

Substrate-induced strain effect in $\text{La}_{0.875}\text{Ba}_{0.125}\text{MnO}_3$ thin films grown on ferroelectric single-crystal substrates

R. K. Zheng,^{1(a)} Y. Wang,¹ H. L. W. Chan,¹ C. L. Choy,¹ and H. S. Luo²

¹Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hong Kong, People's Republic of China

²State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201800, People's Republic of China

(Received 21 November 2007; accepted 28 January 2008; published online 28 February 2008)

The authors have studied the substrate-induced strain effect in $\text{La}_{0.875}\text{Ba}_{0.125}\text{MnO}_3$ (LBMO) thin films grown on ferroelectric $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.33\text{PbTiO}_3$ (PMN-PT) single-crystal substrates. Both the strain and resistance of the films can be *in situ* varied by applying an electric field across the PMN-PT substrates. X-ray diffraction analysis indicates that the variations of strain and resistance result from the induced strain in the PMN-PT substrate due to the ferroelectric polarization or the converse piezoelectric effect. The relationships between the resistance and the induced strain in the LBMO film and PMN-PT substrate have been quantitatively analyzed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2870100]

The substrate-induced strain effect in perovskite manganites is far from fully understood.¹⁻⁷ Zhang *et al.*¹ reported that the substrate-induced tensile strain reduces the resistivity and enhances Curie temperature T_C of $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ (LBMO) ($0 \leq x \leq 0.2$) films, while the substrate-induced compressive strain enhances resistivity and reduces T_C . These results are different from those of well studied manganese thin films, e.g., $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$,² $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$.³ Kanki *et al.*⁴ pointed out that this anomalous strain effect is due to enhanced charge carrier transfer resulting from strain-induced modification of Mn–O–Mn networks and that the oxygen nonstoichiometry plays a negligible role. In contrast, Murugavel *et al.*^{5,6} and Orgiani *et al.*⁷ reported that, irrespective of whether the strain is compressive or tensile, the oxygen content plays a dominant role in controlling the hole doping level, Mn–O–Mn bond angle, Mn–O bond length, and the transport and magnetic properties of LBMO films, which strongly highlight the very important role of oxygen content in determining the electrical, magnetic, and structural properties of LBMO films. Thus, it is not easy to study the intrinsic substrate-induced strain effect in LBMO films because it is rather difficult to determine the oxygen content and, thus, the property changes due to oxygen nonstoichiometry in the films.

In this letter, we deposit the LBMO films on the ferroelectric $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.33\text{PbTiO}_3$ (PMN-PT) single-crystal substrates and *in situ* induces strain in the PMN-PT substrate via ferroelectric polarization or the converse piezoelectric effect. Using this method, we have studied the effects of the substrate-induced strain on the strain state and transport properties of the LBMO films quantitatively while keeping the oxygen content constant.

PMN-PT substrates show excellent ferroelectricity which is characterized by a well-defined polarization-electric field hysteresis loop with a remnant polarization $P_r \sim 35 \mu\text{C}/\text{cm}^2$ and a coercive field $E_C \sim 2.5 \text{ kV}/\text{cm}$ [inset (a) of Fig. 1]. The LBMO films were grown on the (001)-oriented and polished PMN-PT substrates using dc magnetron sputtering. The resistance of the LBMO film was mea-

sured using the measurement circuit shown in the inset (b) of Fig. 1. X-ray diffraction (XRD) patterns of the PMN-PT and LBMO (002) reflections were recorded under application of a static dc electric field E ($0 \leq E \leq 10 \text{ kV}/\text{cm}$) across the PMN-PT substrate *in situ*.

Figure 1 shows the XRD pattern of a LBMO film grown on a (001)-oriented PMN-PT substrate. A peak arising from the LBMO(002) reflection is observed, indicating that the LBMO film is *c*-axis preferentially oriented. The lattice constant c of the LBMO film was measured to be 3.8823 \AA which is smaller than that of the LBMO single crystals, indicating that the film is under in-plane tensile strain.

Inset (a) of Fig. 2 shows the temperature dependence of the resistance of the LBMO film when the PMN-PT substrate was in the unpolarized state (referred to as P_r^0) and positively polarized state (i.e., electric dipole moments in the PMN-PT substrate point toward the LBMO film, referred to as P_r^+), respectively. When the PMN-PT was in P_r^0 state, the resis-

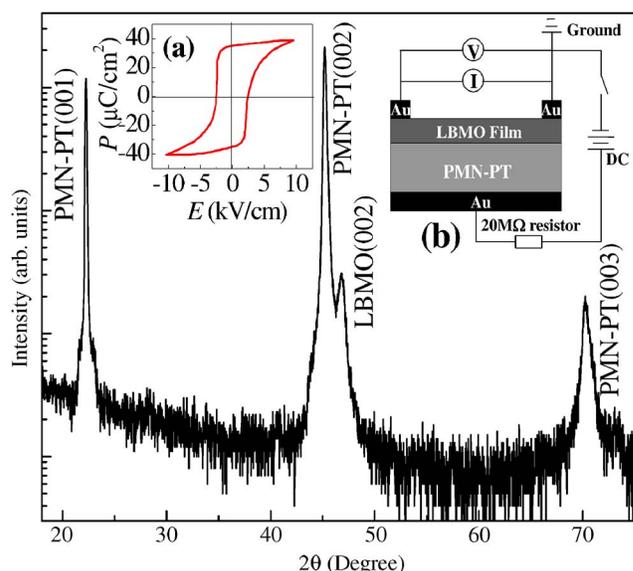


FIG. 1. (Color online) X-ray diffraction pattern of the LBMO/PMN-PT structure. Inset (a) shows the polarization-electric field hysteresis loop of the PMN-PT substrate measured at 296 K. Inset (b) shows a schematic diagram of the LBMO/PMN-PT structure and the electrical measurement circuit.

^aElectronic mail: zrk@ustc.edu.

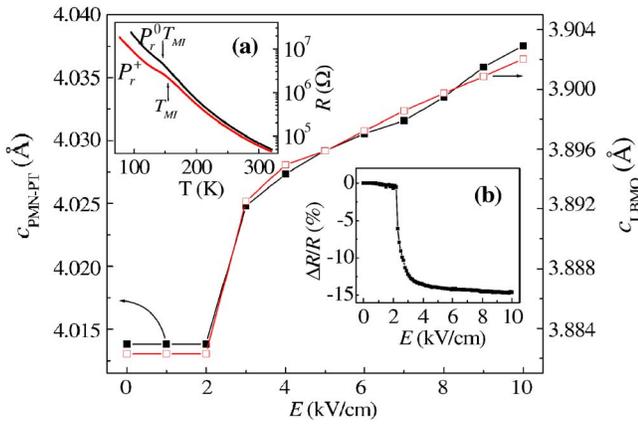


FIG. 2. (Color online) Lattice constant c of the PMN-PT substrate and LBMO film at 296 K as a function of the electric field applied to the LBMO/PMN-PT structure where the initial polarization state of the PMN-PT substrate is in P_r^0 state. Inset (a) shows the temperature dependence of the resistance for the LBMO film when the PMN-PT substrate is in the unpolarized state (P_r^0) and positively polarized state (P_r^+). Inset (b) shows the resistance of the LBMO film at 296 K as a function of the electric field applied to the LBMO/PMN-PT structure where the initial polarization state of the PMN-PT substrate is in P_r^0 state.

tance of the LBMO film increases with decreasing temperature from 320 K to lower temperatures, displaying semiconducting behavior. At $T_{MI} \sim 146$ K (defined as the temperature where the $\ln R-T^{-1/4}$ curve changes its slope), the resistance shows a metal-insulator-like transition. Unfortunately, there is very limited study on the resistance transition near T_{MI} for $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ with x close to $1/8$ doping. Nevertheless, the nature of the resistivity transition near T_{MI} is quite similar to that of $\text{La}_{7/8}\text{A}_{1/8}\text{MnO}_3$ ($A=\text{Ca}, \text{Sr}$) single crystals, where short/long-range polaron ordering has been reported below T_{MI} .^{8,9} Note that T_{MI} of ~ 146 K in our film is lower than that of the LBMO single crystals, which may be due to oxygen deficiency in the LBMO film.⁵⁻⁷

After the measurements of the resistance when the PMN-PT was in P_r^0 state, we polarized the PMN-PT substrate by applying a dc poling field of +10 kV/cm across the LBMO/PMN-PT structure. It is clear that, after the PMN-PT substrate has been positively polarized, the metal-insulator-like transition near T_{MI} becomes more conspicuous. At the same time, T_{MI} shifts to a higher temperature by ~ 9 K and the resistance decreases over a wide temperature range from 77 to 320 K. The relative decrease in the resistance associated with the switching from P_r^0 to P_r^+ state $\Delta R/R$ is about 12.9% at room temperature and increases to $\sim 57.8\%$ at 100 K. We note that the ferroelectric field effect in the LBMO/PMN-PT structure is negligible since the screening length of an electrostatic field in manganite films is only a few unit cells,^{10,11} which is much smaller than the thickness (~ 35 nm) of our LBMO film.

It should be pointed out that the ferroelectric polarization of the PMN-PT substrate will induce a large lattice strain because of the rotation of polarization direction toward the direction of electric field. The induced strain would be transferred to the LBMO film, causing a large change in the strain state and hence the resistance of the LBMO film. The inset (b) of Fig. 2 shows the resistance of the LBMO film at 296 K as a function of the electric field applied to the LBMO/PMN-PT structure, where the initial polarization of the PMN-PT substrate was in P_r^0 state (i.e., piezoelectric coefficient $d_{33}=0$ pC/N). The resistance decreases slightly by

$\sim 0.5\%$ with increasing E from 0 to 2.2 kV/cm, but decreases drastically with further increase in E . $\Delta R/R$ reaches $\sim -14.7\%$ at $E=10$ kV/cm. We note that, after the measurements of the resistance as a function of E , d_{33} was found to be ~ 1900 pC/N, which demonstrates that the large decrease in the resistance near $E=2.5$ kV/cm is associated with the ferroelectric polarization.

Figure 2 shows the lattice constant c of the PMN-PT substrate and LBMO film between $E=2$ and 3 kV/cm, coincident with the large decrease in the resistance of the LBMO film near $E=2.5$ kV/cm. When $E=10$ kV/cm, the electric field induces an increase of the lattice constant c of the PMN-PT substrate by ~ 0.024 Å, corresponding to $\varepsilon_{zz(\text{PMN-PT})} \sim 0.6\%$. Such changes in $\varepsilon_{zz(\text{PMN-PT})}$ would give rise to a large compression in the in-plane lattice constants of the PMN-PT substrate and LBMO film, as a result of the Poisson effect. Consequently, the lattice constant c of the LBMO film increases from 3.882 Å at $E=0$ kV/cm to 3.902 Å at $E=10$ kV/cm. This value (i.e., $c=3.902$ Å) is close to that ($c=3.9015$ Å) of the LBMO single crystals,¹² which indicates that the out-of-plane compressive and in-plane tensile strain in the LBMO film has been almost completely released.

For LBMO films, it is argued that the substrate-induced strain primarily modifies the Mn–O–Mn bond angle θ , with the Mn–O bond length d nearly unchanged.¹³ The same results have also been observed in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x=0.31, 0.39$) (Ref. 14) and $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (Ref. 15) films, where the substrate-induced strain only affects the Mn–O–Mn bond angle. Thus, if the Mn–O bond length is assumed to be fixed for the LBMO film, the electronic bandwidth W ($W \propto \sin(\theta/2)/d^{3.5}$) would be reduced by the ferroelectric polarization-induced in-plane compressive strain which reduces θ , which would increase the resistance of the film. Clearly, the strain-induced modification of the electronic bandwidth cannot explain the observed results [inset (b) of Fig. 2]. According to Millis *et al.*,¹⁶ the substrate-induced strain strongly affects the Jahn–Teller (JT) electron-lattice coupling strength in manganite thin films. A tensile strain will increase the JT electron-lattice coupling and thereby increase the localization of charge carriers, while a compressive strain tends to increase hopping amplitude of charge carriers as a result of the reduction of the JT electron-lattice coupling. As discussed above, when the PMN-PT substrate is in P_r^0 state, the LBMO film suffers from large in-plane tensile and out-of-plane compressive strain, which implies that the MnO_6 octahedra is compressed along the c -axis and elongated in the film plane. Such a large apically compressed distortion of the MnO_6 octahedra (i.e., the Q_2 -mode JT distortion) would localize the charge carriers as polarons due to the strong electron-lattice coupling.^{16,17} As can be seen in Fig. 2, when the PMN-PT substrate is in P_r^+ state (e.g., $E=10$ kV/cm), the out-of-plane compressive strain of the film is almost completely released, which would significantly reduce the magnitude of the Q_2 -mode JT distortion. Consequently, the localization of the charge carriers decreases due to the reduced electron-lattice coupling, which

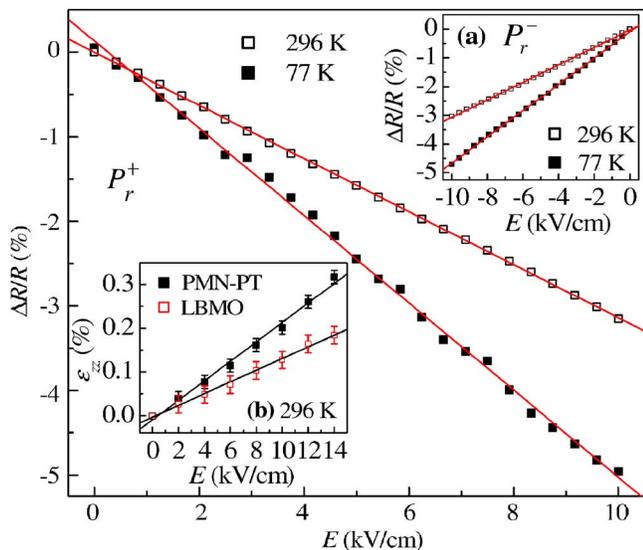


FIG. 3. (Color online) Relative change in the resistance ($\Delta R/R$) of the LBMO film at 77 and 296 K as a function of the electric field E applied to the positively polarized PMN-PT substrate. Inset (a) shows the $\Delta R/R$ as a function of the negative electric field E applied to the negatively polarized PMN-PT substrate. Inset (b) shows the induced out-of-plane strain in the PMN-PT substrate and LBMO film as a function of the electric field E applied to the positively polarized PMN-PT substrate.

would result in a decrease of the resistance. Therefore, it would be reasonable to conclude that the electric-field-induced large decrease in the resistance and enhancement of T_{MI} is mainly due to the reduction of the electron-lattice coupling, resulting from the ferroelectric polarization-induced in-plane compressive strain, which reduces the apically compressed JT distortion of the MnO_6 octahedra.

Figure 3 shows the relative change in the resistance ($\Delta R/R$) of the LBMO film as a function of the electric field E applied to the positively polarized PMN-PT substrate. The resistance shows a linear dependence on E both at high and low temperatures. The resistance decreases by $\sim 5\%$ at 77 K and 3.15% at 296 K, respectively, as E increases from 0 to 10 kV/cm. The relationship between $\Delta R/R$ and E is given by $\Delta R/R = -aE$. The fitting of the experimental data to $\Delta R/R = -aE$ yields $a = 0.51$ at 77 K and 0.31 at 296 K, respectively. When the PMN-PT substrate is in P_r^- state, the resistance is also linearly dependent on the (negative) electric field applied to the PMN-PT substrate [inset (a) of Fig. 3], which can be well described by $\Delta R/R = aE$.

According to the converse piezoelectric effect, when an electric field with the same polarity as the poling field is applied to the polarized PMN-PT substrate, the electric field induces an out-of-plane tensile strain $[\varepsilon_{zz}(\text{PMN-PT})]$ and an in-plane compressive strain $[\varepsilon_{xx}(\text{PMN-PT})]$ in the PMN-PT substrate simultaneously. The magnitude of $\varepsilon_{zz}(\text{PMN-PT})$ and $\varepsilon_{xx}(\text{PMN-PT})$ are linearly dependent on the electric field E . The inset (b) of Fig. 3 shows $\varepsilon_{zz}(\text{PMN-PT})$ and the induced out-of-plane strain in the LBMO film $[\varepsilon_{zz}(\text{LBMO})]$ as a function of E . $\varepsilon_{zz}(\text{PMN-PT})$ increases almost linearly with increasing E . The relationship between $\varepsilon_{zz}(\text{PMN-PT})$ and E can be described by $\varepsilon_{zz}(\text{PMN-PT}) = bE$. This linear dependence of $\varepsilon_{zz}(\text{PMN-PT})$ on E strongly implies the piezoelectric nature of the induced out-of-plane strain. Using $\Delta R/R = -aE$ and $\varepsilon_{zz}(\text{PMN-PT}) = bE$, the relationship between $\Delta R/R$ and $\varepsilon_{zz}(\text{PMN-PT})$ can be simply obtained as $\Delta R/R = -a\varepsilon_{zz}(\text{PMN-PT})/b$. On the other hand, the

converse piezoelectric effect-induced in-plane compressive strain in the PMN-PT substrate $[\varepsilon_{xx}(\text{PMN-PT})]$ was transferred to the LBMO film, which causes the out-of-plane strain of the LBMO film $[\varepsilon_{zz}(\text{LBMO})]$ increases almost linearly with increasing E . The relationship between $\varepsilon_{zz}(\text{LBMO})$ and E can be expressed as $\varepsilon_{zz}(\text{LBMO}) = cE$, where c is a constant. Compared with the strain state of the LBMO film at $E = 0$ kV/cm, the converse piezoelectric effect-induced strain in the PMN-PT substrate imposes in-plane compressive strain on the LBMO film. Thus, the relationship between $[\varepsilon_{zz}(\text{LBMO})]$ and the in-plane strain $[\varepsilon_{xx}(\text{LBMO})]$ can be written as $\varepsilon_{zz}(\text{LBMO}) = -2\nu/(1-\nu)\varepsilon_{xx}(\text{LBMO})$, where ν is the Poisson ratio. Using the $\Delta R/R = -aE$, $\varepsilon_{zz}(\text{LBMO}) = cE$, and $\varepsilon_{zz}(\text{LBMO}) = -2\nu/(1-\nu)\varepsilon_{xx}(\text{LBMO})$, the relationship between $\Delta R/R$ and the induced in-plane strain in the LBMO film can be expressed as $\Delta R/R = (a/c)(2\nu/1-\nu)\varepsilon_{xx}(\text{LBMO})$. This resistance-strain relationship demonstrates that the relative change in the resistance of the LBMO film is proportional to the induced in-plane compressive strain in the LBMO film.

In summary, we have grown LBMO films on ferroelectric PMN-PT substrates and investigated the effects of substrate-induced strain on the transport properties of LBMO films. It was found that the ferroelectric polarization or the converse piezoelectric effect-induced strain drastically affects the strain state and transport properties of the LBMO film, which is interpreted in terms of the strain-induced reduction of the apically compressed JT distortion of MnO_6 octahedra. We also quantified the relationships between the resistance of the LBMO film and the induced strain in the LBMO film and PMN-PT substrate, respectively.

This work was supported by the Hong Kong Research Grants Council (CERG PolyU 5122/07E), PolyU internal Grant No. 1-BB84, and the Center for Smart Materials of the Hong Kong Polytechnic University.

- ¹J. Zhang, H. Tanaka, T. Kanki, J. H. Choi, and T. Kawai, Phys. Rev. B **64**, 184404 (2001).
- ²M. Ziese, H. C. Semmelhack, and K. H. Han, Phys. Rev. B **68**, 134444 (2003).
- ³S. I. Khartsev, P. Johnsson, and A. M. Grishin, J. Appl. Phys. **87**, 2394 (2000).
- ⁴T. Kanki, T. Yanagida, B. Vilquin, H. Tanaka, and T. Kawai, Phys. Rev. B **71**, 012403 (2005).
- ⁵P. Murugavel, J. H. Lee, K. B. Lee, J. H. Park, J. S. Chung, J. G. Yoon, and T. W. Noh, J. Phys. D **35**, 3166 (2002).
- ⁶P. Murugavel, J. H. Lee, J. G. Yoon, T. W. Noh, J.-S. Chung, M. Heu, and S. Yoon, Appl. Phys. Lett. **82**, 1908 (2003).
- ⁷P. Orgiani, A. Guarino, C. Aruta, C. Adamo, A. Galdi, A. Yu. Petrov, R. Savo, and L. Maritato, J. Appl. Phys. **101**, 033904 (2007).
- ⁸Y. Yamada, O. Hino, S. Nohdo, R. Kanao, T. Inami, and S. Katano, Phys. Rev. Lett. **77**, 904 (1996).
- ⁹P. Dai, J. A. Fernandez-Baca, N. Wakabayashi, E. W. Plummer, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. **85**, 2553 (2000).
- ¹⁰C. Thiele, K. Dörr, O. Bilani, J. Rödel, and L. Schultz, Phys. Rev. B **75**, 054408 (2007).
- ¹¹R. K. Zheng, Y. Wang, H. L. W. Chan, C. L. Choy, and H. S. Luo, Appl. Phys. Lett. **90**, 152904 (2007).
- ¹²P. Mandal and B. Ghosh, Phys. Rev. B **68**, 014422 (2003).
- ¹³Q. S. Yuan, Phys. Rev. B **70**, 066401 (2004).
- ¹⁴A. Miniotas, A. Vailionis, E. B. Svedberg, and U. O. Karlsson, J. Appl. Phys. **89**, 2134 (2001).
- ¹⁵H. L. Ju, K. M. Krishnan, and D. Lederman, J. Appl. Phys. **83**, 7073 (1998).
- ¹⁶A. J. Millis, T. Darling, and A. Migliori, J. Appl. Phys. **83**, 1588 (1998).
- ¹⁷X. J. Chen, S. Soltan, H. Zhang, and H.-U. Habermeier, Phys. Rev. B **65**, 174402 (2002).