

Control of the strain and magnetoresistance of $\text{LaMnO}_{3+\delta}$ thin films using the magnetostriction of Terfenol-D alloy

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We have fabricated a magnetoelectric laminate structure composed of magnetostrictive $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_{1.92}$ (Terfenol-D) alloy and $\text{LaMnO}_{3+\delta}$ (LMO)/ $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.33\text{PbTiO}_3$ (PMN-PT) structure where the LMO film is epitaxially grown on the piezoelectric PMN-PT single-crystal substrate. When an external dc magnetic field is applied perpendicular to the film plane, the magnetoresistance of the LMO film at 220 K under a magnetic field of 1.2 T for the LMO/PMN-PT/Terfenol-D structure is enhanced by 31.6% with respect to that for the LMO/PMN-PT structure without Terfenol-D. Measurements of the magnetoelectric effects of the LMO/PMN-PT/Terfenol-D structure indicate that the strain induced by the magnetostriction of the Terfenol-D alloy is transferred to the PMN-PT substrate, which induces changes in the strain state of the PMN-PT substrate, thereby modifying the strain and magnetoresistance of the epitaxial LMO film.

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I. INTRODUCTION

The substrate-induced strain effects in complex oxide thin films including colossal magnetoresistance (MR) manganites, high temperature cuprate superconductors, multiferroic manganites, bismuth ferrite, etc., are quite complicated and still under intensive investigation.¹⁻⁴ In order to obtain the strain effects in these films, researchers usually grow a set of thin films with different thicknesses on lattice-mismatched substrates and compare the properties of these strained thin films. However, one needs to be reminded that, besides the substrate-induced strain, a range of extrinsic variables including oxygen content, film crystallinity, microstructural defects, dead layer at the interface, growth-induced disorder, growth mode, etc., also strongly influence the properties of thin films.⁵⁻⁸ Therefore, it is quite difficult to separate the effects of the substrate-induced strain from those of the above mentioned extrinsic variables on the properties of complex oxide thin films.

Recently, a variety of experimental work⁹⁻¹⁴ have demonstrated that the strain of piezoelectric $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PMN- x PT) single crystals of PMN- x PT/Terfenol-D laminate structure can be dynamically changed by applying an external dc/ac magnetic field. This dynamical control of the strain of PMN- x PT single-crystal using magnetic field opens the possibility that the strain and properties of complex oxide thin films epitaxially grown on PMN- x PT single-crystal substrates could also be dynamically modified via the magnetostriction of a Terfenol-D alloy if a film/PMN- x PT structure is glued to a Terfenol-D alloy to form a film/PMN- x PT/Terfenol-D laminate structure. In this paper, we report that the strain and MR of $\text{LaMnO}_{3+\delta}$ (LMO) thin films epitaxially grown on the

$0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.33\text{PbTiO}_3$ (PMN-PT) single-crystal substrates can be modified using the magnetostriction of the Terfenol-D alloy for the LMO/PMN-PT/Terfenol-D structure. Measurements of magnetoelectric (ME) effects of the LMO/PMN-PT/Terfenol-D structure indicate that the strain induced by the magnetostriction of the Terfenol-D is effectively transferred to the PMN-PT substrate, which is believed to change the strain state of the epitaxial LMO film, and thus leads to changes in the MR of the film.

II. EXPERIMENTAL DETAILS

We have grown the PMN-PT single crystals by a modified Bridgman technique.¹⁵ The single crystals were cut into rectangular plates ($10 \times 2.5 \times 0.5$ mm³) with the plate normal in the (001) crystal direction and polished until the average surface roughness R_a is less than 0.6 nm. Such polished single crystals were used as substrates to grow LMO films using dc magnetron sputtering. The film deposition was carried out in an argon-oxygen flow with 60% Ar and 40% O₂ at a pressure of 5 Pa and a substrate temperature of 700 °C. During deposition, the substrate holder rotates slowly in order to reduce the dispersion of film thickness over the whole film. After deposition, the films were cooled to room temperature and postannealed in air at 700 °C for 30 min using a rapid thermal processor furnace.

The surface morphology of the films was checked using an atomic force microscope (Digital Instruments, Nanoscope IV) working in a contact mode. The rms roughness is measured to be ~ 0.6 nm over 2.5×2.5 μm^2 area, implying a quite smooth film surface. The crystallographic characterization of the films was performed on a Bruker D8 Discover x-ray diffractometer equipped with Cu $K\alpha$ radiation. Thickness of the LMO films was examined using a field-emission scanning electron microscope (JEOL JSM-6335F) and was

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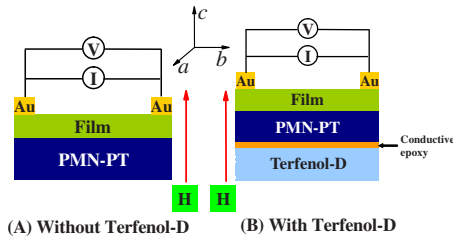


FIG. 1. (Color online) Schematic diagram and electrical measurement circuits for (a) the LMO/PMN-PT structure and (b) the LMO/PMN-PT/Terfenol-D structure.

found to be ~ 36 nm. Figures 1(a) and 1(b) show the electrical measurement circuits for the LMO/PMN-PT structure and the LMO/PMN-PT/Terfenol-D structure, respectively. A constant current of $2 \mu\text{A}$ was applied to the thin film through the two top-top gold electrodes using a Keithley 2400 source meter and the voltage difference between the two top-top gold electrodes was measured by a Keithley 2700 digital multimeter. MR of the LMO films was measured using a Model 7600 LakeShore Hall measurement system (Lake Shore Cryotronics, Inc.). The magnetic properties of the LMO films were measured using a superconducting quantum interference device magnetometer (SQUID-7T, Quantum Design) with the magnetic field applied parallel to the film plane.

ME properties of the LMO/PMN-PT/Terfenol-D structure were characterized at room temperature using a homemade automated measurement system.¹⁴ The induced ME voltages between the top gold electrode and the bottom Terfenol-D alloy were measured as a function of ac magnetic field H_{ac} using a 400 MHz WaveRunner oscilloscope (LeCroy Inc., USA). H_{ac} was provided by Helmholtz coils driven by an AFG320 function generator (Sony Tektronix) via a constant-current Precision Industrial Amplifier (AE Techtron Inc. USA). H_{dc} bias field was supplied by a water-cooled electromagnet.

III. RESULTS AND DISCUSSION

Figure 2 shows the x-ray diffraction (XRD) θ - 2θ scan of the LMO/PMN-PT structure. It is seen that only $(00l)$ ($l=1, 2,$ and 3) reflections from both the LMO film and the

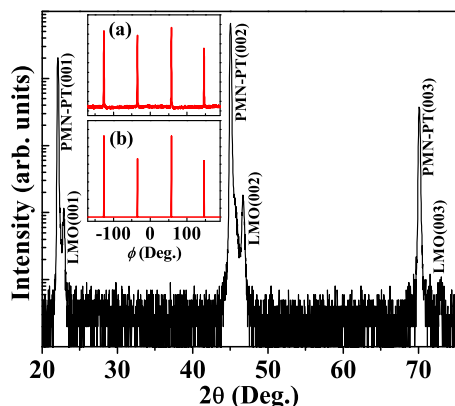


FIG. 2. (Color online) XRD pattern of the LMO/PMN-PT structure. Inset (a) and (b) show the XRD ϕ scans on the LMO(101) and PMN-PT(101) reflections, respectively.

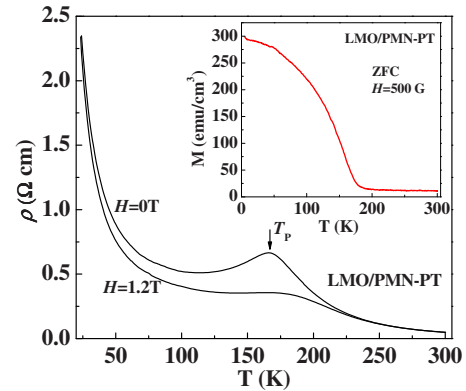


FIG. 3. (Color online) Temperature dependence of the resistivity under $H=0$ and 1.2 T for the LMO/PMN-PT structure without Terfenol-D. The inset shows the temperature dependence of the zero-field-cooled magnetization measured at $H=500$ G for the LMO/PMN-PT structure without Terfenol-D.

PMN-PT substrate appear, indicating that the LMO film and the PMN-PT single-crystal substrate are highly $(00l)$ -oriented and the film has no secondary phases. We have performed XRD ϕ scans on the LMO(101) and PMN-PT(101) reflections, respectively, and obtained fourfold symmetrical reflections for both the LMO film and the PMN-PT substrate [the insets (a) and (b) of Fig. 2, respectively], indicative of the epitaxial growth of the LMO film on the PMN-PT substrate. The out-of-plane or c -axis lattice constant of the film calculated from the LMO(002) reflection is ~ 3.885 Å. This value is smaller than the c -axis lattice constant of LMO bulk materials,¹⁶ indicating that the film is subjected to an out-of-plane compressive and in-plane tensile strain. This is consistent with the fact that the lattice constants of LMO bulk materials are much smaller than those [$a \sim b \sim c \sim 4.02$ Å (Ref. 17)] of PMN-PT single crystals.

Figure 3 shows the temperature dependence of the resistivity under zero magnetic field and a magnetic field of $H=1.2$ T for the LMO/PMN-PT structure without Terfenol-D. With decreasing temperature, the resistivity of the LMO film increases and undergoes an insulator-to-metal transition near $T_p \sim 168$ K. However, with further decrease in the temperature from $T \sim 115$ K, the resistivity starts to increase. The overall resistivity behavior is quite similar to those observed in the $(\text{La}_{0.9}\text{Pr}_{0.1})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$,¹⁸ $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$,¹⁹ and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.125 \leq x \leq 0.145$) (Ref. 20) bulk materials, for which the charged-ordered insulating phase appears at low temperatures. Magnetic measurements performed on the LMO/PMN-PT structure without Terfenol-D show that the LMO film undergoes a paramagnetic to ferromagnetic phase transition near $T=175$ K, which is close to the insulator-to-metal transition temperature. Although the magnetic ground state is ferromagnetic, the resistivity shows insulating behavior for $T < 115$ K, indicating that there exists hole rich $\text{Mn}^{3+}\text{-O-Mn}^{4+}$ ferromagnetically coupled phase which is embedded in the $\text{Mn}^{3+}\text{-O-Mn}^{3+}$ antiferromagnetically coupled matrix with the volume fraction of the latter dominates over the former,²¹ that is, the ferromagnetic metallic phase coexists with the antiferromagnetic insulating phase at low temperatures. Under a relative small magnetic field of $H=1.2$ T, the resistivity decreases remarkably in the whole

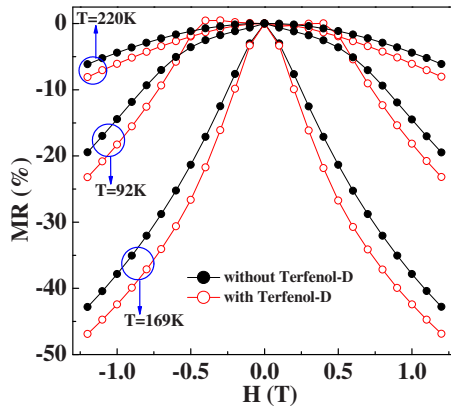


FIG. 4. (Color online) MR of the LMO film for the LMO/PMN-PT structure and the LMO/PMN-PT/Terfenol-D structure at $T=92$ K, 169 K, and 220 K, respectively.

temperature range, implying that the volume fraction of the ferromagnetic metallic phase increases while that of the antiferromagnetic insulating phase decreases under a magnetic field.

In order to observe the effects of the strain induced by the magnetostriction of the Terfenol-D, first, we measured MR of the LMO film at several fixed temperatures for the LMO/PMN-PT structure without Terfenol-D. Here, $MR = [\rho(0) - \rho(H)] / \rho(0)$ where $\rho(0)$ and $\rho(H)$ are the resistivity of the LMO film under zero magnetic field and a magnetic field H , respectively. It is noted that the direction of the magnetic field is perpendicular to the film plane. The MR versus H curves at $T=92$, 169, and 220 K are shown in Fig. 4. After the measurements of MR versus H for the LMO/PMN-PT structure, the same piece of the LMO/PMN-PT structure was glued to a $10 \times 5 \times 1$ mm² Terfenol-D plate using electrically conductive silver loaded epoxy (E-SolderTM 3022, Von Roll Isola, USA) to form a LMO/PMN-PT/Terfenol-D structure. MR of the LMO film for the LMO/PMN-PT/Terfenol-D structure was measured again at $T=92$, 169, and 220 K with the magnetic field also applied perpendicular to the film plane so that the Terfenol-D alloy generates a biaxial in-plane compressive strain due to the magnetostriction effect. Here, the Terfenol-D is textured in the [112] crystallographic orientation, which is parallel with the c -axis (see Fig. 2), and the saturation magnetostriction along the [112] direction of such textured Terfenol-D is ~ 1200 ppm,²² i.e., the saturation strain is $\sim 0.12\%$. As can be seen in Fig. 4, after the LMO/PMN-PT structure had been glued to the Terfenol-D alloy, MR of the LMO film was modified significantly under the same strength of magnetic field, in comparison with the MR values of the LMO/PMN-PT structure without Terfenol-D. Under a magnetic field of 1.2 T (i.e., a strain of 0.12%), MR at 220 K was enhanced by nearly 31.6%.

As is known, the Terfenol-D alloy is a magnetostrictive material. When a dc magnetic field is applied perpendicular to the plane of the Terfenol-D, the Terfenol-D will expand along the direction of the magnetic field and thus generates an in-plane compressive strain. The induced in-plane compressive strain is transferred to the PMN-PT substrate via the silver loaded epoxy, as has been widely observed in PMN-

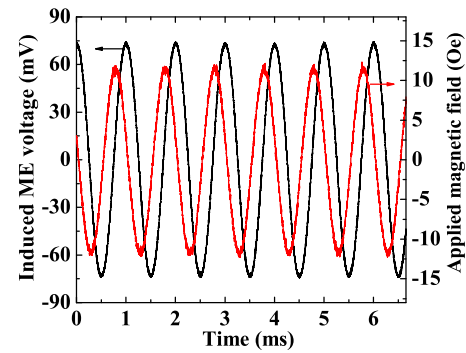


FIG. 5. (Color online) ME voltages induced by a sinusoidal ac magnetic field with a peak value 11.5 Oe as a function of time at a frequency of 1 kHz for the LMO/PMN-PT/Terfenol-D structure.

PT/Terfenol-D structures⁹⁻¹⁴). Consequently, the PMN-PT substrate would be biaxially compressed along the in-plane direction. Such a change in the in-plane strain of the PMN-PT substrate would reduce the in-plane tensile strain of the LMO film since the LMO film is epitaxially grown on the PMN-PT substrate.

To check whether the strain induced by the magnetostriction of Terfenol-D is effectively transferred to the PMN-PT substrate or not, we measured the ME effects of the LMO/PMN-PT/Terfenol-D structure. First, we poled the PMN-PT substrate of the LMO/PMN-PT/Terfenol-D structure by applying a 10 kV/cm dc electric field to the PMN-PT substrate through the conducting LMO film (top electrode) and the Terfenol-D alloy (bottom electrode). Before the measurements of the induced ME voltages, a dc bias field of $H_{dc}=2500$ Oe was applied perpendicular to the plane of the Terfenol-D plate so that the LMO/PMN-PT/Terfenol-D structure has ME effects when an ac magnetic field is applied. Figure 5 shows the ME voltages induced by an applied sinusoidal ac magnetic field with a peak value of 11.5 Oe as a function of time at a frequency of 1 kHz. It is seen that the induced ME voltages are sinusoidally modulated at the same frequency as the driving ac magnetic field. The ME coefficient α_E is calculated to be ~ 156.8 mV/cm Oe. We have also measured the induced ME voltages as a function of time when the same sinusoidal ac magnetic field was applied parallel to the plane of the Terfenol-D plate under a dc bias field of $H_{dc}=1000$ Oe and observed ME coefficient $\alpha_E \sim 86.9$ mV/cm Oe (the results are not shown here). These observed ME effects in the LMO/PMN-PT/Terfenol-D structure strongly indicate that the strain induced by the magnetostriction of the Terfenol-D is effectively transferred to the PMN-PT substrate.

It is generally accepted that MR of perovskite manganites is strongly influenced by the phase separation which is closely related to the lattice distortion of MnO₆ octahedra.²³⁻²⁵ Whether the LMO film is in the high temperature paramagnetic state or the low temperature ferromagnetic insulating state, associated with the reduction in the in-plane tensile strain of the LMO film induced by the magnetostriction of the Terfenol-D, the in-plane tetragonal distortion of MnO₆ octahedra of the film would be reduced, as revealed by the angular resolved x-ray absorption spectroscopy by Souza-Neto *et al.*²⁶ Such a change in the distortion

of MnO_6 octahedra weakens the electron-lattice coupling strength and increases the double-exchange interaction, thereby favoring the active hopping of e_g electrons.²⁷ As a result, the volume fraction of the ferromagnetic metallic phase would increase at the expense of the paramagnetic (or antiferromagnetic) insulating phase. MR of the film thus increases due to enhanced volume fraction of the ferromagnetic metallic phase.

IV. CONCLUSIONS

We have fabricated a LMO/PMN–PT/Terfenol-D laminate structure and induced strain in the Terfenol-D plate via the magnetostriction effect. The induced strain is found to be effectively transferred to the PMN–PT substrate and is believed to reduce the in-plane tensile strain of the epitaxial LMO film. Consequently, MR of the LMO film is remarkably enhanced, e.g., MR is modified by $\sim 31.6\%$ at $T = 220$ K under $H = 1.2$ T, in comparison with that for the LMO/PMN–PT structure without Terfenol-D. This effect of the magnetostrictive strain on MR can be explained by the enhanced volume fraction of the ferromagnetic metallic phase of the LMO film due to the reduction in the tetragonal distortion of MnO_6 octahedra and enhancement of double-exchange interaction. The control of strain using the magnetostriction of Terfenol-D alloy may be further extended to study intrinsic strain effects of other complex oxide thin films without introducing certain effects induced by extrinsic variables since the same piece of thin-film sample is used.

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