Tuning the Electron Gas at an Oxide Heterointerface via Free Surface Charges

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Keywords: Heterointerface, complex oxides, surface charge, atomic force microscopy

Oxide heterointerfaces are emerging as one of the most exciting materials systems in condensed matter science.[1] One remarkable example is the $LaAlO_3/SrTiO_3$ (LAO/STO) interface, a model system in which a highly mobile electron gas forms between two band insulators,[2,3] exhibiting two dimensional superconductivity[4] and unusual magnetotransport properties.[5] An ideal tool to tune such an electron gas is the electrostatic field effect.[6] In principle, the electrostatic field can be generated by bound charges due to polarization (as in the normal and ferroelectric field effects) or by adding excess free charge. In previous studies, a large modulation of the carrier density and mobility of the LAO/STO interface has been achieved using the normal field effect.[7,8,9] However, little attention has been paid to the field effect generated by free charges. This issue is scarcely addressed, even in conventional semiconductor devices, since the free charges are typically not stable. Here, we demonstrate an unambiguous tuning of the LAO/STO interface conductivity via free surface charges

written using conducting atomic force microscopy (AFM). The modulation of the carrier density was found to be reversible, nonvolatile and surprisingly large, ~3×10^{13} cm^{-2}, comparable to the maximum modulation by the normal field effect.[6] Our finding reveal the efficiency of free charges in controlling the conductivity of this oxide interface, and suggest that this technique may be extended more generally to other oxide systems.

The build up of free charges on surfaces is a very common phenomenon in nature, and has been widely used in many fields such as xerography and printing. On the nanoscale, many studies have shown that scanning probe techniques such as AFM can be used to write surface charges on various materials.[10,11] However, these studies concentrate almost exclusively on applications to data storage or nanoxerography.[10,12] Only a few works utilize these surface charges to actively tune the conductivity of the underlying material, for example tuning the carrier density in GaAs/AlGaAs heterostructures at low temperatures.[13] A key feature of the LAO/STO interface is that there exists a critical LAO thickness, d_{LAO} ~ 3-4 uc, below which the interface is insulating.[7] It has been demonstrated that, just below this critical thickness, conducting AFM writing can tune the interface from insulating to conducting.[14,15] This phenomenon is related to the presence of surface charges written by the AFM.[16] Interestingly, these surface charges are found to be stable even far above the critical thickness,[16] providing the possibility to tune the conductivity in samples with a wide range of LAO thicknesses.

First we demonstrate that we can reliably write charges and switch their sign over a relatively large area of the sample. This is necessary to be able to enact significant changes to the conductivity of a micron sized region defined by optical lithography (see Experimental). **Figure 1a** shows the surface potential image of a pattern written on a d_{LAO} = 5 uc sample by raster scanning alternatively with conducting AFM writing biases of V_{write} = -4 V and V_{write} = +6 V over squares of decreasing size. Although the tip velocity used is 100 times greater than that for writing single lines in our previous publication,[16] well defined surface charges are deposited. Consistent with previous results,[16] the surface potential confirms that $V_{write} < 0$

accumulates negative charges, and positive charge for $V_{write} > 0$. The sign of the surface charge can be readily switched by re-scanning using the opposite V_{write}. We stress that the surface charges, even the border contrast between areas of negative and positive charge, are robust for many hours (**Figs. 1b and 1c**).

The surface charges exert significant influence on the conductivity of the LAO/STO interface. **Figure 2** shows a typical tuning using a d_{LAO} = 5 uc sample. In this case a bridge with area of ~5×5 μm^2 was pre-patterned using hard-masking (Fig. 2a).[17] The AFM topography image shown in Fig. 2b confirms that the bridge was well defined. Charge was written over the entire bridge area and the variation in the interface resistance was monitored. As is clear from Fig. 2c, using V_{write} = -4 V (+ 6V) increased (decreased) the resistance. This tuning was reversible and nonvolatile, analogous to conventional ferroelectric field effect devices,[18] although here no evidence for ferroelectricity is found.[16] Initially the resistance showed a fast decay but tends to saturate after ~1 hour, as shown in Fig. 2d. This decay behavior in resistance is consistent with the time-dependent variation of contrast of surface charges (see Fig. 1 and Ref. 16), confirming their close correlation.

To enable more quantitative studies, we also studied patterned Hall bars (see **Fig. 3a**) and performed Hall measurements at various temperatures after writing. **Figures 3b and 3c** show the temperature-dependent sheet resistance R_s and the sheet carrier density n_{2d}, respectively, for a d_{LAO} = 5 uc sample. The transport properties of the initial sample (before writing) are similar to those reported in the literature for these growth conditions.[2,5,9,17,19] After depositing charges over the whole region between the voltage contacts (see Fig. 3a), the transport properties are significantly altered. We note that the tuning in high temperature (> 100 K) and low temperature (< 100 K) regimes is quite different. In the former regime a positive writing decreases the interface resistance and increases the carrier density, and the reverse for a negative writing, in good agreement with simple electrostatic considerations. At lower temperatures, however, the relationship between the sign of the surface charges and n_{2d}

or R_s is more complicated. Indeed we have found no clear relationship in all of the samples we have measured with various d_{LAO} (not shown). At present the complexity in low-temperature transport is not well understood. Certainly the complex temperature and electric field dependence of the dielectric constant in STO[20] must play a role, as well as complexities associated with multiband conduction.[21] Compared with other recent field effect experiments,[7,8,9] our procedure has two significant differences. The first is that the electric field is applied continuously while cooling from room temperature, since the charges have been fixed on the surface, while in other experiments the electric field is only applied at low temperatures after the sharp increase in the dielectric constant of STO. Secondly, the electric field generated by the surface charge penetrates the LAO film, and thus changes the electrostatic condition across LAO film, rather than through the STO. We speculate that this latter point may have significant impact on any surface or interfacial electronic reconstructions occurring in this system in which the divergent electrostatic potential across LAO has been believed to be the driving force.[3]

Figure 3d shows the difference in n_{2d} between positive and negative writing for d_{LAO} = 5, 10, and 15 uc samples at 150 K. The modulation is ~3 × 10^{13} cm^{-2}, comparable to the maximum modulation achieved in conventional metal-insulator-semiconductor field effect devices.[6] Indeed we expect that the true maximum modulation is much higher than this, since these measurements were performed several hours after AFM writing, after which some spreading of the charge will have occurred, reducing the maximum electric field experienced by the electron gas.[16] As for normal field effect devices, the modulation of n_{2d} should be equal to the number of accumulated surface charges. However, assuming that the electric field is generated only by the surface charges, the best estimate from the surface potential image in Fig. 1a gives a surface charge density of ~10^{11} cm^{-2}, two orders of magnitude smaller than the modulation of n_{2d}. This large disagreement is expected since in present system not only the surface charges, but also the induced interface screening charges (opposite in sign to the

surface charges) contribute to the potential features observed using the AFM. This situation is similar to that observed in ferroelectric films in which the measured surface charge density is typically three orders of magnitude smaller than the remnant polarization.[22] Therefore, although the surface potential data give a qualitative measure of the surface charges, the image contrast cannot be directly used as a representation of the amount of charge.

Figure 3d also shows the change in room temperature resistance observed immediately after AFM writing, for d_{LAO} = 3.1, 5, 10, 15 and 25 uc samples. For positive V_{write}, the largest reduction in resistance ~60 % was observed for the d_{LAO} = 3.1 uc sample, whereas a ~40 % reduction was typical for the thicker samples, with no clear trend for increasing d_{LAO}. Using negative V_{write}, the resistance increase was at least 2000 % for all samples. For d_{LAO} = 25 uc and 3.1 uc samples the resistance can be even tuned into a highly insulating state, as discussed below.

Finally, we briefly discuss the tuning of electron gas at room temperature in two particular cases, the relatively thick (d_{LAO} = 25 uc) and thin (d_{LAO} = 3.1 uc, slightly above the critical thickness) samples. For the d_{LAO} = 25 uc sample the electric force microscope phase signal for $V_{write} < 0$ is very strong [16] and thus a strong variation of the interface resistance might be expected. This was confirmed experimentally: scanning with V_{write} = -8 V can drive the sample into an extremely insulating state, > 2 GΩ, as shown in **Fig. 4a**. This insulating state could be stable for more than 12 hours and the conduction can be recovered after scanning with $V_{write} > 0$. However, the insulating character is less stable than previously after switching into low-resistance state and subsequently switching back again into the insulating state, suggesting some fatigue or memory effect. Similar fatigue properties were observed in all samples studied. We note that this behavior might be expected if surface adsorption of molecules plays a facilitating role in stabilizing the surface charges. In this case repeated scanning of the AFM tip can metastably change the adsorbed species.

In the case of d_{LAO} = 3.1 uc, the relatively small carrier density makes it sensitive to small changes in n_{2d}. As shown in **Fig. 4b**, while $V_{write} < 0$ could induce an insulating state, this state was not as stable as for the d_{LAO} = 25 uc sample. After decaying for 3 hours, we then drove the sample into a low-resistance state using V_{write} = +8 V. Remarkably, this state, lower in resistance than the initial value, showed no obvious change in properties after even one month. This extremely long time scale is hard to reconcile with the fading of surface charges. As a perspective, previous observations of a stable low-resistance state for d_{LAO} = 3 uc (tuned by the field effect across STO substrate) sample[7] may be explained by the production and motion of oxygen vacancies in the STO. This process may also be occurring here, when we bias from the LAO side using the surface charges.[23]

In summary, we have demonstrated a reversible and nonvolatile way of tuning of the electron gas at various LAO/STO interfaces using free surface charges written using conducting AFM. We have shown that the modulation in carrier density is as large as ~3×10^{13} cm^{-2}, comparable to conventional field effect tuning achieved using bound charges. Our findings provide a new way to control conducting interfaces in oxides and may be immediately extended to other oxide structures. Due to their robustness and strong influence on the nearby carriers, free surface charges can be utilized in a highly flexible way in future electronic devices based on oxides.

Experimental

All samples were prepared by growing LAO films on TiO_2 terminated (001) STO substrates by pulsed laser deposition. Before growth, the STO substrates were patterned using conventional optical lithography and lift off of an amorphous AlO_x hard mask [17]. After this, the samples were first pre-annealed at 1223 K in 0.67 mPa of O_2 for 30 minutes, before the growth was performed at 1073 K in 2.66 mPa of O_2. The laser repetition rate was 1 Hz. The total laser energy was 20 mJ, and the laser was imaged to a rectangular spot of area

approximately 2.3 × 1.3 mm^2 on the single crystal $LaAlO_3$ target. After growth, each sample was annealed at 873 K in 4×10^4 Pa of O_2 for 1 hour and cooled to room temperature in the same O_2 pressure. The thickness of LAO films was measured using *in-situ* reflection high-energy electron diffraction.

A multimode AFM (Digital Instruments NANOSCOPE 3100, equipped with a NanoScope IV controller) was used throughout this work. The conducting probe was a PtIr5 coated silicon tip (Arrow NCPT, Nanoworld: resonant frequency = 270 kHz, force constant = 40 N/m, and tip radius of curvature ≤ 25 nm). All AFM experiments were performed in air, at room temperature, exposed to room light, with a relative humidity in a range of 40 – 60 %. For writing charges, a voltage bias is applied to the conducting probe and the sample is grounded. The q2DEG was electrically contacted by ultrasonic bonding with Al wire, which provided a simple method to break through the top insulating LAO layer. The AFM was operated in tapping mode with amplitude feedback. A relatively small amplitude setpoint (1-3% of the imaging value) was used to approach close to the surface. The tip velocity was 30 μm/s for the writing of the bridge samples (Figs. 1, 2 & 4) and 200 μm/s for the Hall bar samples (Fig. 3). For measuring the surface potential (Fig. 1), the tip lift height was 100 nm.

Acknowledgements

We thank M. Lippmaa for the use of clean room facilities. Y. W. X acknowledges funding from the Japan Society for the Promotion of Science (JSPS). H.Y.H. acknowledges support by the Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-76SF00515.

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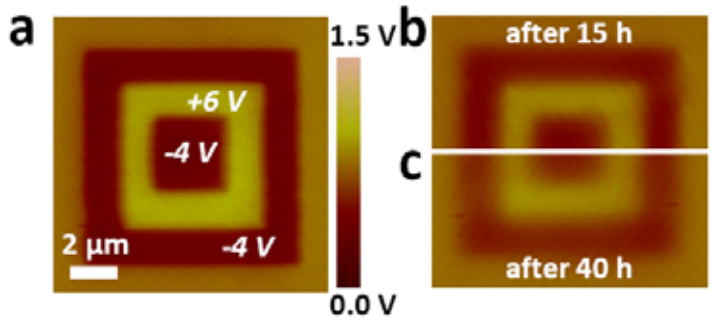

Figure 1. (a), Surface potential image of an electrostatic pattern written on a d_{LAO} = 5 uc sample. The pattern was achieved by first writing a 9 × 9 μm^2 square with V_{write} = -4 V, then a 6 × 6 μm^2 square with V_{write} = +6 V on the top of the first square, and finally a 3 × 3 μm^2 square with V_{write} = -4 V at the center of the image. (b) The surface potential image of the same pattern after 15 hours and (c), 40 hours. Scale bar used in (a) is the same for all images.

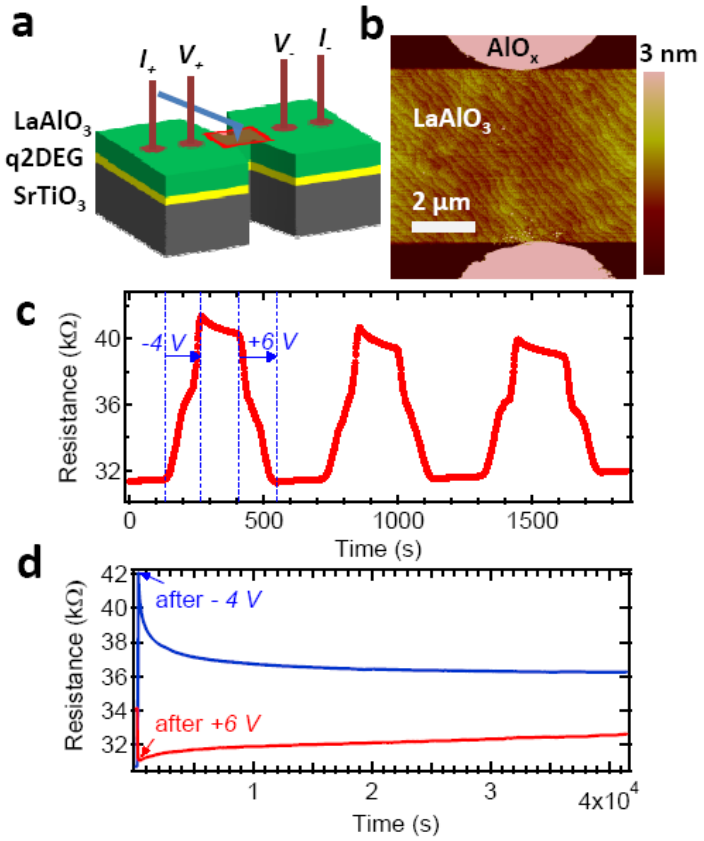

Figure 2. Tuning the electron gas of a d_{LAO} = 5 uc sample. (a), Schematic view of the bridge configuration, with the conducting interface (q2DEG) between the LAO and STO. The surface charges were written in the area shown by the red box. (b), AFM topographic image of the bridge area. The 1 uc terrace structure caused by the miscut of the substrate can be clearly seen. (c), The interface resistance alternatively increases and decreases during repeated writing with V_{write} = - 4 V and V_{write} = +6 V. Areas between blue vertical lines, connected by the blue arrows, indicate the writing process. (d), Decay of the interface resistance after writing surface charges with V_{write} = -4 V and V_{write} = +6 V. Arrows indicate the end of the writing process.

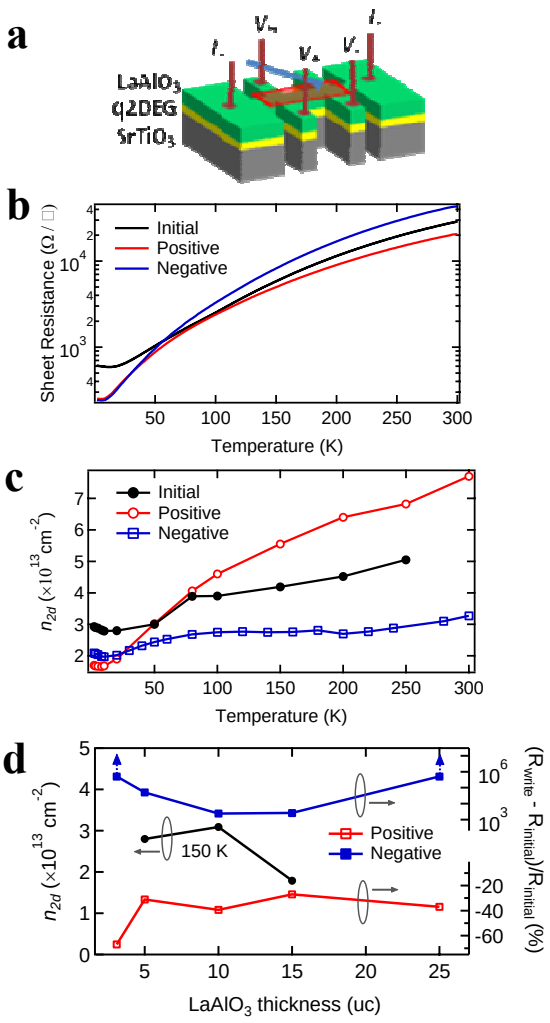

Figure 3. Transport properties measured using a Hall bar configuration. (a), Schematic view of the Hall bar configuration. The width of the bar is 10 μm and the distance between voltage contacts is 50 μm. Temperature dependence of (b) sheet resistance and (c) n_{2d} for a d_{LAO} = 5 uc sample. The measurements were performed at least 5 hours after writing (V_{write} = ±8 V). (d), Left scale: The difference in n_{2d} between positive and negative writing, measured at 150 K, for 5, 10, and 15 uc samples. Right scale: The maximum modulation of the resistance measured immediately after AFM writing charge at room temperature, for d_{LAO} = 3.1, 5, 10, 15 and 25 uc. For d_{LAO} = 3.1 and 25 uc, the maximum resistance exceeded the measurement limit (indicated by the vertical arrows).

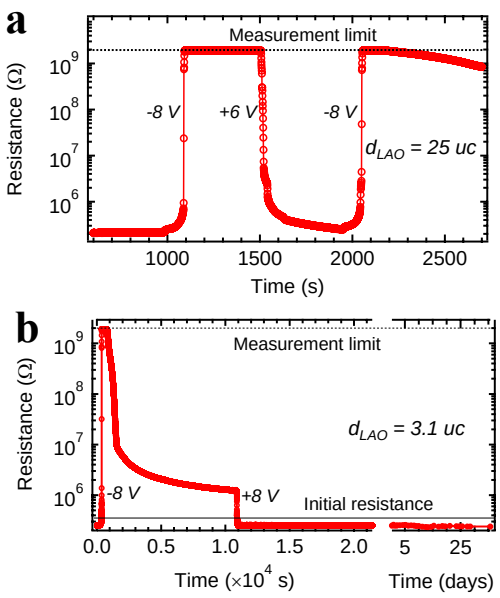

Figure 4. Tuning the d_{LAO} = 25 uc and d_{LAO} = 3.1 uc samples. (a) A scanning with V_{write} = -8 V drives the d_{LAO} = 25 uc sample into an extremely insulating state. A subsequent scan using V_{write} = +6 V recovers the low-resistance state. Switching back into the insulating state with V_{write} = -8 V. (b) V_{write} = -8 V drives the d_{LAO} = 3.1 uc sample into an insulating state. After the resistance decays for ~ 3 hours, AFM scanning with V_{write} = +8 V creates a low-resistance state that is extremely stable, (note the abscissa unit change to "days".)