Effects of ferroelectric-poling-induced strain on the transport and magnetic properties of La$_{7/8}$Ba$_{1/8}$MnO$_3$ thin films

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We have investigated the effects of the strain induced by ferroelectric poling on the transport and magnetic properties of La$_{7/8}$Ba$_{1/8}$MnO$_3$ (LBMO) thin films epitaxially grown on ferroelectric 0.67Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$–0.33PbTiO$_3$ (PMN–PT) single-crystal substrates. The ferroelectric poling reduces the in-plane tensile strain of the film, giving rise to a decrease in the resistivity and an increase in the magnetization, Curie temperature, and magnetoresistance of the LBMO film. These strain effects are explained within the framework of coexisting phases whose volume fractions are modified as a result of the reduction in the tetragonal distortion of MnO$_6$ octahedra induced by ferroelectric poling. An investigation of the effects of polarization reversal on the transport properties of the LBMO film indicates that the ferroelectric-poling-induced strain effects dominate over the ferroelectric field effects in the LBMO/PMN–PT structure. © 2010 American Institute of Physics. [doi:10.1063/1.3464226]

I. INTRODUCTION

The effects of substrate-induced strain on the properties of perovskite manganite thin films are quite complex and still under investigation.1–11 Zhang et al.1 reported that lightly doped La$_{1-x}$Ba$_x$MnO$_3$ (0.05 ≤ x ≤ 0.2) thin films show anomalous strain effects, which is different from those previously observed in La$_{0.9}$Sr$_{0.1}$MnO$_3$,2 La$_{0.7}$Ca$_{0.3}$MnO$_3$,3 La$_{0.7-x}$Sr$_{0.3+x}$MnO$_3$4,5 and La$_{0.67-x}$Pr$_x$Ca$_{0.33}$MnO$_3$ (x =0.13,0.2,0.27) (Ref. 5) thin films. They observed that the substrate-induced in-plane tensile strain dramatically reduces the resistivity and enhances the ferromagnetism and Curie temperature ($T_C$) of La$_{1-x}$Ba$_x$MnO$_3$ (0.05 ≤ x ≤ 0.2) thin films and suggested that the tensile strain-induced stabilization of $d_{z^2-r^2}$ orbital is responsible for the enhanced ferromagnetism and $T_C$. Using hall measurements, Kanki et al.6 found that the tensile strain-induced enhancements in ferromagnetism and $T_C$ of La$_{1-x}$Ba$_x$MnO$_3$ (0.05 ≤ x ≤ 0.2) thin films are due to enhanced carrier mobility arising from strain-induced modification of Mn–O–Mn network. In contrast, Murugavel et al.7–9 reported that, irrespective of whether the substrate-induced strain is compressive or tensile, the oxygen nonstoichiometry, which depends on the oxygen pressure during film deposition and postannealing process, strongly influences the structural, transport, and magnetic properties of the lightly doped La$_{1-x}$Ba$_x$MnO$_3$ (x =0.08,0.2) thin films. Orgiani et al.10 reported similar effects of oxygen nonstoichiometry on the transport properties and $T_C$ of La$_{0.3}$Ba$_{0.7}$MnO$_3$ thin films. These results demonstrate the important role of the oxygen content in determining the structural and physical properties of La$_{1-x}$Ba$_x$MnO$_3$ thin films.

In order to obtain further insight into the effects of substrate-induced strain on the transport and magnetic properties of lightly doped La$_{1-x}$Ba$_x$MnO$_3$ thin films, we epitaxially grown lightly doped La$_{7/8}$Ba$_{1/8}$MnO$_3$ (LBMO) thin films on ferroelectric 0.67Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$–0.33PbTiO$_3$ (PMN–PT) single-crystal substrates and in situ dynamically reduces the in-plane tensile strain of the LBMO film via ferroelectric poling, such that the effects of extrinsic variables such as oxygen nonstoichiometry are kept constant since we used the same piece of LBMO/PMN–PT sample. We found that the ferroelectric poling induces an in-plane compressive strain which is transferred to the film, thus giving rise to a reduction in the in-plane tensile strain of the LBMO film. As a result, the resistivity is reduced while the magnetoresistance (MR), ferromagnetism, and $T_C$ are enhanced. The analysis of the results show that the reduction in the lattice distortion of MnO$_6$ octahedra induced by ferroelectric poling plays a crucial role in understanding the strain effects in LBMO films.

II. EXPERIMENTAL DETAILS

We have grown the PMN–PT single crystals by a modified Bridgman technique. The crystals were cut into small plates (10 × 2.5 × 0.5 mm$^3$) with the plate normal in the ⟨001⟩ crystal direction and polished to a surface roughness less than 1 nm. LBMO films were deposited on the ⟨001⟩-oriented and polished PMN–PT substrates using dc magnetron sputtering.11 The deposition was carried out in an argon–oxygen flow with 60% Ar and 40% O$_2$ at a pressure of 5 Pa.
and a substrate temperature of 700 °C. After deposition, the films were cooled to room temperature and postannealed in 1 atm of flowing O2 at 700 °C for 30 min using a rapid thermal processor furnace. Although the lattice constants (a ≈ b ≈ c ≈ 3.902 Å (Ref. 12)) of the LBMO bulk material, recent work by Thiele et al.13 and Zheng et al.11,14 demonstrate that it is still possible to epitaxially grow manganite on LBMO film in fact serves as the top electrode for poling the PMN–PT substrate. This was achieved by applying a dc poling field /H9258/ of flowing O2 at 700 °C for 30 min using a rapid thermal processor furnace. Although the lattice constants of the LBMO film when the PMN–PT substrate is in +10 kV/cm to the LBMO/PMN–PT structure at room temperature and turned off the poling field after 15 min. Since the PMN–PT substrate has a ferroelectric Curie temperature of ~155 °C (much higher than room temperature), the polarization direction will remain toward the poling direction after the poling field has been turned off. It can be seen that, associated with the switch of the poling state from /P/0 to /P/+ state, the resistivity decreases noticeably in the whole temperature range and in/MI shifts to a higher temperature by ~9 K. /In situ/ XRD measurements indicate that, associated with the poling of the PMN–PT substrate, the /2θ/ value of the LBMO(002) reflection shifts from 46.79° to 46.65° [inset (b) of Fig. 2], corresponding to an increase in the lattice constant /c/ from ~3.883 to 3.894 Å. Therefore, the out-of-plane compressive strain /ε/zz = (/ε/cfilm–/ε/bulk)//ε/bulk is reduced from ~0.49% to ~0.21% (i.e., /Δ/ε/zz = 0.28%). Assuming approximate volume preserving distortion, an increase in /ε/x/y by 0.28% would be accompanied by a decrease in the in-plane tensile strain /ε/x/x by 0.14% (i.e., /Δ/ε/x/x = −0.14%) using the expression /Δ/ε/x/x = −2/[(1−/ν)/Δ/ε/x/x], where /ν/ = 0.5 is the Possion’s ratio. Such a decrease in the in-plane tensile strain would reduce the tetragonal distortion of MnO6 octahedra of the film, as recently revealed by the angular resolved x-ray absorption spectroscopy study of epitaxially strained La0.6Sr3.5MnO8 thin films by Souza-Neto et al.15 and thus weakens the electron-lattice coupling strength, as pointed out by Millis et al.16 As a result, the itinerancy of the /e/ electrons would be enhanced, giving rise to a decrease in the resistivity of the LBMO film.

Figure 2 shows the temperature dependence of the resistivity for the LBMO film when the PMN–PT substrate is in the unpoled state (referred to as /P/0) and positively polied state (i.e., electric dipole moments point to the LBMO film, referred to as /P+/), respectively. For /P/0 state, the resistivity of the film increases with decreasing temperature and shows an appreciable insulator-to-metal-like transition near /TMI/ ~ 146 K, which can be more clearly seen from the ln ρ versus /T/1/4 curves shown in the inset (a) of Fig. 2. The measurements of the resistivity as a function of temperature for /P/+ state, we /in situ/ poled the PMN–PT substrate by applying an electric field of +10 kV/cm to the LBMO/PMN–PT structure at room temperature and turned off the poling field after 15 min. Since the PMN–PT substrate has a ferroelectric Curie temperature of ~155 °C (much higher than room temperature), the polarization direction will remain toward the poling direction after the poling field has been turned off. It can be seen that, associated with the switch of the poling state from /P/0 to /P+, the resistivity decreases noticeably in the whole temperature range and /TMI shifts to a higher temperature by ~9 K. /In situ/ XRD measurements indicate that, associated with the poling of the PMN–PT substrate, the /2θ/ value of the LBMO(002) reflection shifts from 46.79° to 46.65° [inset (b) of Fig. 2], corresponding to an increase in the lattice constant /c/ from ~3.883 to 3.894 Å. Therefore, the out-of-plane compressive strain /ε/zz = (/ε/cfilm–/ε/bulk)//ε/bulk is reduced from ~0.49% to ~0.21% (i.e., /Δ/ε/zz = 0.28%). Assuming approximate volume preserving distortion, an increase in /ε/x/y by 0.28% would be accompanied by a decrease in the in-plane tensile strain /ε/x/x by 0.14% (i.e., /Δ/ε/x/x = −0.14%) using the expression /Δ/ε/x/x = −2/[(1−/ν)/Δ/ε/x/x], where /ν/ = 0.5 is the Possion’s ratio. Such a decrease in the in-plane tensile strain would reduce the tetragonal distortion of MnO6 octahedra of the film, as recently revealed by the angular resolved x-ray absorption spectroscopy study of epitaxially strained La0.6Sr3.5MnO8 thin films by Souza-Neto et al.15 and thus weakens the electron-lattice coupling strength, as pointed out by Millis et al.16 As a result, the itinerancy of the /e/ electrons would be enhanced, giving rise to a decrease in the resistivity of the LBMO film.

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FM clusters while the long-range antiferromagnetic (AFM) order in the host lattice is supported predominantly by the Mn$^{3+}$–O–Mn$^{4+}$ exchange coupling which is weaker than the Mn$^{3+}$–O–Mn$^{3+}$ double-exchange interaction. Because the concentration of FM clusters is not high enough, they do not interact with one another, thereby giving rise to the FM insulating behavior of the resistivity at low temperatures. Associated with the establishment of FM ordering within FM clusters below $T_C$ ($\sim 150$ K), faster hopping of $e_g$ electrons within FM clusters is expected, which could lead to the insulator-to-metal-like transition near $T_{Mf}$. We note that, associated with the switch of the poling state from $P_{0}$ to $P_{r}$, both ferromagnetism and $T_C$ are clearly enhanced. At 4.2 K, the magnetization was enhanced by $\sim 8.2\%$. As discussed above, a decrease in the in-plane tensile strain weakens the electron-lattice coupling and enhances the electron hopping amplitude. The enhanced electron hopping would increase the ferromagnetism of the FM clusters since the FM double-exchange interaction, which could also contribute to the enhancement of the ground state ferromagnetism of the film.

The ferroelectric-poling-induced reduction in the in-plane tensile strain also influences MR of the LBMO film. The inset (b) of Fig. 3 shows MR of the film at $T=100$ K as a function of magnetic fields applied parallel (or perpendicular) to the film plane. MR is defined as $MR=(\rho(0)-\rho(H))/\rho(0)$ where $\rho(0)$ and $\rho(H)$ are the resistivity of the LBMO film in zero magnetic field and a magnetic field $H$, respectively. Whether the magnetic field is applied parallel or perpendicular to the film plane, associated with the reduction in the in-plane tensile strain, MR of the film is enhanced appreciably. It is noted that similar strain-induced enhancement of MR has been observed in the La$_{0.7}$Ba$_{0.3}$MnO$_3$ films epitaxially grown on PMN–PT substrates. The underlying mechanism that is responsible for the enhancement of MR for the LBMO/PMN–PT structure is probably the same as that for the La$_{0.7}$Ba$_{0.3}$MnO$_3$/PMN–PT structure. Namely, the effects of the induced strain on MR can be explained in terms of strain-induced modification of phase separation. At 100 K, the film is in FM insulating state. That is, FM metallic clusters are embedded in the AFM insulating matrix with the volume fraction of the latter dominating over that of the former. Associated with the reduction in the in-plane tensile strain, the volume faction of the FM metallic phase increases at the expense of the AFM insulating phase (as reflected by the decrease in the resistivity and the increase in magnetization and $T_C$). Consequently, MR of the film increases due to enhanced volume fraction of FM metallic phase.

Figure 4 shows the relative change in the resistivity of the LBMO film as a function of electric field applied to the PMN–PT substrate. The resistivity-electric field ($\rho$-$E$) hysteresis loop shows a butterflylike shape with the resistivity change exhibiting the same sign for opposite directions of applied electric field. This is a typical behavior of the resistivity change due to the strain induced by the reversal of the polarization direction in the PMN–PT substrate. If the ferroelectric field effect plays a dominant role in influencing the resistivity, one would observe a rectanglelike $\rho$-$E$ hysteresis loop with the resistivity change exhibiting opposite signs for opposite directions of applied electric field, as previously observed in the La$_{1-x}$Ba$_x$MnO$_3$($x=0.1,0.15$)/Pb(Zr$_{0.7}$Ti$_{0.3}$)O$_3$ structures. Thus, the butterflylike $\rho$-$E$ hysteresis loop gives further evidence that the strain induced by poling plays a dominant role in influencing the transport properties of the LBMO film while the ferroelectric field effect is minor and negligible.
direction of ferroelectric domains in the PMN–PT substrate. As can be seen in the inset of Fig. 4, with the change of the electric potential in the sequence of $0 \rightarrow -20\, V \rightarrow +20\, V \rightarrow 0\, V$, the polarization direction of ferroelectric domains rotates by $180^\circ$, as reflected by the $180^\circ$ change in the PFM phase, giving evidence that the strain induced by the polarization reversal is responsible for the resistivity modulation.

IV. CONCLUSIONS

In summary, we have studied the effects of ferroelectric-poling-induced strain on the transport and magnetic properties of lightly doped La$_{7/8}$Ba$_{1/8}$MnO$_3$ thin films epitaxially grown on ferroelectric PMN–PT substrates. The ferroelectric poling in situ reduces the in-plane tensile strain of the film, giving rise to a decrease in the resistivity and an increase in the Curie temperature, ferromagnetism, and MR of the film. We discussed these strain effects within the framework of the phase separation which is significantly influenced by the strain induced by ferroelectric poling. The results also demonstrate that the strain induced by ferroelectric poling play a dominant role in influencing the transport and magnetic properties of the film while the ferroelectric field effect is minor and negligible in the LBMO/PMN–PT structure.

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