Static and dynamic strain effects in $La_{0.7}Ce_{0.3}MnO_3$ thin films

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Both static and dynamic strain effects of $La_{0.7}Ce_{0.3}MnO_3$ (LCeMO) thin films that were grown on (001) oriented $SrTiO_3$ (STO) and $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$ (PMN-PT) substrates were investigated. A charge-orbital ordering (COO) transition was found in the region of low temperature for strained (001)-LCeMO/STO films. The gradual vanishing of the COO transition with the relaxation of tensile epitaxial strain indicates the key role of tensile strain in the formation of COO. Furthermore, the results of dynamic strains on (001)-LCeMO/PMN-PT film show that even a small strain modification of $\sim -0.1\%$ could evidently change the magnetotransport properties around T_{COO}, verifying the dominant role of the tensile strain. © *2011 American Institute of Physics*. [doi:10.1063/1.3544511]

Tetravalent cation-doped perovskite-type manganites (La,Ce)MnO_3 have attracted much attention since the first report by Mandal and Das.[1] The realization of possible electron-doped manganites may enable new types of functional spintronic devices, such as p-n homojunctions of both hole- and electron-doped manganites,[2] which raised further research interest to reveal the fundamental physics in the emergence of ferromagnetism (FM) with relative electronic configuration. Accurate x-ray diffraction (XRD) analyses showed that the bulk Ce-doped $LaMnO_3$ always included CeO_2 impurity phase[3] or even a multiphase mixture which leads to the hole-doped behavior.[4,5] Fortunately, Raychaudhuri *et al*.[6] and Mitra *et al*.[7,8] found that the single phase of Ce-doped $LaMnO_3$ showing no impurity in the XRD data could be fabricated in the form of epitaxial thin films using a pulsed laser deposition (PLD) technique. Various experimental approaches, such as Hall measurements,[9] thermopower measurements,[10] photoexcitation,[11] x-ray absorption spectroscopy,[12,13] x-ray magnetic circular dichroism,[13] or x-ray absorption near-edge-structure spectroscopy,[14] have been followed so far to clarify the intrinsic doping type and thus the nature of FM and metal-insulator transition. Although the presence of Mn^{2+} within the (La,Ce)MnO_3 thin films has been demonstrated,[12,13] strong controversies still exist with whether Mn^{2+} contributes to FM. The question whether $LaMnO_3$ accepts Ce doping as an electron- doped nature has to be answered for each sample individually. More recently, our group demonstrated that the as-prepared single-phase $La_{0.7}Ce_{0.3}MnO_3$ films show hole-doping due to overoxygenation while the deoxygenation by annealing in vacuum drives the system into the electron-doped state, concomitantly leading to an insulating character of the films.[15]

On the other hand, elastic strain plays an important role in controlling the properties of manganite thin films due to the pronounced coupling of lattice and electronic degrees of freedom.[16–18] For instance, the ferromagnetic Curie temperature T_C of $La_{0.6}Sr_{0.4}MnO_3$ can be reduced from 370 K for bulk to 310 K in tensile strained $La_{0.6}Sr_{0.4}MnO_3/SrTiO_3$ (001) films.[16] Thiele *et al*. also reported that the resistivity and magnetization could be modulated continuously by reversible strain induced by electric bias field.[18] Since the biaxial strain could change the strength of Jahn-Teller coupling (JT) and double-exchange (DE) interaction via modifying Mn-O-Mn bond lengths and angles, thorough knowledge of strain effect would help to improve the understanding of the transport nature. However, only few studies of the strain effect in (La,Ce)MnO_3 films was reported so far, partially due to the properties of (La,Ce)MnO_3 films are much more sensitive to the oxygen content and thus to the preparation conditions.[19]

In this work, we present the results of both static and dynamic strain effects of $La_{0.7}Ce_{0.3}MnO_3$ (LCeMO) thin films that were grown on (001) oriented commercial $SrTiO_3$ (STO) and (001)-$0.7Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$ (PMN-PT) substrates by pulsed laser deposition (PLD) technique.

The deposition of LCeMO thin films was performed at an oxygen pressure of 1 mbar and a substrate temperature of 750 °C. The deposition of films with thickness of 160 nm on STO and PMN-PT substrates was simultaneously performed to ensure identical growth conditions. The stoichiometric target was ablated by KrF excimer laser (248 nm) with a pulsed energy of 200 mJ and a frequency of 2 Hz. After deposition, in a pure oxygen atmosphere of 1 atm, the film were cooled to room temperature and postannealed at 800 °C for 1 h. The crystalline structure and c-axis lattice constant were determined by x-ray diffraction measurements (Fig. 1). No impurity peaks of CeO_2 were found in all films. It was found that the tensile strain in the film of 160 nm LCeMO on PMN-PT was $\sim -0.23\%$ (compared with bulk one), which is much larger than the one in films of LCeMO/STO (-0.13% for 40 nm, -0.11% for 80 nm, and -0.008% for 160 nm)

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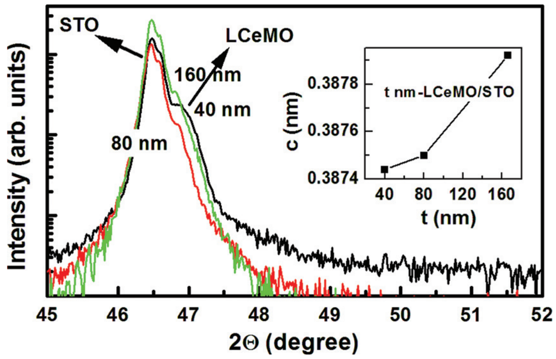

FIG. 1. (Color online) XRD results of LCeMO/STO films with different thickness. The inset shows the c-axis value increases with increasing thickness.

due to the large difference of lattice mismatch between LCeMO/PMN-PT (∼3.42%) and LCeMO/STO (∼0.65%).

Magnetic and transport measurements were performed by a superconducting quantum interference device magnetometer. To investigate the influence of the modification of strain state on the behavior of LCeMO/PMN-PT film, a static bias field up to 12 KV/cm was applied across the PMN-PT substrate (for protection, a 20 MΩ resistor is presented in the circuit, see inset of Fig. 3). The resistance of the PMN-PT, measured using a Keithley 6517A electrometer, was ∼10 GΩ, and a negligible small leakage current was observed (less than 25 nA under a 20 KV/cm electric field).

Figure 2 presents temperature dependent magnetization and resistivity for LCeMO/STO films with thickness of 40, 80, 160 nm, respectively. A clear metal-insulator transition (MIT)/ferromagnetism-paramagnetism transition was found in all three samples. The transition temperature T_{IM}/T_C varies from 215 to 231 K with thickness increasing from 40 to 160 nm, which could be ascribed to the relaxation of expitaxial strains in LCeMO/STO films. It is known that the epitaxial tensile strain will cause an increase in the in-plane Mn-O-Mn bond distance and the compressive MnO_6 octahedral distortion. Consequently, the in-plane transfer integral for the FM DE significantly decreases, resulting in a lower T_C in comparison with that of bulk. With thickness increasing, the relaxation of strains leads to an enhancement of FM DE and thus of T_C.

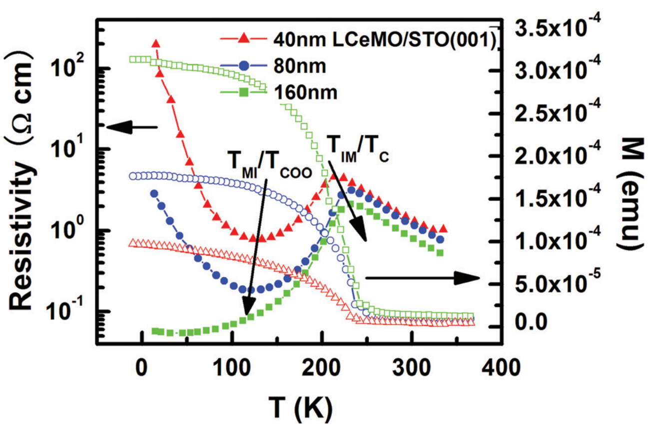

FIG. 2. (Color online) Temperature dependent magnetization (H = 0.05 T) and resistivity for LCeMO/STO films with thickness of 40, 80, 160 nm, respectively.

Moreover, a second MIT at T_{MI}/T_{COO} was observed in the region of low temperature for strained films, which might be related to the formation of ferromagnetic charge/orbital ordering phase (COO). Such ordering formation has been found to be strongly related to the epitaxial tensile strain in other hole-doped manganites.[20] The carriers could be trapped in a local lattice distortion due to tensile strains.[21–23] Thus, a polaron ordering would be constructed[22,23] and the mobilization of carriers between lattice is suppressed upon cooling, resulting in the upturn of resistivity at low temperature. It was believed that the epitaxial tensile strain provide an extra source of octahedral distortion besides the JT distortion, leading to a large compression of the MnO_6 octahedrons in the out-of-plane direction with simultaneous elongation in the in-plane directions.[20] In such a situation, the freedom for the occurrence of COO would be provided, allowing the transition between COO and non-COO phases as reported in other hole-doped manganites thin films.[20,24] It was also noted that the COO-like behavior at low temperature diminishes gradually as the film thickness increases ($T_{MI}/T_{COO} \approx 127$ K for 40 nm, 121 K for 80 nm, and vanishing for 160 nm), which gives a collateral evidence for the close relations between tensile epitaxial strains and the ferromagnetic insulatorlike state.

However, many other elements, such as oxygen-nonstoichiometry, defects, and even multiphase mixtures may change together with the strain in the statically strained films, affecting the double exchange coupling, JT coupling and thus transport properties. To rule out these unexpected effects and measure the true effect of strain on magnetic and transport properties in LCeMO films, we investigate the dynamic influence of the biaxial strain on transport behaviors of 160nm-LCeMO/PMN-PT film based upon the inverse piezoelectric effect of PMN-PT. Figure 3 illustrates the resistivity as a function of temperature under magnetic and electric fields. First of all, when the external electric and magnetic fields are zero, a clear MIT in the region of low temperature ($T_{MI}/T_{COO} \sim 38$ K) could be distinguished for the 160 nm-LCeMO/PMN-PT film. While 5 T magnetic field is applied, the insulating behavior below T_{COO} becomes weak and the T_{COO} shifts to low temperature ($T_{MI}/T_{COO} \sim 30$ K), indicating a strong modification of the competition between COO and ferromagnetic metallic phases. Whereas the bias electric field seems only reducing the resistivity at the first glance. Previous researches have shown that a field of 13 KV/cm could induce an in-plane contradiction of $\sim -0.13\%$ in the PMN-PT substrate.[25] Such in-plane compressive strain could transfer to the film and reduce the epitaxial tensile strain.[25] Therefore the reduction of the resistance should be ascribed to the reduction of tensile strain.

To further clarify the effect of field induced strain and magnetic field on the transport properties, we present the relative change in resistance induced by external magnetic and electric fields in Fig. 4. First of all, one could find that magnetoresistance (MR = (R(5T) − R(0T)/R(0T)) exhibits a minimum value around T_{COO} due to the strong alteration of the competition between COO and FM metallic states [Fig. 4(a)]. More importantly, the MR enhances distinctly around T_{COO} under a bias electric field of 12 KV/cm while remaining unchanged around and above T_C. The divergence of the

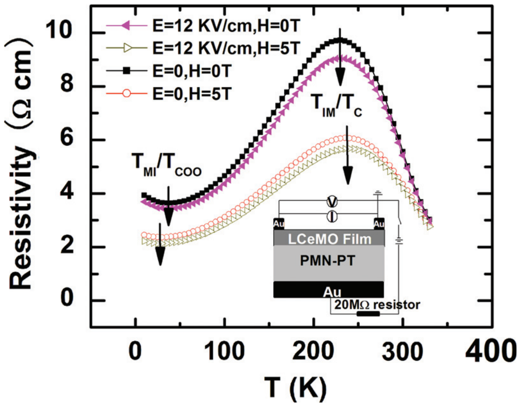

FIG. 3. (Color online) Temperature dependent resistivity in 160 nm-LCeMO/PMN-PT film with magnetic field $\mu_0H = 0$, 5 T and bias field $E = 0$, 12 KV/cm. The inset shows a schematic diagram of the LCeMO/PMN-PT structure and the circuit for electrical measurements.

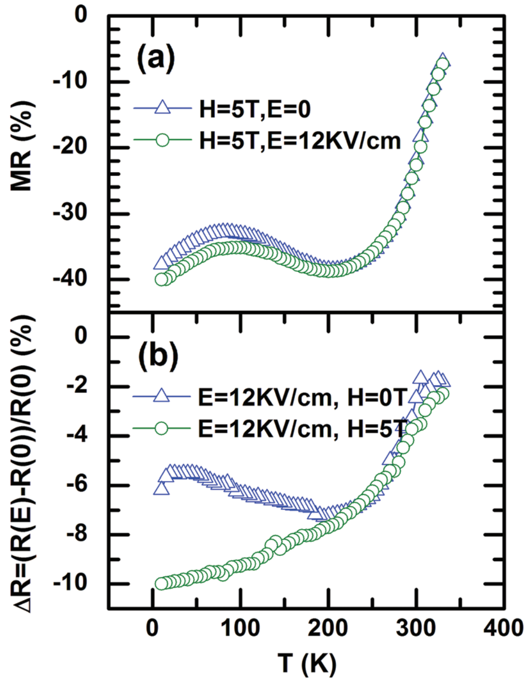

FIG. 4. (Color online) (a) Temperature dependent MR under 5 T for the LCeMO film with bias field $E = 0$ and 12 KV/cm. (b) Relative change in resistance $\Delta R = (R(E) - R(0))/R(0)$, under a electric field of 12 KV cm, as a function of temperature with magnetic field $\mu_0H = 0$, 5 T.

curves around T_{COO} [see Fig. 4(a)] shows that even a small strain modification of $\sim -0.1\%$ could evidently change the magnetotransport properties around T_{MI}/T_{COO}. This result demonstrates that the alteration of the strain state would lead to a change of COO state in the film of LCeMO, verifying the dominant role of the tensile strain in the occurrence of COO transition. The opposite response of MR, at different temperature region, to the bias electric field indicates that the observed COO phase in present LCeMO film are more sensitive to the strain effect than other phases such as PM insulating phase, which has been reported in other hole-doped $La_{7/8}Sr_{1/8}MnO_3$ films.[20] However, different from the reported case, the observed COO in present LCeMO films could be easily moved and even melted by applying magnetic field. Figure 4(b) shows the influence of magnetic field on the temperature dependent relative change in resistance ($\Delta R/R = [R(E) - R(0)]/R(0)$) due to bias electric field. One can find that a field of 5 T expunges configuration both from PM-FM and COO transitions. Such different characteristics from other hole-doped manganite film probably reflect the intrinsic doping mechanism of LCeMO.

In summary, the effect of tensile strain on the magnetotransport properties of (001)-LCeMO thin films was investigated by using both static and dynamic methods. It was found that an additional transition from ferromagnetic metal to ferromagnetic insulator appears in the region of low temperature for strained (001)-oriented LCeMO/STO films, indicating the formation of ferromagnetic charge/orbital ordering phase (COO). The observed COO-like transition gradually diminishes with the relaxation of the tensile epitaxial strain in films, showing the close relations between tensile strains and the formation of COO. Further measurements of dynamic strain effects on (001)-LCeMO/PMN-PT film shows that even a small strain modification of $\sim -0.1\%$ could evidently change the magnetotransport properties around T_{COO}, verifying the dominant role of the tensile strain in the occurrence of COO transition.

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