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Effects of ferroelectric polarization switching on the electronic transport and magnetic properties of $La_{0.8}Ce_{0.2}MnO_3$ epitaxial thin films

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The authors report the electronic transport and magnetic properties of the $La_{0.8}Ce_{0.2}MnO_3$ (LCEMO) thin film epitaxially grown on the ferroelectric $0.67Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.33PbTiO_3$ (PMN-PT) single-crystal substrate and their dependence on the polarization state of the PMN-PT substrate. Upon electric-field-induced polarization switching, the electrical resistance and magnetization of the LCEMO film were modulated reversibly. The underlying coupling mechanism that is responsible for the electric-field-control of the resistance and magnetization strongly depends on temperature, being strain-mediated type at relatively high temperatures but becoming charge-mediated type with decreasing temperature. The knowledge about the evolution of the coupling mechanism with temperature not only helps to understand the drive force for multiferroic properties but also is important for theoretical modeling and device fabrication. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4817080]

I. INTRODUCTION

The magnetoelectric coupling in multiferroic heterostructures consisting of ferromagnetic (FM) complex oxide thin films epitaxially grown on ferroelectric (FE) substrates has sparked a surge of research activity due to fundamental scientific interest and potential new avenues for data storage and processing.[1–7] A model system for this study is hole doped manganites $R_{1-x}A_xMnO_3$ (R = La, Pr, etc., A = Ca, Sr, or Ba), characterized by inseparable energy overlaps of the spin-charge-lattice-orbital interactions and a diversity of unique behaviors.[8,9] Manganite films have been epitaxially grown on FE single-crystal substrates, e.g., $BaTiO_3$ (Refs. 4, 5, and 10) and $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$,[6,11] to form FM film/FE crystal heterostructures. For these heterostructures, the resistance and magnetization of manganite films can be modulated continuously via reversible strain induced by electric field applied to FE substrates.[4,12,13] The elastic strain transferred from FE substrates could change the strength of Jahn-Teller (JT) effect and double-exchange (DE) interaction through modifying Mn-O bond lengths and/or Mn-O-Mn bond angles. Additionally, these heterostructures can also be considered as ferroelectric field effect configuration.[14] The induced electric polarization at substrates produces an accumulation of positive or negative electric charge at interface, which is screened by an equal number of charge carriers of the opposite sign (i.e., the ferroelectric field effect), thereby changing the effective doping level of manganite films. Underlying the ferroelectric field approach is the prominent role of charge in the double-exchange, hopping integral, and orbital overlap. Most previous reports hold the view that the screening length in magnetic films with metallic carrier doping level is merely a few angstroms; consequently only in ultrathin ferromagnetic layers can one observe measurable ferroelectric field effect.[15–18] Recently, we focused on the impact of electric field on the transport and magnetic properties in manganite films. Our studies revealed that the ferroelectric field effect may significantly affect the balance of multiphase coexistence at low temperatures and cause a series of changes in physical properties for manganite films.

Tetravalent cation-doped perovskite manganites $(La,Ce)MnO_3$ have stimulated wide interest due to the potential application in functional spintronic devices, such as p-n junctions of both hole- and electron-doped manganites.[19] Various experimental approaches have been followed so far to clarify the intrinsic doping type and the nature of ferromagnetic metallic to paramagnetic insulating transitions.[14,20–23] Controversies still exist with whether $LaMnO_3$ accepts Ce doping as an electron-doped nature. In this paper, we report the effects of polarization switching on the electronic transport and magnetic properties of $La_{0.8}Ce_{0.2}MnO_3$ (LCEMO) film/$0.67Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.33PbTiO_3$ (PMN-PT) crystal heterostructures. Combining measurements of transport and magnetic properties, the doping nature of LCEMO film is proven as hole conductive nature owing to overoxygenization, and the coupling mechanism in this multiferroic heterostructure was found to be temperature-dependent.

II. EXPERIMENTAL DETAILS

LCEMO films were grown on single-crystal substrates of PMN-PT with (001) orientation by pulsed laser deposition

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using a 248 nm KrF excimer laser. The deposition was carried out in pure oxygen of 27 Pa with the substrate temperature kept at 700 °C. After deposition, LCEMO films were *in situ* cooled to room temperature and postannealed in air at 700 °C for 30 min using a rapid thermal processor furnace to increase the crystallinity of films. The surface morphology of LCEMO films was checked by atomic force microscopy (AFM) (Nanocute SII, Seiko, Japan) in tapping mode. The thickness of films was measured to be ~31 nm using a JSM-6700F scanning electron microscope. X-ray diffraction (XRD) measurements were made using a Bruker D8 Discover x-ray diffractometer equipped with Cu $K_{\alpha 1}$ radiation ($K_{\alpha 1} = 1.5406$ Å) to explore the phase purity and epitaxial relationship between films and substrates. The strain versus electric field loop for the PMN-PT substrate at $T = 296$ K was analyzed by employing a laser interferometer (SIOS NT-04 Sensor).

Gold film was deposited on the surface of LCEMO films to form two top-top electrodes in order to measure electronic transport properties of LCEMO films.[7] The back of PMN-PT substrates was also deposited with gold film as bottom electrodes. The reversal of the polarization direction was achieved by applying an external dc electric field to the PMN-PT substrate through the top and bottom gold electrodes. The transport properties of LCEMO films were measured with a two probe technique since the contact resistance (less than several Ohms) between the gold electrode and the LCEMO film is negligible compared with that (>72 kΩ) of LCEMO films. A superconducting quantum interference device (SQUID) magnetometer (MPMS-5T, Quantum Design) was employed to determine the magnetic properties of LCEMO films.

III. RESULTS AND DISCUSSION

XRD θ-2θ scan of the LCEMO/PMN-PT structure indicates that the LCEMO film is c-axis preferentially oriented and has no secondary phase. The rocking curve taken around the LCEMO (002) diffraction peak has a full width at half maximum of 0.23°, indicating the good crystallinity of the film. The off-axis ϕ-scans of the LCEMO (101) and PMN-PT (101) planes reveal a "cube-on-cube" epitaxial growth mode of the LCEMO film on the PMN-PT substrate. We calculate c- and a-axis lattice constants of the film to be ~3.88 and ~3.93 nm, respectively. The LCEMO bulk material holds a pseudocubic unit cell with lattice parameters $a \sim b \sim c \sim 3.89$ Å, thus the film is subjected to an out-of-plane compressive ($\Delta\varepsilon_{zz} = -0.26\%$) and in-plane tensile ($\Delta\varepsilon_{xx} = 1.01\%$) strain, consistent with the fact that the lattice constants of the LCEMO bulk material are smaller than those ($a \sim b \sim c \sim 4.02$ Å) of the PMN-PT substrate. The AFM image in Fig. 1(d) shows that the surface of the LCEMO film is rather flat with a root-mean-square roughness of ~1.28 nm. The PMN-PT substrate exhibits excellent piezoelectric activities, evidenced by a well-defined butterfly-like strain-electric field loop [Fig. 1(c)].

It is noted that the LCEMO/PMN-PT heterostructure can be viewed as a ferroelectric field effect transistor where the LCEMO film and the PMN-PT substrate are the

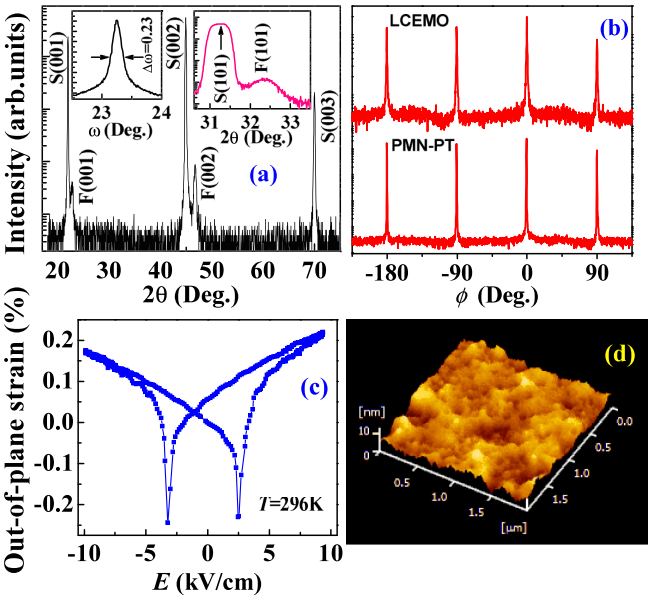

FIG. 1. (a) XRD θ-2θ scan for the LCEMO/PMN-PT structure. Left panel: the rocking curve taken around LCEMO (002) diffraction peak. Right panel: the off-axis θ-2θ scan data obtained by tilting the film plane at an angle of 45°. (b) XRD phi scans taken on the LCEMO (101) and PMN-PT (101) diffraction peaks, respectively. (c) Out-of-plane piezo-strain versus E curve for the PMN-PT substrate at $T = 296$ K. (d) The AFM image of the LCEMO film.

conductive channel and the insulating gate, respectively. An application of a positive electric bias through the top and bottom electrodes polarizes the PMN-PT domains towards the LCEMO film (denoted by P_r^+) and causes a buildup of negative electric charge at interface, which would deplete hole carriers in the LCEMO film. Similarly, an application of negative electric bias will add hole carriers to the LCEMO channel (denoted by P_r^-). Figure 2 shows the resistance (R) versus temperature (T) curves for different polarized states of the PMN-PT substrate. One can see that the resistance of the LCEMO film at any fixed temperature for the P_r^- state is smaller than that for the P_r^+ state. The

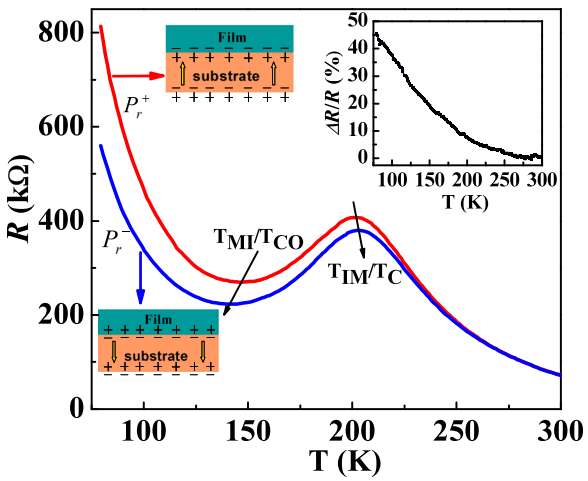

FIG. 2. Temperature dependence of the resistance for the LCEMO film when the PMN-PT substrate was in positively and negatively polarized states. The inset shows the relative change in the resistance, $\Delta R/R$ [$\Delta R/R = [R(P_r^+) - R(P_r^-)]/R(P_r^-)$], of the LCEMO film with the reversal of the polarization direction.

divergence of the resistance is minor at high temperatures while enhances distinctly with decreasing temperature, which is directly illustrated by the increase of $\Delta R/R$ ($\Delta R/R = [R(P_r^+) - R(P_r^-)]/R(P_r^-)$) with decreasing temperature (see the inset of Fig. 2). If the charge carriers in the LCEMO channel is of electron-type, the increased (decreased) carrier density upon positive (negative) polarization would cause a decease (an increase) in the channel resistance. Nevertheless, opposite results were observed, revealing holes as the dominant charge carriers in the LCEMO film.

Upon cooling, the *R-T* curves in Fig. 2 show a clear insulator-to-metal transition near 200 K. Below $T = 150$ K, the resistance shows an upturn with decreasing temperature, which might be related to the formation of antiferromagnetic charge-ordered (CO) phase.[23,24] The carriers could be trapped in a local lattice distortion. Thus, the mobilization of hole carriers is suppressed upon cooling, resulting in the upturn of resistance at low temperature. Changing the polarization state of the PMN-PT substrate from P_r^+ to P_r^-, the insulator-to-metal transition temperature (T_{IM}) increases slightly, accompanied by a decrease in T_{MI}/T_{CO}, presumably due to the ferroelectric field effect. The negative poling accumulates hole carriers, corresponding to converting a portion of Mn^{3+} ions to Mn^{4+} ions in the films.[15,16] Namely, the effective hole carrier concentration increases. As a result, the DE interaction between Mn^{3+} and Mn^{4+} ions gets stronger, which leads to an increase in T_{IM} and a decrease in the resistance. This interpretation is also supported by the results from the measurement of magnetic properties, which will be discussed further below. Meanwhile, the number of Jahn-Teller active Mn^{3+} decreases when negative bias is applied to the PMN-PT substrate, weakening the Jahn-Teller distortion of the local lattice and suppressing the CO phase.

A more direct visualization of the resistance modulation can be seen in Fig. 3, which shows the $R(E)$ curves of the LCEMO film, taken at several fixed temperatures with bipolar electric field E applied across the PMN-PT substrate.

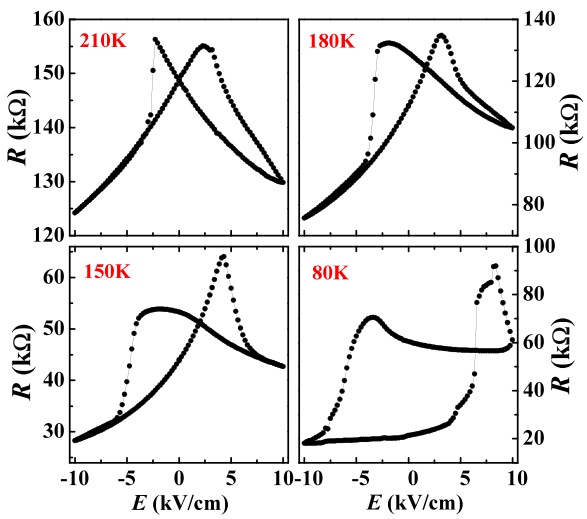

FIG. 3. Electric-field-induced change in the resistance of the LCEMO film at several fixed temperatures as a function of bipolar electric field applied to the PMN-PT substrate.

Reversible changes of R are observed as a function of E at a high temperature ($T = 210$ K) with the loop exhibiting a butterfly-like shape. This indirectly proves that the elastic strain is the driving force for the butterfly-like change in the resistance here.[7,11,17] Due to the epitaxial nature of the interface, strain in the PMN-PT substrate [see Fig. 1(c)] is effectively transferred to the LCEMO film and, thus, giving rise to a remarkable modulation of the resistance. The resistance of the LCEMO film does not depend on the polarization history of the PMN-PT substrate at 210 K, so it is concluded that the ferroelectric field effect has a minor effect on the electronic transport properties of the LCEMO film at 210 K. However, when temperature decreases, the symmetry of the $R(E)$ curves decreases with the resistance switching hysteretically between two discrete values in response to the ferroelectric polarization reversal. This characteristic, commensurate with the *P-E* hysteresis curve of the PMN-PT substrate, demonstrates that the difference in the resistance at $E = 0$ kV/cm probably tracks the switching of the polarization direction in terms of a nonvanishing influence of the surface charge from ferroelectric polarization on the resistance of the LCEMO thin film [i.e., the aforementioned ferroelectric field effect].[17,25] Attribution of strain to the resistance can be excluded from symmetry considerations as strain effect should yield $R(E)$ loops with even symmetry with respect to $E = 0$ kV/cm. With temperature further decreasing (e.g., at $T = 80$ K), the $R(E)$ curve turns into a hysteresis loop. The evolution of the *R-E* loops from a butterfly-like shape to a rectangular-like shape gives collateral evidence that the relative importance of the ferroelectric field effect increases while that of the strain effect decreases with decreasing temperature. The enhanced ferroelectric field effect at low temperatures consents to the feature that the relative change in the resistance of the LCEMO film caused by switching the polarized state of the PMN-PT substrate grows with temperature decreasing (see the inset of Fig. 2). We note that in $Ni/Pb(Zr_{0.52}Ti_{0.48})O_3$,[26] $Ni/BaTiO_3$,[27] and $La_{1-x}Sr_xMnO_3(x = 0.13,\ 0.3)/Pb(Zr,Ti)O_3$ (Refs. 3, 15, 16, 28–30) heterostructures, the authors also attributed the quite asymmetric feature of the voltage induced magnetization variation to the interfacial charge effect arised from polarization switching. It's reasonable to believe that the ferroelectric field effect is the dominated coupling in our samples at low temperatures. To elaborate our proposal more convincingly, the M(T) curves taken at a constant magnetic field $H = 100$ Oe applied in the LCEMO film plane are presented in Fig. 4. We found a drop in the magnetic moment when switching the polarization direction from P_r^- to P_r^+ at low temperatures, albeit no obvious change in the critical temperature was observed. For a given low temperature, the difference of saturation magnetization between the two polarized states (the inset of Fig. 4) indicates a change in the magnetic state with the applied electric field, demonstrating the presence of magnetoelectric coupling in this system. The strong spin-charge coupling via the DE interaction explains the correlation between the ferroelectric field effect and the magnetic modulation: the decrease in hole carriers in the LCEMO film after the positive polarization of the PMN-PT substrate would change a portion of Mn^{4+} ions to Mn^{3+}

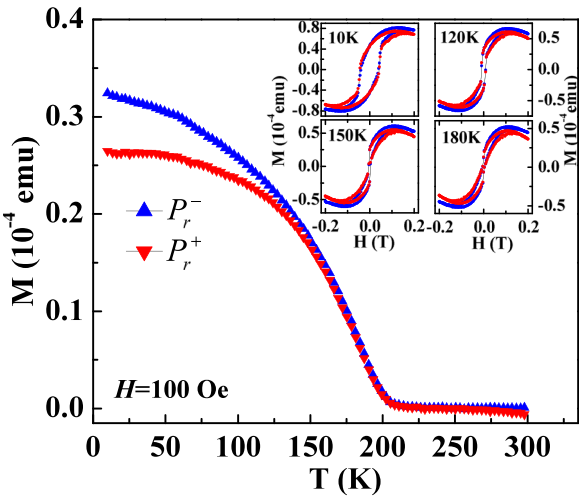

FIG. 4. Temperature dependence of the magnetization for the LCEMO film when the PMN-PT substrate was in positively and negatively polarized states, respectively. The inset shows the in-plane magnetic hysteresis loops $M(H)$ for the two polarization states of the PMN-PT substrate.

ions, concomitantly reducing the number of Mn^{3+}–Mn^{4+} pairs and weakening the DE interaction. This observation is also consistent with the picture of electrostatic hole doping of the LCEMO film.

The coupling mechanism in the LCEMO/PMN-PT heterostructure shows strong temperature dependence. On one hand, at relatively high temperature, elastic strain plays a pivotal role in controlling the properties of LCEMO films due to the pronounced coupling between the lattice and the charge degrees of freedom. On the other hand, both the transport and magnetic properties could be altered electrostatically via the ferroelectric field effect at low temperatures. These results are interpreted in the framework of the changes in effective carrier doping level, modulated by the ferroelectric polarization reversal. It is believed that the enhanced ferroelectric field effect with temperature decreasing can be more reasonably interpreted as a consequence of electronic inhomogeneity and phase separation in the LCEMO film.[14,24] Around T_{IM}, the paramagnetic insulator and ferromagnetic metallic phases coexist. With temperature further lowered through T_{MI}/T_{COO}, the ferromagnetic metallic and antiferromagnetic charge/orbital ordering phases coexist. Consequently, in the low temperature range, the phase boundary between metallic and insulating phases allows the electric field induced effect to penetrate more deeply into the LCEMO film, thus significantly affecting the balance of multiphase coexistence and leading to a series of changes in physical properties.

IV. CONCLUSIONS

The responses of transport and magnetic properties to polarization switching have been investigated for the LCEMO film/PMN-PT crystal heterostructure. It is believed that the ferroelectric field effect plays a significant role in controlling the properties of manganite films with distinct response of resistance and magnetization to the reversal of the ferroelectric polarization at low temperature. However, with increasing temperature, the observed divergence gradually diminishes and the strain effect dominates over the ferroelectric field effect, reflected by the butterfly-like $R(E)$ loop at relatively high temperatures. The obtained knowledge of the interaction between the strain effect and ferroelectric field effect would improve the understanding of the coupling mechanism in manganite film/FE crystal heterostructures.

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