEG is confined to within $\sim$1 nm of the LaO/TiO$_2$ interface.$^3$ The polar interface exhibits superconducting and magnetic ground states$^{4,5}$ which originates from electronic phase separation. The conductivity of the interface has been drastically modulated by external electric fields.$^6$ More excitingly, bistable conductivities of the interface have been demonstrated using scanning probe microscopy techniques, suggesting the potential application to non-volatile memories.$^9,10$ Due to the strong surface-interface coupling, the interfacial conductivity is also controlled by the surface adsorbates.$^{11,12}$ In addition to external perturbations, the interfacial conductivity of the LaAlO$_3$/SrTiO$_3$ interface could be tuned via structural deformation. Bark et al.$^{13}$ showed that biaxial strain can be used to tailor 2DEG properties of the LaAlO$_3$/SrTiO$_3$ heterointerface. Also Jang et al.$^{14}$ demonstrated that both biaxial strain and octahedral distortion greatly influence conductivities of oxide heterointerfaces, making them either conducting or insulating.

In this letter, we report tunable conductivity in LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$ heterointerfaces. By changing Sr content in Sr$_x$Ca$_{1-x}$TiO$_3$ films epitaxially grown on SrTiO$_3$ substrates, the orthorhombicity of the films are varied, while the in-plane lattice parameters of the Sr$_x$Ca$_{1-x}$TiO$_3$ films are kept constant by coherent growth. Electrical measurements reveal that the interfacial conductivity at the LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$ heterointerfaces is tuned over 6 orders of magnitude, showing that the transition from metal to insulator is controlled by the Sr content in the films. Our results in this study clearly demonstrate that the control of crystallographic structure in complex oxide heterostructures is a remarkably powerful tool to control the conductivity of buried 2DEG for oxide-based high on/off ratio switching and memory devices.

SrTiO$_3$ is an ideal cubic perovskite material with the $Pm3m$ symmetry and the lattice constant of 3.905 Å. The oxygen octahedra are perfectly regular, exhibiting the Ti-O-Ti angle of 180° [Fig. 1(a)]. In contrast, CaTiO$_3$ has an orthorhombically distorted perovskite structure with the $Pbnm$ symmetry and the lattice constants are $a$ = 5.379 Å, $b$ = 5.436 Å, and $c$ = 7.639 Å (JCPDS #04-011-8341). The $Pbnm$ symmetry is dictated by an $a' \cdot a' \cdot c''$ Glazer notation, in which the oxygen octahedra rotate in antiphase around the [100]$_p$ and [010]$_p$ axes with equal magnitude and in-phase around [001]$_p$. (The subscript $p$ denotes pseudocubic).$^{15}$ Such an octahedral rotation is characterized by the Ti-O-Ti angle of 153.5° along [001]$_p$ [Fig. 1(b)]. This suggests that the Ti-O-Ti angle can

be tailored between 153.5° and 180° for ternary Sr_xCa_{1-x}TiO_3 (0 ≤ x ≤ 1) compounds by varying the Sr composition.

Polycrystalline single-phase Sr_xCa_{1-x}TiO_3 (x = 0, 0.5, 0.75, 0.88, and 1.0) targets were prepared by conventional solid state sintering. Epitaxial Sr_xCa_{1-x}TiO_3 (x = 0, 0.5, 0.75, 0.88, and 1.0) films were grown on TiO_2-terminated (001) SrTiO_3 substrates by pulsed laser deposition (PLD) using KrF excimer laser (λ = 248 nm). During the growth, the oxygen partial pressure, substrate temperature, laser fluence, repetition rate, and target-substrate distance were 1 × 10^{-3} Torr, 700 °C, 2 J/cm², 2 Hz, and 5 cm, respectively. Subsequently, 5-nm-thick LaAlO_3 layer was deposited on the Sr_xCa_{1-x}TiO_3/SrTiO_3 structure under the same deposition condition. The surface morphology of the grown films was examined using a tapping mode atomic force microscopy (AFM). Structural characterizations of the films were performed using a high-resolution X-ray diffractometer (HRXRD, X’PertPro, PANalytical) with a (220) Ge crystal 2-bounce hybrid monochromator (λ = 1.5406 Å) and a high-resolution transmission electron microscope (HRTEM, Titan, FEI) operated at 300 kV. The interfacial conductivity at 300 K was evaluated using both current-voltage (I-V) and Hall measurements. I-V measurements have been carried out using indium ohmic contacts on the diagonal corners of 5 mm × 5 mm samples. The four-probe Van der Pauw method was used for the Hall measurements. For each sample, electrical measurements have been conducted for 10–20 times.

Figure 2(a) shows a 20 μm × 20 μm AFM image of a LaAlO_3 (5 nm)/CaTiO_3 (10 nm) film. The surface is smooth with the steps and terraces of the original SrTiO_3 substrate surface, indicating high-quality growth. The RMS surface roughness of the Sr_xCa_{1-x}TiO_3 and LaAlO_3 films (0.10–0.13 nm) was comparable to that of SrTiO_3 substrates (~0.10 nm). Figure 2(b) shows out-of-plane θ-20 HRXRD scans of LaAlO_3 (5 nm)/Sr_xCa_{1-x}TiO_3 (25 nm), LaAlO_3 (5 nm)/Sr_xCa_{1-x}TiO_3 (50 nm), and LaAlO_3 (5 nm)/Sr_xTiO_3 (50 nm) films. The shift of the orthorhombic (002) peak toward the lower angle with increasing the Sr content indicates an increase in the out-of-plane lattice parameter of the film. The out-of-plane lattice parameter of the CaTiO_3 film is determined to be 3.797 Å, which is smaller than the pseudocubic lattice parameter of bulk CaTiO_3 (3.8235 Å). This means that the film is subjected to a biaxial tensile strain in the plane of the film due to the lattice mismatch between the SrTiO_3 substrate and the CaTiO_3 film. The FWHM value of the (002)_p rocking curve was determined to be 0.078° for the 25 nm-thick CaTiO_3 and 0.061° for the 50-nm-thick Sr_xCa_{0.5}TiO_3 film. The in-plane phi scan of the LaAlO_3 (5 nm)/CaTiO_3 (25 nm)/SrTiO_3 structure in Fig. 2(c) confirms cube-on-cube epitaxy for the CaTiO_3 film.

A cross-sectional HRTEM image of a LaAlO_3/CaTiO_3/SrTiO_3 structure is shown in Fig. 3(a). It is clear that the CaTiO_3 film is single domain with high crystalline quality and has sharp interfaces with the substrate and the overlayer, as confirmed by high-magnification HRTEM images in Figs. 3(b) and 3(c). Selected area electron diffraction (SAED) in Fig. 3(d) shows that CaTiO_3 is aligned with SrTiO_3 and both are single domain. The weak spots such as (121) mean that the strained CaTiO_3 film is orthorhombically distorted and possesses octahedral tilting, which is confirmed by the fast Fourier transformed (FFT) diffraction pattern acquired from the CaTiO_3 layer in Fig. 3(a). For the LaAlO_3/Sr_xCa_{0.5}TiO_3/SrTiO_3 structure in Fig. 3(e), it is found that the Sr_xCa_{0.5}TiO_3 film retains the octahedral tilting and remains orthorhombic. From the SAED patterns, the crystallographic orientation relationship between the Sr_xCa_{1-x}TiO_3 film and SrTiO_3 substrate is found to be Sr_xCa_{1-x}TiO_3 [001]//SrTiO_3 [100], Sr_xCa_{1-x}TiO_3 [110]//SrTiO_3 [010], and Sr_xCa_{1-x}TiO_3 [110]//SrTiO_3 [001], which is analogous to the Sr_xRuO_3/SrTiO_3 system. For bulk CaTiO_3, the pseudocubic in-plane lattice parameters are calculated to be 3.824 Å and 3.820 Å which are close enough for the pseudocubic growth of CaTiO_3 layer on the cubic SrTiO_3 substrate. From AFM, TEM, and HRXRD reciprocal space mapping, we have confirmed that the CaTiO_3 and Sr_xCa_{0.5}TiO_3 films are fully strained on the SrTiO_3.
substrates without dislocations as seen the cross-sectional TEM images. The average in-plain tensile stain is calculated to be 2.1% for the CaTiO$_3$ film and 1.05% for the Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ film.

Figure 4(a) shows $I-V$ curves of LaAlO$_3$ (5 nm)/Sr$_x$Ca$_{1-x}$TiO$_3$ (10 nm)/SrTiO$_3$ heterostructures. For the LaAlO$_3$/CaTiO$_3$/SrTiO$_3$, the curve is identical to bulk SrTiO$_3$, which means that the sample is insulating. The $I-V$ curve of the LaAlO$_3$/SrTiO$_3$/SrTiO$_3$ is very similar to that of LaAlO$_3$/SrTiO$_3$, indicating that the insertion of the SrTiO$_3$ layer has no considerable effect on the $I-V$ characteristics. As the Sr content increases, the current at 5 V increases gradually from $<0.2$ nA to $>100$ nA. This is a very interesting result because the interfacial conductivity can be tuned about 6 orders of magnitude. In the previous reports, the tuning of conductivity at LaO/TiO$_2$ interfaces resulted in metal-insulator transitions. In this respect, the fact that various intermediate conductivities can be obtained by changing the Sr content is exciting. The consistent result has been obtained from Hall measurements [Fig. 4(b)] and the sheet conductance increases by similar orders of magnitude with Sr content. It is noteworthy that the sheet conductance ($5 \times 10^{-3} \Omega^{-1}$) of the LaAlO$_3$/SrTiO$_3$/SrTiO$_3$ is same as the previously reported values, indicating that the measured conductance comes from the carriers confined near the interface.

In ABO$_3$, the distortions of BO$_6$ octahedra lead to the localization of carriers, making even heavily doped A$^{3+}$TiO$_3$ systems insulating. In the LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$ (x < 1) heterointerfaces, orthorhombic Sr$_x$Ca$_{1-x}$TiO$_3$ (x < 1) layers with $Pbnm$ symmetry as shown in Fig. 3 should possess bent Ti-O-Ti bond angles of TiO$_6$ units ($\geq 180^0$), which are absent in cubic SrTiO$_3$. Such a change in crystallographic structure at the interface affects the interfacial conductivity. By changing the Sr content, we could minutely tune the magnitude of structural distortions, and in turn, modify the interfacial conductivity. We suggest that controlling the orthorhombicity of pseudo-substrates (or templates) via chemical doping or alloying is a fascinating route to tune sheet conductance at oxide heterointerfaces. In addition, dramatically different electronic properties of the heterointerfaces from the bulk counterparts can be exploited using the orthorhombic pseudo-substrates. We note that we were not able to quantify the magnitude of orthorhombic distortions (octahedral tilt angles along the out-of-plane direction) with the TEM data. Thus, further studies are needed to clarify the conductivity dependence on the octahedral tilt angles.

In summary, we have grown epitaxial LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$ heterostructures on SrTiO$_3$ substrates. The Sr$_x$Ca$_{1-x}$TiO$_3$ (0 < x < 1) films were orthorhombically distorted. With the Sr content in the Sr$_x$Ca$_{1-x}$TiO$_3$ films, the heterostructures exhibited gradual increases in the conductivity over a range of 6 orders of magnitude. Such a tunable conductivity was attributed to the variation in the crystallographic structure of the pseudo-substrate by changing the A-site cation composition, suggesting the creation of new functionalities in oxide heterointerfaces via the control of crystallographic geometry.
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FIG. 4. (a) Typical $I-V$ curves of LaAlO$_3$ (5 nm)/Sr$_x$Ca$_{1-x}$TiO$_3$ (10 nm)/SrTiO$_3$ structures. For comparison, $I-V$ curves of LaAlO$_3$/SrTiO$_3$ and bulk SrTiO$_3$ are presented. (b) Current at 5 V and sheet conductance of the LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$/SrTiO$_3$ structures as a function of Sr content.