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Asymmetric electroresistance of cluster glass state in manganites
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Asymmetric electroresistance of cluster glass state in manganites

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We report the electrostatic modulation of transport in strained Pr0.65(Ca0.75Sr0.25)0.35MnO3 thin films grown on SrTiO3 by gating with ionic liquid in electric double layer transistors (EDLT). In such manganite films with strong phase separation, a cluster glass magnetic state emerges at low temperatures with a spin freezing temperature of about 99 K, which is accompanied by the reentrant insulating state with high resistance below 30 K. In the EDLT, we observe bipolar and asymmetric modulation of the channel resistance, as well as an enhanced electroresistance up to 200% at positive gate bias. Our results provide insights on the carrier-density-dependent correlated electron physics of cluster glass systems. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4870480]

Coexistence of competing electronic and magnetic phases of comparable energies, a phenomenon often referred to as phase separation (PS), lies at the root of exotic physical phenomena like colossal magnetoresistance (CMR) in manganites.1,2 Because of PS from nanometer to submicrometer scales, both experimental and theoretical investigations propose that the transport in manganites has a percolative nature.3,4 In addition, PS in manganites is responsible for the magnetic glassy behavior where spins of isolated ferromagnetic regions are “frozen” in random orientations.5 Since the electronic and magnetic properties are strongly correlated in such transition metal oxides, the glassy behavior is expected to bear implications for the transport properties in manganite thin films. Prototypical PS manganites like La3/8–xPryCa3/8MnO3 (LPCMO) and Pr0.65(Ca0.75Sr0.25)0.35MnO3 (PCSMO) have been extensively investigated.5–11 In general, the dynamic fluid-like state of PS states and their glassy nature sensitively depend on the external parameters like temperature, magnetic field, and electric field.12–14 Additionally, since the long-range strain significantly affects the energetics of PS in manganites, thin films provide a viable platform, unavailable in the bulk counterparts, to elucidate the physics in such glassy PS systems.15–17 Compared with the chemical doping which invariably introduces disorders, electrostatic gating can modulate the carrier concentration in manganite thin films in a convenient and reversible manner.18 So far, most electric field effect experiments have been carried out on double-exchange ferromagnetic metallic (FMM) manganites.19–21 That of STO. Fig. 1(a) shows the XRD data of glassy cobaltates with tuned compositions, it was previously reported that the glassy magnetic order is sensitive to the hole doping level.22 Indeed, by carrying out electrostatic experiments on strained PCSMO thin films using EDLT, we observed a large electroresistance of 200% below the spin freezing temperature.

The epitaxial PCSMO films were grown on (001)-oriented STO substrates (cubic with a = 3.905 Å) using pulsed laser deposition, and the growth conditions are similar to previous reports.23–26 XRD measurements were performed using a X-ray diffractometer (SmartLab, Rigaku) in the high-resolution mode. Transport and gating measurements were carried out in a physical property measurement system (PPMS-14 T, Quantum Design) with externally connected meters. DC magnetization measurements were conducted using a superconducting quantum interference device SQUID magnetometer (MPMS XL-5, Quantum Design). EDLT devices were fabricated by patterning the films with a six-probe Hall-bar configuration (300 µm × 900 µm) with photolithography and wet etching. Au electrodes were then sputtered through a shadow mask and silicone paste was used to separate the electrodes from the exposed channel. To complete the fabrication of EDLT, we applied the ionic liquid N,N-diethyl-Nmethyl-N-(2-methoxyethyl)ammonium bis(trifluoromethyl-sulphonyl)imide (DEME-TFSI) to the channel and gate areas. Proper cares were taken to make sure that the ionic liquid is free from contamination during transport measurements.

We chose the STO substrate with the purpose of producing a tensile strain in the films since the bulk lattice parameters of PCSMO (orthorhombic Pnma) with equivalent a = 3.851 Å, b = 3.840 Å, and c = 3.848 Å are smaller than that of STO. Fig. 1(a) shows the XRD θ-2θ data for a typical PCSMO film with a thickness of 40 nm and only (00n) peaks in the pseudo-cubic notation are observed. Fig. 1(b) shows the dependence of the out-of-plane lattice parameter on the film thickness. As expected, thinner films exhibit smaller out-of-plane lattice parameters and hence they are under larger tensile strain from substrate. In Fig. 1(c), the

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reciprocal space mapping data taken around the (022) spot of PCSMO and STO indicate that the film has the same in-plane lattice parameter as the substrate, consistent with the coherent and epitaxial growth.

Different from the double-exchange manganites like (La, Sr)MnO₃, PCSMO with PS is much insulating, and the device channel would be too insulating to measure if the films were too thin. Strain effects further modify the transport properties of manganite thin films by promoting long-range charge ordering.²⁷–²⁹ We found that the resistance of films with thicknesses from 30 to 75 nm falls in the measurement range of our experimental setup. The transport properties of PCSMO films with various thicknesses are shown in Fig. 1(d). No metal-insulator transition was observed in films thinner than 30 nm, which is consistent with the larger strain observed in these films. For thicker films, the temperature of peak resistances, $T_P$, monotonously increases with film thickness. In the 40 nm PCSMO film, the resistance change modestly around $T_P$, indicating competing ground states in the low-temperature PS region. In our experiments, we focused on this particular thickness and investigated the electric field effect on the transport of mixed phases.

Temperature dependent zero-field cooled (ZFC) and field cooled (FC) measurements for the 40 nm PCSMO films were performed for various fields $H = 100, 200, 1000,$ and $5000$ Oe. The magnetization versus temperature curves present a λ-shape (Fig. 2(a)), which is the signature of magnetically inhomogeneous systems, and can be attributed to

FIG. 1. (a) X-Ray diffraction pattern of the 40 nm PCSMO film grown on STO. (b) Out-of-plane lattice parameter as a function of the film thickness as determined from X-Ray diffraction spectra. (c) RSM data of the (022) reflection measured on the 40 nm PCSMO film. (d) Resistivity vs. temperature curves of the PCSMO films grown on STO substrates for various thicknesses. The arrows mark the resistance peak temperatures $T_P$.

FIG. 2. (a) Temperature dependent magnetization in both FC (solid symbols) and ZFC (open symbols) modes measured on the 40 nm thick PCSMO film under different magnetic fields. The spin-freezing temperature $T_f$ and the merging temperature $T_m$ are indicated for the 1000 Oe data as an example. (b) Magnetic field dependent magnetization data measured at various temperatures. Inset shows the low-field part of the hysteresis loops to highlight the coercive field of the PCSMO film. (c) Field dependence of spin freezing temperature fitted by Eq. (1). (d) Magnetic field dependence of $T_f$ and $T_m$. The solid lines are guide to the eye demarcating different magnetic orders.
FC magnetization is almost constant. Since the data of merging temperature imbedded in the AFM matrix. As shown in Fig. 2(a), the merging temperature $T_m$ decreases on increasing field; above $T_m$, the same FM state is achieved for both the ZFC and FC processes, and the CG state is destroyed.

At temperatures 10 K, 50 K, and 100 K, we measured the M-H curves for the PCSMO film, and the data are shown in Fig. 2(b). The saturation magnetization $M_S$ was found to be $2.71 \mu_B$/Mn estimated from the M-H curve at 10 K. For an ideal double-exchange manganite with $x = 0.35$, the $M_S$ should be $3.35 \mu_B$. In manganites, the smaller experimental value of $M_S$ can be attributed to the spin-freezing behavior. As shown in the inset of Fig. 2(b), all the M-H curves exhibit hysteresis behavior which is a signature of ferromagnetism, and the coercive field monotonously increases with decreasing temperature.

For glassy systems, the magnetic field dependence of the freezing temperature $T_f$ should follow the Almeida-Thouless (AT) line

$$H(T) = H_0(1 - T/T_0)^p,$$

where $T_0$ is the spin freezing temperature and $p$ is normally $3/2$. In Fig. 2(c), we plot $T_f$ as a function of magnetic field, and fitting to Eq. (1) yields $p = 1.12 \pm 0.28$, $T_0 = 99 \pm 6$ K, and $H_0 = 2044 \pm 313$ Oe. This suggests the existence of AT critical line with the glassy behavior of disordered spin. The magnetic phase diagram, as established from the ZFC and FC magnetization measurements, is shown in Fig. 2(d).

Fig 3(a) shows a schematic of the EDLT device using the PCSMO manganite film as the channel. When a positive gate voltage $V_g$ is applied, holes are depleted in the channel due to the migration of cations (DEME$^+$) towards the channel/ionic liquid interface leading to a higher resistance. On the other hand, a negative gate voltage $V_g$ induces hole accumulation in the conducting channel, thereby reducing the resistance. In most field effect devices, the channel is a homogeneous single-phase materials. But in our EDLT device, the channel contains competing FMM and COI phases as illustrated in Fig. 3(b). Since the hole doping promotes the growth of FMM phase, a strong electric field is expected to modulate the size of hole-rich clusters, or even cause the seeding of new clusters, which are responsible for the low-temperature conduction in PCSMO.

The data of resistance versus temperature measured under different gate biases for the 40 nm PCSMO film are shown in Fig. 3(c). The largest field-induced transport modulation appears in the low-temperature region where the resistance is in the range of $10^9$ Ohm, whereas the high-temperature transport is not much affected by the electric field. There is a large difference in resistance between the cooling and the warming curves, and the thermal hysteresis is a signature of PS state. The resistance reaches peak values at the temperature $T_p$, and the insulator-to-metal transition clearly has a percolation nature. However, the metal-like state is not robust, and as the temperature lowers further ($<30$ K), the conduction path is broken and there is a reentrant insulating behavior at the temperature $T_R$. This anomalous reentrant insulating behavior was reported previously, and it was attributed to various factors including the magnetic glassy state. As shown in the ZFC magnetization curves in Fig. 2(a), there is a continuous suppression of magnetization at temperatures lower than $T_f$, thus the emergence of reentrant insulating state is clearly related to the freezing of spin clusters.

As a distinct feature of the electric field effect in our EDLT devices, the most significant modulation occurs in the low-temperature CG state. As illustrated in Fig. 3(d), in the

![Fig. 3. (a) Schematic experimental setup of the EDLT device with the PCSMO film as the channel. (b) Schematic illustration of the electrostatic tuning of phase separation in the PCSMO channel. $V_{g1}$ (on) and $V_{g2}$ (off) correspond to the application of negative and positive biases, respectively. (c) Temperature dependent resistance with various applied gate voltages ($-3$ V, $-2$ V, $0$ V, $+1$ V, and $+3$ V) measured for the 40 nm PCSMO EDLT channel. As example, for the cooling cycles under applied gate voltages of $+3$ V and $-3$ V, the peak temperatures are indicated as $T_{R1}$ and $T_{R2}$, while the reentrant temperatures are indicated by $T_{R1}$ and $T_{R2}$, respectively. (d) Electroresistance defined as $\Delta R/R = (R(V_g) - R(0 V))/R(0 V)$ vs. temperature data. For clarity, only the data of cooling cycles are shown. Characteristic temperatures are marked, including $T_f$ and $T_m$ from the 100 Oe magnetization measurements, as well as $T_R$ and $T_P$ from the cooling data under the +3 V gate bias.](image-url)
depletion mode of the field effect device, there is a giant increase of resistance in the reentrant insulating state. The largest electroresistance, which is defined as $\Delta R/R = ((R(V_g)) - R(0 V))/R(0 V))$, is $-200\%$ for $V_g = +3$ V around the temperature $T_R$. On the other hand, the magnitude of field effect in the accumulation mode is much weaker: the electroresistance is about 43% at the gate bias of $-3$ V. The electric field not only induces changes in resistance but also modulates the values of $T_R$. The shifts of $T_R$ due to gating are asymmetric for cooling and warming processes: it is about 1 K during cooling and 3 K during warming. Furthermore, we found that the $T_R$ can also be electrostatically tuned by about 5 K during cooling as indicated in Fig. 3(c).

One implication of the asymmetric gating characteristics is that the insulating cluster glass state is quite robust and the reentrant insulating behavior persists even under the highest applied gate bias. The electroresistance at the negative bias is much weaker compared to that at the positive bias, and a connected network of metallic domains is not electrostatically achieved at low temperatures. One reason for this gating asymmetry may lie in the fact that the chosen chemical composition of PCSMO is near the boundary of the robust COI phase in the bulk phase diagrams but far apart from the pure FMM phase. Therefore, the accumulated holes at a negative bias is not enough to trigger the overall phase transition and the resistive switching. The significant positive electroresistance is in agreement with this picture since the depletion of charge carriers move the system towards the more stable COI state with less FMM clusters. Moreover, our results suggest a strong nature of carrier localization in the reentrant insulating phase so that the accumulation of holes in the PCSMO channel changes little the insulating ground state.

In addition, recent reports proposed that an electric field can align fluid-like FMM domains embedded in the COI matrix, leading to improved connectivity and transport properties. Detailed time and voltage dependent studies pointed out the fluid-like dynamic nature of FMM domains in the COI matrix. Guo et al. reported that in the phase separated state, a laterally applied gating voltage induces electrophoretic-like domain movement and resistive switching at intermediate temperatures, while the electric field effect is suppressed at lower temperatures where the domain movement is restricted in the glassy phase. In our EDLT experiments, notable electric field effect extends to the low-temperature glassy region, suggesting the dominant role of electrostatic doping and possible field-induced seeding of new FMM domains in the transport modulation.

We should note that a large electric field may also induce strain and oxygen migration which are possible scenarios in producing field effects in oxides. The electric field induced strain effect can be excluded in EDLT experiments because the mechanical interaction between the ionic liquid and the oxide channel is quite weak. Furthermore, it was previously reported that the electric field effect produced by strain is ambipolar; in other words, the channel resistance increases for both positive and negative biases. Therefore, the bipolar field effect observed in our PCSMO devices indicates that the strain is not the dominant factor.

The scenario of oxygen vacancies moving in and out of the manganite channel under the influence of an applied electric bias is more difficult to rule out. In manganites, it has been reported that oxygen vacancies lead to increased resistance. Therefore, in principle, a positive bias may extract negatively charged oxygen ions out of the manganite film, and the resulting larger channel resistance is consistent with the experimental observation. To examine this scenario, we measured the response of the EDLT device using a designed sequence of gate bias. Fig. 4(a) shows the typical temperature-dependent resistance data for not only two different gate voltages of 0 V and $+3$ V, but also the repeated 0 V data after the gating cycle ($+3$ V, $+1$ V, 0 V, $-2$ V, and $-3$ V). The recorded time difference between two zero-bias measurements was 15 h, and during the experiment the device was kept in the PPMS chamber which is maintained at a pressure of $\sim 7$ Torr. The fact that the second zero-bias curve does not exactly overlap with the first one suggests that the chemical redox process involving oxygen ions or other kinds of electrochemical reactions at the manganite channel surface may play a certain role. However, the electrostatic doping should be a dominating factor; otherwise, a much stronger memory effect and dependence on gating history should have been observed. Furthermore, the good reproducibility of the zero-bias data is indicative of the fact that our gating experiments did not irreversibly damage the film.

We also examined an EDLT device with 30 nm PCSMO as the channel, and as shown in Fig. 1(c), this thinner film shows only insulating transport without insulator-metal transition. Unlike the 40 nm PCSMO films, the electric field effect of the 30 nm channel is much weaker and there is no pronounced temperature dependence (Fig. 4(b)).
thin PCSMO films, the FMM domains remain small and isolated throughout the whole temperature regime, and the electric field effect is suppressed because the transport is dictated by the COI matrix. This comparison suggests that phase separation near the percolation threshold is indispensable for achieving sizable field effect.

In summary, we have observed an unambiguous signature of cluster glass state in PCSMO thin films which is accompanied by an unusual reemergent insulating behavior near about 30 K. A large electric field effect with an electroresistance as large as ~200% also emerges in this reentrant insulating phase with FMM cluster. We believe that the observed asymmetrical characteristics of electrostatic modulation may be general for the glassy states in mixed-valence oxides with correlated electron, and EDLT experiments should be a powerful tool to reveal the physics in such complex materials systems.