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Investigation of substrate-induced strain effects in $La_{0.7}Ca_{0.15}Sr_{0.15}MnO_3$ thin films using ferroelectric polarization and the converse piezoelectric effect

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We have fabricated manganite film/ferroelectric crystal heterostructures by growing $La_{0.7}Ca_{0.15}Sr_{0.15}MnO_3$ (LCSMO) films on ferroelectric $0.67Pb(Mg_{1/3}Nb_{2/3})O_3-0.33PbTiO_3$ (PMN-PT) single-crystal substrates. The efficient mechanical coupling at the interface, originated from ferroelectric polarization or the converse piezoelectric effect in the PMN-PT substrate, gives rise to large changes in the strain state, electrical resistance, magnetoresistance, and insulator-to-metal transition temperature (T_P) of the film. We interpreted all these changes in terms of substrate-induced strain, which modifies the tetragonal distortion of MnO_6 octahedra and the electron-lattice coupling strength in the film. Quantitative relationships between T_P and induced strain in the LCSMO film have been established. © *2008 American Institute of Physics*.
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Many experimental and theoretical studies have shown that the substrate-induced strain strongly affects the structural, electrical, and magnetic properties of manganite thin films.[1–3] Generally, the approach to characterize the strain effects is achieved by analyzing the thickness dependence of the properties of thin films grown on different substrates. However, in real practice, it is quite difficult to ensure that the studied thin films have the same oxygen content and similar microstructure irrespective of their thickness. As is known, the oxygen content, structural disorder, and defects also strongly influence the properties of manganite thin films.[3–5] Therefore, in order to obtain the intrinsic substrate-induced strain effects, one has to rule out the effects of these extrinsic variables. Recently, it was reported that the strain state of manganite thin films grown on ferroelectric single-crystal substrates, e.g., $BaTiO_3$ (Ref. 6) or $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$,[7,8] can be *in situ* modulated via ferroelectric polarization or the converse piezoelectric effect, which demonstrates the possibility that one can *in situ* modulate the strain state and properties of thin films by using ferroelectric crystals as substrates.

In this letter, we deposited $La_{0.7}Ca_{0.15}Sr_{0.15}MnO_3$ (LCSMO) films on ferroelectric $0.67Pb(Mg_{1/3}Nb_{2/3})O_3-0.33PbTiO_3$ (PMN-PT) single-crystal substrates and studied the substrate-induced strain effects in the LCSMO film by *in situ* inducing strain in the PMN-PT substrate via ferroelectric polarization or the converse piezoelectric effect without introducing the effects of extrinsic variables.

LCSMO films were deposited on (001)-cut and polished PMN-PT single-crystal substrates using dc magnetron sputtering. The resistance of the films was measured using the measurement circuit shown in inset (b) of Fig. 1. The magnetoresistance (MR) of the films were measured under application of magnetic fields parallel to the film plane.

Figure 1 displays the temperature dependence of the resistance for the LCSMO film when the PMN-PT substrate is in the unpolarized state (referred to as P_r^0) and positively polarized state (referred to as P_r^+), respectively. When the PMN-PT substrate is in the P_r^0 state, the resistance increases with decreasing temperature and undergoes an insulator-to-metal transition at ~228 K, exhibiting typical electrical behaviors of CMR materials. To observe the ferroelectric-polarization-induced strain effect, we *in situ* polarized the PMN-PT substrate at 296 K by applying an electric field of +10 kV/cm to the PMN-PT substrate and turned off the electric field after poling for 15 min. It can be seen that the

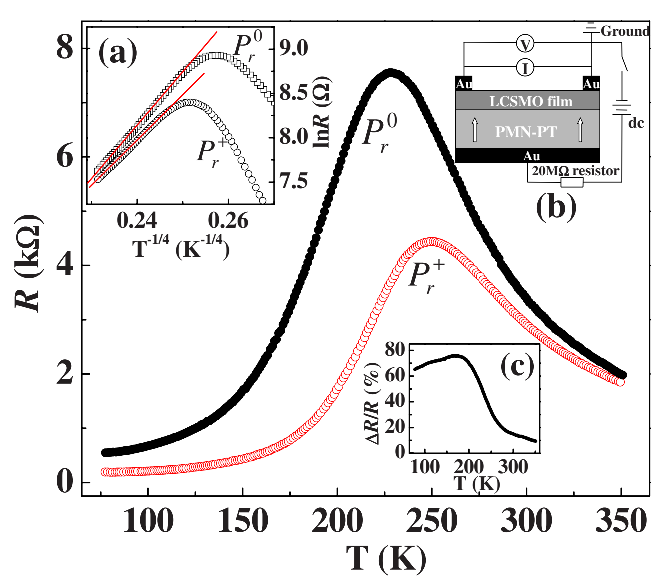

FIG. 1. (Color online) Temperature dependence of the resistance for the LCSMO film when the PMN-PT substrate is in the P_r^0 and P_r^+ states, respectively. Inset (a) shows the ln R vs $T^{-1/4}$ curves. Inset (b) shows the schematic diagram of the LCSMO/PMN-PT structure and the electrical measurement circuit. The arrows represent the polarization direction. Inset (c) shows the ferroelectric-polarization-induced relative change in the resistance, $\Delta R/R$, as a function of temperature.

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ferroelectric polarization induces T_P shifts to a higher temperature by $\sim$20 K and the resistance decreases over a wide temperature range. The relative decrease in the resistance associated with the switching of the polarization state from P_r^0 to P_r^+, $\Delta R/R$, is about 15.1% at 300 K and increases to a maximal value of $\sim$75.8% at 175 K, as illustrated in inset (c) of Fig. 1. We point out that the ferroelectric field effect plays a negligible effect since the electronic screening length in similar manganite films, e.g., $La_{1-x}Sr_xMnO_3$, is less than a few unit cells,[7] which is much smaller than the thickness ($\sim$65 nm) of our LCSMO film.

Ferroelectric polarization will simultaneously induce large out-of-plane tensile and in-plane compressive strains in the PMN-PT crystals The induced in-plane compressive strain would be transferred to the LCSMO film, causing decreases in the in-plane lattice constants and an increase in the out-of-plane lattice constant of the film. To verify this point, we measured the out-of-plane or c-axis lattice constant of the LCSMO film by *in situ* measuring the position of the LCSMO(002) reflection when the PMN-PT substrate is in the P_r^0 and P_r^+ states, respectively. We found that the c-axis lattice constant of the film is 3.8524 Å for the P_r^0 state. This value is smaller than that (i.e., $c=3.8878$ Å for pseudocubic structure, as obtained by Rietveld refinement analysis of the powder XRD data of our LCSMO ceramic target) of the LCSMO ceramic target, indicating the film is under in-plane tensile strain. Associated with the ferroelectric polarization, the c-axis lattice constant increases from 3.8524 to 3.8686 Å. This indicates that the in-plane tensile strain was significantly reduced after the PMN-PT has been polarized.

The ferroelectric-polarization-induced reduction in the in-plane tensile strain would modify the distortion of the MnO_6 octahedra in the LCSMO film. When the PMN-PT is in the P_r^0 state, the film is under in-plane tensile strain. This implies that the MnO_6 octahedra are compressed along the c axis and elongated in the film plane.[9] Such a tetragonal distortion of the MnO_6 octahedra leads to an increase in the splitting of the e_g levels, tending to localize charge carriers due to the electron-lattice coupling.[1,2,10] When the PMN-PT substrate is in the P_r^+ state, the in-plane tensile strain of the film is significantly reduced, which would reduce the electron-lattice coupling strength associated with the reduction in the tetragonal distortion of the MnO_6 octahedra, favoring the delocalization of the charge carriers. Our experimental results are consistent with the theoretical works by Millis *et al.*[1] and Perroni *et al.*[10] who pointed out that a small reduction in electron-lattice coupling strength can induce a large decrease in the resistance and a large enhancement in the transition temperature in the CMR region.

We found that whether the PMN-PT substrate is in the P_r^0 or P_r^+ state, the resistance data for $T>T_P$ can be best fitted by the equation $R(T)=R_0\exp[(T_0/T)^{1/4}]$,[11] where T_0 is a characteristic temperature obtained from the slope of the $\ln R$ versus $T^{-1/4}$ curve [inset (a) of Fig. 1], supporting Mott's variable-range-hopping model in three dimensions as the mechanism for electronic transport for $T>T_P$. The fit to the data gives $T_0=6.7\times10^7$ K for the P_r^0 state. By taking the value of charge carrier localization length ξ to be 4 Å, roughly the distance between neighboring Mn atoms, and using $k_BT_0\approx18/[N(E_F)\xi^3]$ where $N(E_F)$ is the density of states at the Fermi level,[11] $N(E_F)$ is estimated to be about 4.87×10^{19} eV^{-1} cm^{-3}. Associated with the switching of the polarization state from P_r^0 to P_r^+, T_0 was found to decrease from 6.7×10^7 to 5.2×10^7 K. Using $N(E_F)=4.87\times10^{19}$ eV^{-1} cm^{-3} and $T_0=5.2\times10^7$ K, ξ is estimated to be $\sim$20.2 Å for the P_r^+ state, five times larger than that for the P_r^0 state. At the same time, the mean electron hopping distance $R_{hopping}$ at 300 K, inferred from $R_{hopping}=\frac{3}{8}\xi(T_0/T)^{1/4}$,[12] increases from 32.4 Å for the P_r^0 state to 154.8 Å for the P_r^+ state. These estimations of ξ and $R_{hopping}$ indicate that the ferroelectric-polarization-induced strain strongly influences the electronic transport in the film. Correspondingly, the mean hopping energy difference between sites Δ_{hop}^{VRH}, inferred from $\Delta_{hop}^{VRH}(T)=\frac{1}{4}k_BT_0^{1/4}T^{3/4}$, is reduced from 140.5 to 131.8 meV when the polarization state is switched from the P_r^0 to the P_r^+ state. That is, Δ_{hop}^{VRH} decreases with decreasing biaxial distortion in the film. It is clear that the decrease in Δ_{hop}^{VRH} and increases in ξ and $R_{hopping}$ are closely related to the ferroelectric-polarization-induced strain which reduces the tetragonal distortion of MnO_6 octahedra and the electron-lattice coupling strength in the film.[1,2,9,10]

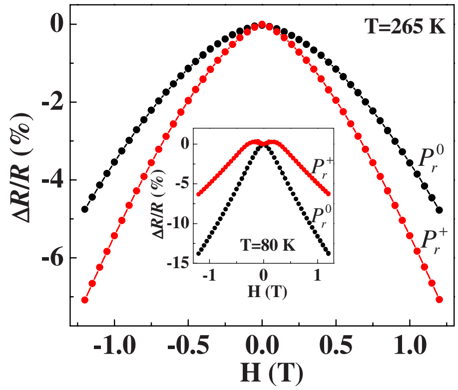

FIG. 2. (Color online) MR of the LCSMO film vs magnetic field H at 265 K when the PMN-PT substrate is in the P_r^0 and P_r^+ states, respectively. The inset shows MR of the film vs magnetic field H at 80 K when the PMN-PT substrate is in the P_r^0 and P_r^+ states, respectively.

Figure 2 shows the MR of the LCSMO film versus the magnetic field H when the PMN-PT substrate is in the P_r^0 and P_r^+ states, respectively. We found that the ferroelectric-polarization-induced in-plane compressive strain (in comparison with the strain state when the PMN-PT substrate is in the P_r^0 state) reduces the MR effect significantly for $T<T_P$. As an example, the MR hysteresis curve at $T=80$ K is shown in the inset of Fig. 2. One can find that the induced in-plane compressive strain reduces the MR in a wide field range from 0 to 1.2 T. At $H=1.2$ T, MR is about 13.7% for the P_r^0 state and is reduced to 6.3% for the P_r^+ state. This in-plane compressive-strain-induced reduction in MR is also observed at several other temperatures that are lower than T_P. In contrast, MR for $T>T_P$ is enhanced when an in-plane compressive strain is applied to the film. A typical MR hysteresis curve at 265 K is shown in Fig. 2. MR at $H=1.2$ T is about 4.8% for the P_r^0 state and increases to 7.1% when polarization is switched to the P_r^+ state. We observed that even at a high temperature of 335 K, the ferroelectric polarization induces an enhancement in MR by 9.4% at $H=1.2$ T.

Many experimental techniques have pointed out that the magnetotransport properties of manganite thin films are strongly associated with the coexisting insulating and metallic phases, i.e., phase separation,[9,10,13,14] whose competition

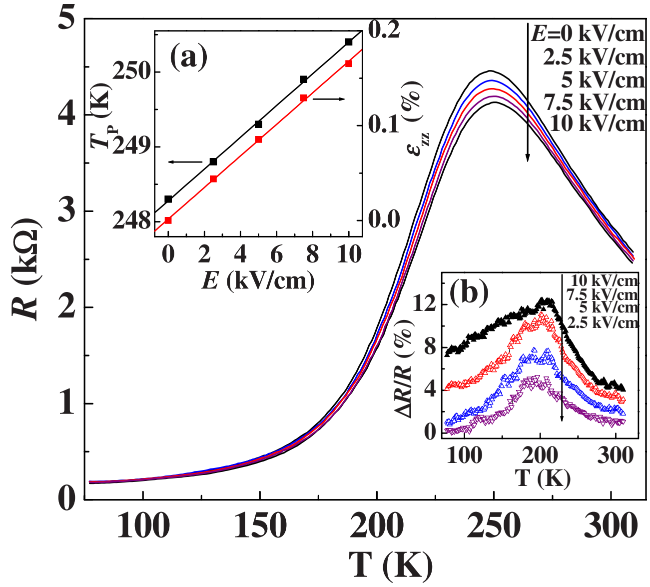

FIG. 3. (Color online) The resistance of the LCSMO film as a function of temperature under application of dc electric fields E to the LCSMO/PMN-PT structure. Inset (a) shows T_P and ε_{zz} of the film as a function of E. Inset (b) shows the converse-piezoelectric-effect-induced relative changes in the resistance, $\Delta R/R$, as a function of temperature.

and subtle balance are closely related to the electron-lattice coupling linked to substrate-induced strain.[9,10,13,14] Generally, the maximal MR effect is observed near T_P where the insulating phase and the metallic phase coexist and strongly compete with each other. The application of a magnetic field near T_P can easily destroy the subtle balance of the coexisting phases favoring ferromagnetic metallic phase. At a high temperature insulating state, i.e., $T>T_P$, the paramagnetic insulating phase dominates over the ferromagnetic metallic phase. The competition between the two coexisting phases is weaker than that at T_P. After the PMN-PT substrate has been polarized, the induced in-plane compressive strain reduces the electron-lattice coupling strength, favoring the metallic phase. As a result, the volume fraction of the metallic phase increases and that of the insulating phase decreases, which would enhance the competition between the coexisting phases and thus favor the CMR effect. In contrast, at a low temperature metallic state, e.g., $T=80$ K, the metallic phase dominates over the insulating phase. The ferroelectric-polarization-induced reduction in the electron-lattice coupling strength would increase the volume fraction of the metallic phase at the expense of the insulating phase, weakening the competition between the coexisting phases, which disfavors the CMR effect.

Figure 3 shows the resistance of the LCSMO film as a function of temperature under application of electric fields E to the LCSMO/PMN-PT structure where the PMN-PT substrate is in the P_r^+ state. With increasing E, the resistance systematically decreases. The relative decrease in the resistance under electric fields, $\Delta R/R$ versus T, is shown in inset (b) of Fig. 3. Accompanied with the decrease in the resistance, T_P was found to increase linearly with increasing E [inset (a) of Fig. 3]. The relationship between T_P and E can be described by $T_P(E)=T_P(0)+aE$, where a is a constant. In order to quantify the relationship between T_P and the induced strain in the film, we calculated the induced out-of-plane strain ε_{zz} in the film by *in situ* measuring the position of the LCSMO(002) reflection under application of electric fields to the LCSMO/PMN-PT structure. As shown in inset (a) of Fig. 3, ε_{zz} increases linearly with increasing E, whose relationship can be described by the equation $\varepsilon_{zz}=bE$, where b is a constant. Such linear dependence of ε_{zz} on E is clearly due to the converse-piezoelectric-effect-induced strain in the PMN-PT substrate.[8] We found that, under application of $E=10$ kV/cm, the c-axis lattice constant of the film is elongated from 3.8686 to 3.8744 Å, indicating that the tensile strain in the film is further reduced. Thus, the electric-field-induced decrease in the resistance and increase in T_P are due to the converse-piezoelectric-effect-induced in-plane compressive strain which reduces the electron-lattice coupling strength associated with the reduction in the tetragonal distortion of MnO_6 octahedra.[8]

The in-plane strain ε_{xx} is related to the out-of-plane strain ε_{zz} by the expression $\varepsilon_{zz}=-[2\nu/(1-\nu)]\varepsilon_{xx}$ where ν is the Poisson ratio. Thus, the relationship between T_P and the induced in-plane compressive strain in the film can be expressed as $T_P(E)=T_P(0)-[(a/b)2\nu/(1-\nu)]\varepsilon_{xx}$, where ε_{xx} is a negative value. This T_P-ε_{xx} relationship demonstrates that T_P is proportional to the induced in-plane strain in the film.

In summary, the substrate-induced strain effects in LCSMO films have been *in situ* studied utilizing ferroelectric PMN-PT single crystals as substrates. Ferroelectric polarization significantly reduces the tensile strain in the film, which reduces the electron-lattice coupling strength and thus gives rise to a large decrease in resistance and increase in T_P of the film. Associated with the reduction in the tensile strain, MR effect for $T<T_P$ decreases while that for $T>T_P$ increases, which we interpreted in terms of phase separation and the variations in the electron-lattice coupling strength linked to substrate-induced strain.

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