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Influence of ferroelectric poling induced strain on magnetic and electric properties in tetravalent cation-doped $La_{0.9}Hf_{0.1}MnO_3$ films

Z. P. Wu,[1] L. Wang,[1] E. J. Guo,[2] and J. Gao[1,a)]
[1]*Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong*
[2]*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*

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Electron-doped manganites $La_{0.9}Hf_{0.1}MnO_3$ (LHMO) films were epitaxially grown on 0.67Pb $(Mg_{1/3}Nb_{2/3})O_3$-0.33$PbTiO_3$ (PMN-PT) substrates. The effects of the strain induced by ferroelectric poling on the magnetic and electric properties have been investigated. The polarization of the PMN-PT crystal reduces the biaxial tensile strain in the formed LHMO layer. It results in a significant decrease in resistance and an enhancement of the phase transition temperature as well as the magnetization of the grown LHMO films. Our study shows that the strain-induced distortion of MnO_6 octahedron plays an important role in impacting the properties of LHMO films. © *2012 American Institute of Physics*. [doi:10.1063/1.3670971]

I. INTRODUCTION

Since the observation of the colossal magnetoresistance (CMR) effects, much effort has been devoted to the doped manganites due to their complicated underlying physical mechanisms and potential oxide electronic device applications.[1] It has been found that the properties of such compounds are sensitive to the external interference, such as magnetic fields, electric fields, light, and mechanical strain.[2–4] The strain effects on the manganite thin films have been intensively studied. It is generally accepted that a change in the magnitude of the Jahn-Teller (JT) distortion would lead to significant modifications in the volume fraction of coexisting phases.[5,6] Hence, the electric and magnetic properties of manganites can be modulated by the substrate-induced strain. The common method for the study of the substrate-induced strain is to grow epitaxial films on specific substrates with certain lattice mismatch. Generally, it is difficult to control the strain in manganite films continuously and reversely by using conventional substrates.

Recently, Thiele *et al.* and Zheng *et al.* reported that the strain state of films could be tuned by applying electric fields on $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ferroelectric single crystals.[6,7] However, much works are focused on the hole-doped manganites, i.e., the electrical conductivity is *p*-type for these compounds, like $La_{1-x}Sr_xMnO_3$, $La_{1-x}Ca_xMnO_3$, and $La_{1-x}Ba_xMnO_3$. They usually exhibit a traditional CMR effect and magnetic phase transition at low temperatures due to the double exchange (DE) interaction between Mn^{3+} and Mn^{4+} ions. In the electron-doped manganites, the tetravalent cation substitutes the La site ion of the parent compound $LaMnO_3$, which leads to an *n*-type conducting. The study of such electron-doped may open a door for the design of whole manganites function devices. Up to now, several electron-doped manganites, like $La_{1-x}A_xMnO_3$ (A represented Sn^{4+}, Ce^{4+}, Sb^{4+}, Hf^{4+}, and Te^{4+}), have been investigated.[8–10] Our previous studies demonstrated that strain-induced lattice deformation and oxygen deficiency significantly influence the transport property in low-doped $La_{1-x}Hf_xMnO_3$ films by growing films with different thicknesses.[9] So far, the studies on the *in situ* strain effect in electron-doped manganites have seldom been reported. In this paper, we report our study on electron-doped $La_{0.9}Hf_{0.1}MnO_3$ (LHMO) manganite. The LHMO films were epitaxially grown on $0.67Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.33PbTiO_3$ (PMN-PT) ferroelectric crystal. The ferroelectric-poling-induced strain effects on the magnetic and electric properties of LHMO films are studied. We suggest that strain may induced JT lattice distortion, which is responsible for our observations.

II. EXPERIMENTAL

LHMO thin films were epitaxially grown on the ferroelectric PMN-PT (001) substrates by pulsed laser deposition (PLD).[11] Pulsed KrF excimer laser was used with wavelength of 248 nm, a repetition of 2 Hz, and energy of ~2 J/cm^2. The substrates temperature and oxygen pressure were kept at 700 °C and 0.5 mbar during the deposition, respectively. In order to avoid the oxygen deficient, the as-grown samples were *in situ* annealed in pure oxygen of 1 atm for 30 min. The thickness of LHMO films was ~50 nm, controlled by the deposition time. Then, four silver contact pads with diameter of 200 μm were prepared on films by thermal evaporation. The magnetization (M) of films was measured by Physical Property Measurement System (PPMS) (Quantum Design) with the magnetic field applied parallel to the film plane. The electric measurement was carried out using standard four-probe method. The resistance of PMN-PT substrate was about 2 GΩ, which is much larger than the resistance of LHMO films (~kΩ). Hence, the LHMO films play a role of top electrode when dc electric field applied to the substrates for ferroelectric poling.

[a)] Author to whom correspondence should be addressed. Electroic mail: jugao@hku.hk.

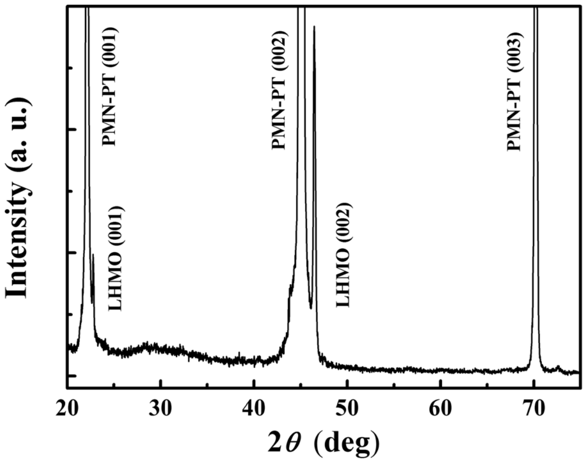

FIG. 1. The XRD θ-2θ scanning curves of LHMO/PMN-PT structure.

III. RESULTS AND DISCUSSIONS

The crystallinity and crystallographic orientation of LHMO films were examined by x-ray diffraction (XRD). Figure 1 shows the XRD θ-2θ patterns of LHMO/PMNPT structure. Besides the (00*l*) diffraction peaks from the films and substrates, no other peaks from the impurities or misorientation were observed, indicating the films are *c*-axis preferentially grown. The out-of-plane lattice parameter of LHMO on PMN-PT was calculated ~3.871 Å, which is smaller than that of LHMO (~3.882 Å) on STO.[9] This is because the larger lattice parameter of 4.020 Å in PMN-PT, which resulting in a larger tensile in-plane strain to the LHMO films.

In our previous works, hall measurements were performed to clarify that LHMO is an electron-doped manganite.[10,12] Figure 2 presents the temperature dependence of resistance of LHMO film when the substrate was under unpolarized (referred to as P_r^0) and positive polarized (referred to as P_r^+) state. The schematic circuit of measurement was shown in the inset (b) of Fig. 2. The resistance of LHMO film grown on PMN-PT substrate increases with decreasing temperatures and undergoes an insulator-to-metal (IM) transition from paramagnetic (PM) insulating phase to ferromagnetic metallic (FM) phase at ~180 K. After poling the PMN-PT substrate, the resistance of LHMO film decreases over the whole temperature range and the insulator to metal transition temperature (T_{IM}) shifts ~10 K toward higher temperature. Since PMN-PT substrate has a pseudocubic unit cell with lattice parameter $c_{PMN\text{-}PT} \sim 4.022$ Å and LHMO has a pseudocubic lattice parameter $c_{film} \sim 3.895$ Å,[9] for coherent growth on the PMN-PT substrates, the LHMO films should be subjected to in-plane biaxial tensile strain and out-of-plane compressive strain. The inset (a) of Fig. 2 presents the XRD patterns for (002) peaks of LHMO/PMNPT structure when PMN-PT is in P_r^0 and P_r^+ states, respectively. Compared to those in the P_r^0 state, the PMN-PT (002) peaks in P_r^+ state shifts to lower degrees. It indicates that the lattice is stretching along the *c*-axis. Due to the Poisson effect, the lattice elongation in *c*-axis would be accompanied by a lattice shrinking in the *a*-*b* plane. Therefore, the polarized PMN-PT substrates can cause a decrease in the in-plane *a*- and *b*-axis lattice constants of the PMN-PT, and then a reduction of the biaxial tensile strain in LHMO films. It is believed that the reduction of tensile strain in LHMO films is the main reason for the reduced resistance and the enhanced T_{IM}, which is in agreement with the previous investigations in other manganites.[3,5]

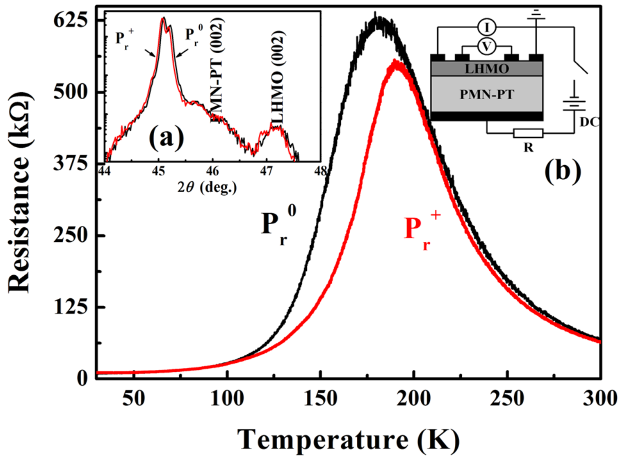

FIG. 2. (Color online) The temperature dependence of resistance for the LHMO film when the PMN-PT substrate is in P_r^0 and P_r^+ states. The inset (a) presents the XRD patterns for (002) peaks of LHMO/PMNPT structure when PMN-PT is in P_r^0 and P_r^+ states. The inset (b) gives out the schematic diagram of measurement circuit.

Similar to the electrical transport, the magnetization (*M*) of the LHMO films can also be influenced by the strain. Figure 3 shows the temperature dependence of *M* for the LHMO/PMN-PT structure when the PMN-PT substrate is in P_r^0 and P_r^+ states. Data were recorded during warming in a magnetic of 200 and 1000 Oe after field cooling (FC) and zero-field-cooling (ZFC). The huge divergence between the FC and ZFC curves is consistent with the previous reports in other manganites and should be related to a spin-glass phase existed in the films.[13,14] Comparing to those in the P_r^0 state, both *M* and T_C values estimated from the temperature-dependent *M* curves are increased for FC mode when PMN-PT is in P_r^+ state. As mentioned earlier, the polarized PMN-PT substrates can cause a reduction of the biaxial tensile

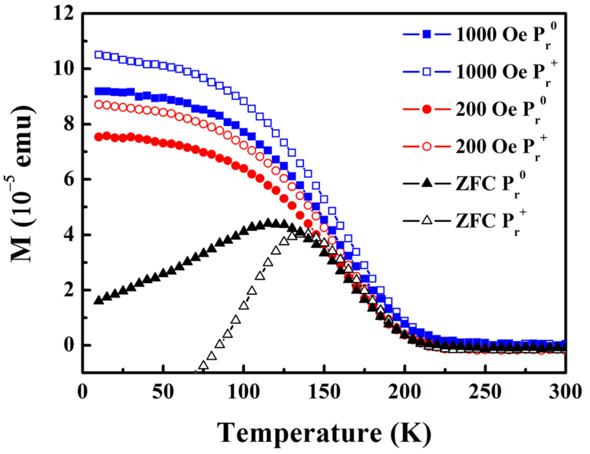

FIG. 3. (Color online) Temperature dependence of the zero-field-cooled magnetization (*M*) for the LHMO/PMN-PT structure at 200 and 1000 Oe when the PMN-PT substrate is in P_r^0 and P_r^+ states.

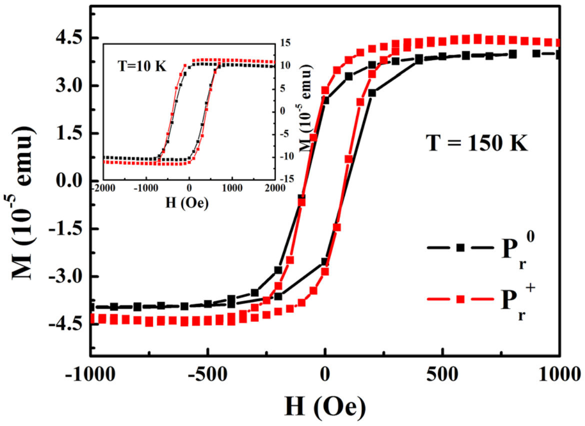

FIG. 4. (Color online) The magnetic hysteresis loops of the LHMO/PMN-PT structure at 150 K when the PMN-PT substrate is in P_r^0 and P_r^+ states. The inset shows the magnetic hysteresis loops measured at 10 K at the same conditions.

strain in LHMO films. Since the effect of this ferroelectric compression in the layer plane is similar to that of the piezoelectric compression, we believe that the increased M should be the result of partial release of the tensile strain in LHMO films. As reported by Dörr *et al.*,[15] the biaxial strain may induce a distortion of MnO_6 octahedron. With decreasing tensile strain, the distortion is relieved and then the double exchange interaction is enhanced. Hence, this strain-induced distortion of MnO_6 octahedron may play an important role in these enhanced M and T_C.

The magnetic hysteresis loops of the LHMO/PMN-PT structure were measured at 150 and 10 K when the PMN-PT substrate is in P_r^0 and P_r^+ states. As shown in Fig. 4, at both temperatures, there is no detectable difference in the coercive field (H_C) between P_r^0 and P_r^+ states, but a larger remnant (M_R) and saturated magnetization (M_S) in P_r^+ state. The negligible effect on H_C was also found in other manganites and attributed to the small change in the strain state.[16] As mentioned before, the strain-induced distortion of MnO_6 octahedral is considered as essential origin of the increasing T_C. It is well known that the distortion of MnO_6 can directly influence the electron hopping integral and the e_g level splitting. When the PMN-PT substrates are polarized, the tensile strain in LHMO films is partially released and the distortion of MnO_6 octahedral is reduced. As a result, the electron hopping rate is enhanced and the e_g electrons in ferromagnetic manganites are delocalized, which favors the FM phase in LHMO films and then increases magnetization.

IV. CONCLUSION

In conclusion, the strain effect on the electric and magnetic properties of LHMO films have been investigated by using ferroelectric PMN-PT substrates. The polarized PMN-PT substrates can cause a reduction of the biaxial tensile strain in LHMO films, and then a decrease of resistance and an enhancement of T_{IM}, T_C and magnetization in LHMO films. It is believed that the strain-induced distortion of MnO_6 octahedron is the main reason to impact the properties of LHMO films.

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