Determination of the strain dependence of resistance in $La_{0.7}Sr_{0.3}MnO_3$/PMN-PT using the converse piezoelectric effect

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We have deposited $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films on piezoelectric $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ ($x\sim0.3$) (PMN-PT) single-crystal substrates and studied the effects of substrate-induced lattice strain on the resistance of the LSMO films. By applying electric fields across the PMN-PT substrate, we *in situ* induce an in-plane compressive (tensile) strain in the PMN-PT substrate via the converse piezoelectric effect. The induced strain is transferred to the LSMO film, which then imposes an in-plane compressive (tensile) strain on the LSMO film, thereby causing a linear decrease (increase) in the resistance of the LSMO film. Based on the experimental results, we establish quantitative relationships between the resistance of the LSMO film and the converse piezoelectric-effect-induced out-of-plane and in-plane strains in the PMN-PT substrate and LSMO film, respectively.

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The colossal magnetoresistance (CMR) manganites of $R_{1-x}A_xMnO_3$ (R and A are trivalent rare-earth and divalent alkaline-earth ions, respectively) have attracted considerable attention due to their potential applications and a range of novel properties such as the CMR effect, phase separation, and charge ordering.[1–6] Because of the strong interplay among the spin, charge, lattice, and orbital degrees of freedom, the properties of CMR materials are very sensitive to subtle structural changes. The substrate-induced lattice strain, which could change the strength of the double-exchange (DE) interaction and Jahn-Teller (JT) electron-lattice coupling via modifying Mn-O bond lengths and/or Mn-O-Mn bond angles, is one of the most important factors that strongly affect the properties of thin films—e.g., Curie temperature, CMR, and phase separation.[5–7] Although the substrate-induced lattice strain effect in manganite thin films has been studied extensively, a quantitative understanding of substrate-induced lattice strain effect is still needed from fundamental and technological viewpoints. In particular, the establishment of quantitative relationships between the properties of thin films and the lattice strains in both thin films and substrates would be highly desired for device fabrication and theoretical modeling of the lattice strain effect.

The commonly applied method for the study of the substrate-induced lattice strain effect is the growth of thin films on substrates with a certain lattice mismatch, with the thickness of these thin films varying over a relatively large range. However, it should be noted that the properties of thin films are not only sensitive to substrate-induced lattice strain but also to other extrinsic factors including oxygen nonstoichiometry, crystalline quality, strain relaxation, growth-induced disorder, grain sizes and boundary, and growth mode.[4,8–10] Therefore, a quantitative understanding of the intrinsic effects of substrate-induced lattice strain on the properties of thin films is still very limited since it is quite difficult to rule out the property changes resulting from these extrinsic factors. One good method for the study of the intrinsic lattice strain effect is to produce biaxial strain in thin films by *in situ* inducing lattice strain in substrates using the same thin-film sample, so that aforementioned extrinsic factors could be kept fixed.

Ferroelectric $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PMN-xPT) single crystals with PT compositions near the morphotropic phase boundary region (i.e., $0.28\leqslant x\leqslant0.35$) exhibit excellent piezoelectric activity after they have been polarized. This means that the lattice strain in PMN-xPT single crystals can be *in situ* induced by applying an electric field across the PMN-xPT single crystals via the converse piezoelectric effect.[11,12] Very recently, Thiele *et al.*[12–14] reported that the resistance, magnetization, and Curie temperature of the $La_{0.7}Sr_{0.3}MnO_3$ thin films grown on (001)-oriented $0.72Pb(Mg_{1/3}Nb_{2/3})O_3-0.28PbTiO_3$ single-crystal substrates can be modulated by the converse piezoelectric effect of the $0.72Pb(Mg_{1/3}Nb_{2/3})O_3-0.28PbTiO_3$ substrate. Similar electric-field-induced modulation of the resistance via the converse piezoelectric effect has also been observed in the $La_{0.7}Sr_{0.3}MnO_3/PbZr_{0.52}Ti_{0.48}O_3$,[15] $La_{0.7}Sr_{0.3}MnO_3/0.68Pb(Mg_{1/3}Nb_{2/3})O_3-0.32PbTiO_3$,[16] and $La_{0.5}Sr_{0.5}MnO_3/BaTiO_3$ (Ref. 17) structures. These results demonstrate the possibility that one can study the sole effects of controlled strain by using the converse piezoelectric effect, while keeping the aforementioned extrinsic factors fixed.

In this work, we deposited $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films on the $0.7Pb(Mg_{1/3}Nb_{2/3})O_3-0.3PbTiO_3$ single-crystal substrates and presented a further study of the effects of substrate-induced lattice strain on the strain state and resistance of the LSMO films by *in situ* inducing lattice strain in the PMN-PT substrates via the converse piezoelectric effect. We established quantitative relationships between the resistance of the LSMO films and the induced lattice strains in the PMN-PT substrates and LSMO films, respectively.

The details for the growth of the PMN-PT single crystals and LSMO films are described in Refs. 16 and 18. X-ray diffraction (XRD) measurements indicate that the LSMO films are of single phase and c-axis preferentially oriented. Low-frequency ferroelectric measurements show that the polarization–electric-field hysteresis loop of the PMN-PT substrate has a square shape and remnant polarization

$\sim 25\ \mu C/cm^2$ and coercive field $E_C \sim 0.35$ kV/mm. The electric-field-induced longitudinal lattice displacement of the PMN-PT substrate, due to the converse piezoelectric effect, was measured using a modified double-beam laser interferometer. The resistance of the LSMO films was measured using the electrical measurement circuit shown in the inset of Fig. 2. The leakage current was measured using a Keithley 6517A electrometer and was less than 0.35 and 2.5 nA under 0.1- and 1 kV/mm bias fields, respectively.

Before the measurements of the resistance of the LSMO film, we polarized the PMN-PT substrate by applying a dc poling field of +1 kV/mm across the LSMO/PMN-PT structure near the Curie temperature of the PMN-PT substrate in a silicone oil bath so that the PMN-PT substrate was polarized and thus possesses the converse piezoelectric effect. Piezoelectric measurements using a Berlincourt-type quasistatic d_{33} meter indicate that the polarized PMN-PT substrate has a longitudinal piezoelectric coefficient $d_{33} \sim 1320$ pC/N at room temperature.

Figure 1(a) shows the resistance response ($\Delta R/R$) of the LSMO film at 296 K as a function of time when a sinusoidal electric field with a peak-to-peak magnitude of 0.2 kV/mm was applied to the polarized PMN-PT substrate. Here, $\Delta R/R=[R(E)-R(0)]/R(0)$ where $R(E)$ and $R(0)$ are the resistance of the LSMO film under an electric field E and zero electric field, respectively. One can see that the resistance of the LSMO film was modulated at the same frequency as that of the driving sinusoidal electric field. Applying a positive (negative) electric field to the PMN-PT substrate leads to a decrease (increase) in the resistance of the LSMO film. A relative change in the resistance ($\Delta R/R$) of $\sim 0.6\%$ is observed when a 0.1 kV/mm electric field is applied to the PMN-PT substrate. It should be pointed out that applying a small electric field of $E=0.1$ kV/mm ($E<E_C$) at 296 K to the polarized PMN-PT cannot switch the polarization state of the PMN-PT substrate. On the other hand, the electric-field-induced relative change in areal carrier density in the LSMO film is given by $\Delta n/n=\varepsilon_0\varepsilon_r V_g/et_i n_0 t_{ch}$,[19,20] where ε_0 and ε_r are the permittivities of free space and the PMN-PT substrate, respectively, V_g is the gate voltage, e is the unit charge, t_i is the thickness of the PMN-PT substrate, and n_0 and t_{ch} are the volume carrier density and thickness of the LSMO film, respectively. Assuming a volume carrier density of $1\times 10^{22}/cm^3$ in the LSMO film,[21,22] $V_g=55$ V, $t_{ch} \sim 30$ nm, $\varepsilon_r=2550$, and $t_i=0.55$ mm, one obtains $\Delta n/n \sim 0.0048\%$. In a free electron model, one could obtain the relationship that $\Delta R/R=-\Delta n/n$.[23–25] Thus, the field effect in the LSMO/PMN-PT structure is negligibly small. In fact, if only the field effect is considered, the resistance of the LSMO film should increase (decrease) when a positive (negative) electric field is applied to the PMN-PT substrate, because of the depletion (accumulation) of holes in the LSMO film.[25–27] As seen in Fig. 1(a), the actual signs of the change in the resistance of the LSMO film are opposite to those expected from the field effect.

Polarized ferroelectric materials possess the converse piezoelectric effect; that is, applying a small electric field E ($E<E_C$) with the same (opposite) polarity as the poling field to the polarized ferroelectric materials will result in an expansion (compression) of the lattice of the materials along the direction of the electric field.[28] To check this effect, we have measured the longitudinal lattice displacement (Δl) of the PMN-PT substrate when a sinusoidal electric voltage with a peak-to-peak magnitude of 40 V is applied to the PMN-PT substrate. As shown in Fig. 1(b), the lattice of the PMN-PT substrate expands and contracts along the c axis at the same frequency and phase as those of the driving sinusoidal electric field. Applying a positive (negative) 20 V voltage to the PMN-PT substrate causes the lattice expands (contracts) along the c axis by ~ 26.2 nm. The electric-field-induced lattice displacement (Δl) in ferroelectric materials due to the converse piezoelectric effect can be calculated using $\Delta l=d_{33}V$.[28] Here, $\Delta l=l(E)-l(0)$ where $l(E)$ and $l(0)$ are the thicknesses of the PMN-PT substrate under an electric field E and zero electric field, respectively. Using $d_{33}=1320$ pm/V and $V=20$ V, one obtains $\Delta l=26.4$ nm. This calculated value agrees well with the Δl value obtained from the piezoelectric displacement measurements. Thus, the results unambiguously indicate that the electric field induces a modulation of the lattice strain in the PMN-PT substrate via the converse piezoelectric effect.

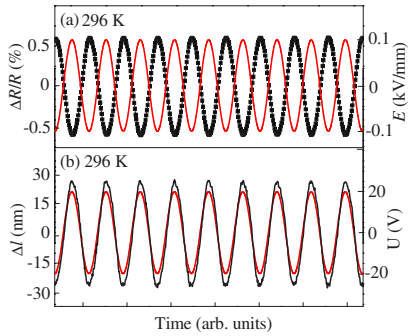

FIG. 1. (Color online) (a) Resistance response ($\Delta R/R$) of the LSMO film at 296 K as a function of time when a sinusoidal electric field with a peak-to-peak magnitude of 0.2 kV/mm (solid red curve) is applied to the positively polarized PMN-PT substrate. (b) The converse piezoelectric effect induced longitudinal lattice displacement (Δl) of the PMN-PT substrate as a function of time when a sinusoidal electric voltage with a peak-to-peak magnitude of 40 V (solid red curve) is applied to the positively polarized PMN-PT substrate.

Theoretical and experimental investigations have shown that the DE interaction and JT electron-lattice coupling in manganite thin films are very sensitive to biaxial strain.[5,6,29] A change in the strain state of the LSMO film is expected to result in a change in the strength of the DE interaction and JT electron-lattice coupling. When a positive electric field is applied to the positively polarized PMN-PT substrate, the field will induce an in-plane compressive strain in the PMN-PT substrate via the converse piezoelectric effect.[12,28] The induced compressive strain will be transferred to the LSMO film, causing a reduction of the tensile strain in the LSMO film,[12,16] which, on the one hand, reduces the JT distortion and thus increase the tendency of the charge carriers to become delocalized.[5,6,29] On the other hand, a reduction of the biaxial tensile strain also gives rise to a decrease in the in-plane Mn-O bond length and hence an enhancement of the strength of DE interaction and hopping amplitude of charge

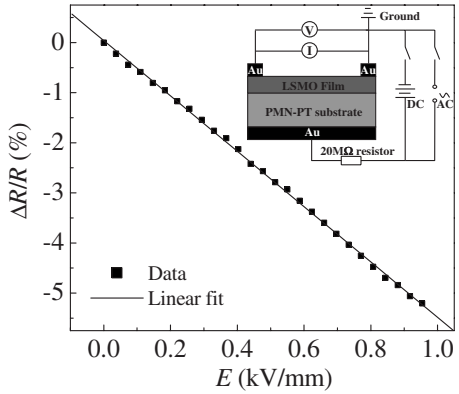

FIG. 2. The relative change in the resistance ($\Delta R/R$) of the LSMO film at 296 K as a function of electric field E applied to the positively polarized PMN-PT substrate. The inset shows the LSMO/PMN-PT structure and the electrical measurement circuit.

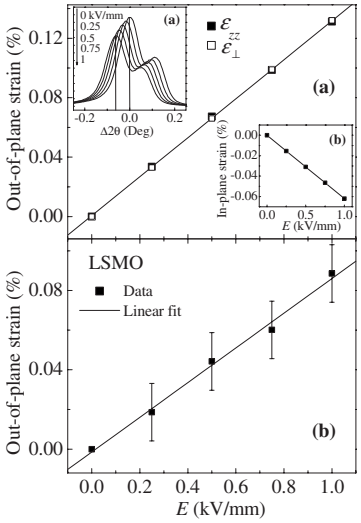

FIG. 3. (a) Electric-field-induced out-of-plane strains in the PMN-PT substrate at 296 K as a function of electric field. The solid and open squares represent the out-of-plane strains in the PMN-PT substrate obtained from XRD measurements and calculated using $\varepsilon_{\perp(PMN\text{-}PT)}=d_{33}E$, respectively. Inset (a) shows the XRD patterns for the PMN-PT(002) reflection under electric fields. Inset (b) shows the electric-field-induced in-plane strains in the PMN-PT substrate as a function of electric field. (b) The induced out-of-plane strains in the LSMO film as a function of electric field.

carriers. This also results in a decrease in the resistance of the LSMO film. For the same arguments, when a negative electric field is applied to the positively polarized PMN-PT substrate, the induced strain in the PMN-PT substrate will increase the tensile strain in the LSMO film and hence an increase in the resistance of the LSMO film. From the above analysis, the modulation of the resistance of the LSMO film with the same frequency (but the opposite phase) as those of the driving sinusoidal electric field (Fig. 1) can be understood on the basis of the combined effect of the DE interaction and JT electron-lattice coupling whose strength are modulated by the induced lattice strain in the LSMO film, resulting from the converse piezoelectric effect induced lattice strain in the PMN-PT substrate.

Figure 2 shows the relative change in the resistance ($\Delta R/R$) of the LSMO film at 296 K as a function of the electric field E applied to the PMN-PT substrate. The resistance decreases linearly with increasing E, being similar to those reported in Refs. 12 and 16. The relationship between $\Delta R/R$ and E can be described by

$$\Delta R/R = -aE, \tag{1}$$

where a is a positive constant. Using Eq. (1) and $\Delta l = d_{33}V$, the relationship between $\Delta R/R$ and $\Delta l/l$ can be expressed as $\Delta R/R = -\frac{a}{d_{33}}\frac{\Delta l}{l}$. This relationship indicates that the relative change in the resistance of the LSMO film is proportional to the relative lattice displacement in the PMN-PT substrate.

To obtain a quantitative understanding of the effects of the electric-field-induced lattice strain on the resistance of the LSMO film, we have examined the electric-field-induced lattice strain in the PMN-PT substrate by measurements of XRD under electric fields. The inset (a) of Fig. 3(a) shows that the PMN-PT(002) reflection shifts to lower 2θ angles with increasing electric field from 0 to 1 kV/mm, which implies that the lattice parameter c of the PMN-PT substrate has been elongated by the electric field. Based on these XRD results, the electric-field-induced lattice strain along the direction of the electric field in the PMN-PT substrate (i.e., out-of-plane strain $\varepsilon_{zz(PMN\text{-}PT)}$) can be estimated using $\varepsilon_{zz(PMN\text{-}PT)} = \frac{c_{PMN\text{-}PT}(E) - c_{PMN\text{-}PT}(0)}{c_{PMN\text{-}PT}(0)}$ where $c_{PMN\text{-}PT}(E)$ and $c_{PMN\text{-}PT}(0)$ are the lattice parameter c of the PMN-PT substrate under an electric field E and zero electric field, respectively. As seen in Fig. 3, $\varepsilon_{zz(PMN\text{-}PT)}$ increases linearly with increasing E. The relationship between $\varepsilon_{zz(PMN\text{-}PT)}$ and E can be described by

$$\varepsilon_{zz(PMN\text{-}PT)} = bE, \tag{2}$$

where b is a positive constant. Combining Eq. (1) with Eq. (2), the relationship between the resistance of the LSMO film and the converse piezoelectric-effect-induced out-of-plane strain in the PMN-PT substrate can be expressed as

$$\Delta R/R = -a\varepsilon_{zz(PMN\text{-}PT)}/b. \tag{3}$$

The electric-field-induced lattice strain along the direction of electric field (i.e., $\varepsilon_{\perp(PMN\text{-}PT)}$) due to the converse piezoelectric effect in the PMN-PT substrate can be calculated using $\varepsilon_{\perp(PMN\text{-}PT)}=d_{33}E$.[28] Using $d_{33}=1320$ pC/N, we calculated the values of $\varepsilon_{\perp(PMN\text{-}PT)}$ and plotted them as a function of E in Fig. 3(a). The calculated values of $\varepsilon_{\perp(PMN\text{-}PT)}$ agree well with those of $\varepsilon_{zz(PMN\text{-}PT)}$ obtained from XRD measurements, which gives further evidence that the electric-field-induced lattice strain in the PMN-PT substrate is caused by the converse piezoelectric effect.

On the other hand, the electric-field-induced lattice strain perpendicular to the direction of electric field in the PMN-PT substrate (i.e., in-plane compressive strain $\varepsilon_{\parallel(PMN\text{-}PT)}$) can be calculated by[28]

$$\varepsilon_{\parallel(PMN\text{-}PT)} = -d_{31}E, \tag{4}$$

where d_{31} is the transverse piezoelectric coefficient of the PMN-PT substrate. Using $d_{31}=620$ pC/N obtained by a resonance technique using a HP4294A impedance analyzer,

we plot $\varepsilon_{\parallel}$ as a function of E in the inset (b) of Fig. 3(a). The linear decrease in $\varepsilon_{\parallel}$ indicates that the in-plane lattice of the PMN-PT substrate was compressed with increasing E. Combining Eq. (1) with Eq. (4), the relationship between the resistance of the LSMO film and the converse piezoelectric-effect-induced in-plane strain in the PMN-PT substrate can be expressed as

$$\Delta R/R = a\varepsilon_{\parallel(PMN\text{-}PT)}/d_{31}. \quad (5)$$

Equations (3) and (5) indicate that the relative change in the resistance of the LSMO film, due to substrate-induced lattice strain, depends linearly on the induced out-of-plane and in-plane strains in the PMN-PT substrate.

The induced in-plane compressive strain in the PMN-PT substrate can be transferred to the LSMO film and thus causes a decrease in the in-plane lattice parameters and an increase in the out-of-plane lattice parameter in the LSMO film. The induced out-of-plane strain $\varepsilon_{zz(LSMO)}$ in the LSMO film can be estimated using $\varepsilon_{zz(LSMO)}=\frac{c_{LSMO}(E)-c_{LSMO}(0)}{c_{LSMO}(0)}$ where $c_{LSMO}(E)$ and $c_{LSMO}(0)$ are the lattice parameter c of the LSMO film obtained from XRD measurements under an electric field E and zero electric field, respectively. We plot $\varepsilon_{zz(LSMO)}$ as a function of electric field in Fig. 3(b). It can be seen that $\varepsilon_{zz(LSMO)}$ increases with increasing electric field and can be roughly described by

$$\varepsilon_{zz(LSMO)} = cE, \quad (6)$$

where c is a positive constant. Using Eqs. (2) and (6), the relationship between the out-of-plane strain in the LSMO film and the out-of-plane strain in the PMN-PT substrate can be obtained as $\varepsilon_{zz(LSMO)}=c\varepsilon_{zz(PMN\text{-}PT)}/b$. Moreover, one may obtain the relationship between $\Delta R/R$ and $\varepsilon_{zz(LSMO)}$ in the LSMO film using Eqs. (1) and (6), which can be written as

$$\Delta R/R = -a\varepsilon_{zz(LSMO)}/c. \quad (7)$$

Equation (7) indicates that the relative change in the resistance is proportional to the induced out-of-plane strain in the LSMO film. Compared with the strain state of the LSMO film when $E=0$ kV/mm, the PMN-PT substrate imposes an in-plane compressive strain on the LSMO film when a positive electric field is applied to the positively polarized PMN-PT substrate. With in-plane strain $\varepsilon_{xx(LSMO)}=\varepsilon_{yy(LSMO)}$, the relationship between $\varepsilon_{zz(LSMO)}$ and $\varepsilon_{xx(LSMO)}$ in the LSMO film can be expressed as $\varepsilon_{zz(LSMO)}=-\frac{2\nu}{1-\nu}\varepsilon_{xx(LSMO)}$ where ν is Poisson's ratio.[30] Thus, the relationship between $\Delta R/R$ and the induced in-plane strain $\varepsilon_{xx(LSMO)}$ in the LSMO film can be written as

$$\Delta R/R = (a/c)[2\nu/(1-\nu)]\varepsilon_{xx(LSMO)}. \quad (8)$$

Equation (8) indicates that the relative change in the resistance is proportional to the induced in-plane compressive strain in the LSMO film. From Figs. 2 and 3, one may find that applying an electric field of 1 kV/mm to the PMN-PT substrate resulted in $\Delta R/R \sim 5.5\%$ and $\varepsilon_{zz(LSMO)} \sim 0.088\%$. Assuming $\nu=0.35$ for the LSMO film,[31,32] one obtains $\varepsilon_{xx(LSMO)} \sim -0.082\%$. This means that a change of in-plane strain by 0.082% leads to a relative change in the resistance by ~5.5% for the LSMO film at 296 K, a resistance-strain coefficient of $\frac{\Delta R/R}{\varepsilon_{xx(LSMO)}}=67.1$.

In summary, we have reported that the lattice strain and resistance of the $La_{0.7}Sr_{0.3}MnO_3$ thin films grown on piezoelectric PMN-PT substrates can be modulated by applying a sinusoidal electric field across the PMN-PT substrates. The origin of the modulation of the resistance has been explained with a model based on the converse piezoelectric effect of the PMN-PT substrates. Moreover, we have established quantitative relationships between the resistance of the LSMO film and the electric-field-induced in-plane and out-of-plane strains in the PMN-PT substrate and LSMO film, respectively, which could be important for understanding the physics of substrate-induced lattice strain effects.

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