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Strong tensile strain induced charge/orbital ordering in (001)-$La_{7/8}Sr_{1/8}MnO_3$ thin film on $0.7Pb(Mg_{1/3}Nb_{2/3})O_3-0.3PbTiO_3$

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The substrate-induced strain effect in $La_{7/8}Sr_{1/8}MnO_3$ (LSMO) thin films grown on (001)-oriented $SrTiO_3$ and ferroelectric $0.7Pb(Mg_{1/3}Nb_{2/3})O_3-0.3PbTiO_3$ (PMN-PT) substrates was investigated. A metal-insulator transition was observed at low temperature in LSMO/PMN-PT, which was ascribed to charge/orbital ordering (COO) formation due to a large tensile strain. The impact of strain modification on the transport properties around COO transition was investigated by using converse piezoelectric effect in PMN-PT. We found the magnetoresistance reduction due to the strain modification at COO state was much larger than that at disordering one, indicating the sensitivity of the COO phase to strain state. This fact presents a collateral evidence for the tensile strain origin of the COO transition. © *2010 American Institute of Physics*. [doi:10.1063/1.3298360]

Hole doped $La_{1-x}Sr_xMnO_3$ compounds, depending on the value of x and temperature, exhibit a variety of phase transitions, such as paramagnetic (PM) to ferromagnetic (FM) transition, insulator to metal transition, and charge/orbital ordering (COO) transition, due to the strong coupling among spin, charge, orbital, and lattice degrees of freedom.[1] COO plays an important role in lightly doped $La_{1-x}Sr_xMnO_3$. This ordering phenomenon was found to be restricted to a small doping regime ($0.1<=x<=0.15$) close to the value giving a commensurate fraction of charge carriers.[2]

On the other hand, thin films of manganites exhibit properties quite different from the bulk partly due to the epitaxial strain induced by the lattice mismatch between the substrate and bulk. One of the remarkable features is the suppression of COO in the (001)-oriented films.[3–6] The in-plane isotropic lattice deformation in the (001)-oriented film is fixed to the substrate independent of temperature and makes the transition between COO and non-COO states unlikely occur.[4,7,8] Recently, Ogimoto *et al.*[8] and Nakamura *et al.*[4] demonstrated that clear COO transitions could be achieved in (110)-oriented $Pr_{0.5}Sr_{0.5}MnO_3$ and $Nd_{0.5}Sr_{0.5}MnO_3$ films by introducing anisotropic strains. Very recently, Chen *et al.*[6] also observed a clear COO transition in $La_{7/8}Sr_{1/8}MnO_3$ thin films grown on (011) $SrTiO_3$ (STO) substrate. These works showed that the anisotropic strain in such films provides an opportunity for the lattice deformation within the orbital ordering plane, which is required by the Jahn-Teller (JT) effect concurrent with the formation of COO.[4–6,8]

In this letter, we report a different route to control the COO pattern in the (001)-oriented $La_{7/8}Sr_{1/8}MnO_3$ (LSMO, $a_{LSMO}=3.920$, $b_{LSMO}=3.907$, and $c_{LSMO}=3.896$ for bulk[9]) thin films. By introducing large tensile strains, we obtained a clear COO transition at low temperature. The commercial (001)-oriented $0.7Pb(Mg_{1/3}Nb_{2/3})O_3-0.3PbTiO_3$ (PMN-PT) single crystal was chosen as the substrate due to its perovskite cubic structure ($a_{PMN-PT}=4.017$ Å) and outstanding ferroelectric and converse piezoelectric effects (remnant polarization $Pr\sim22.9$ $\mu C/cm^2$ and coercivity field E_c ~2.8 kV/cm),[10–13] which makes it a well platform in investigating the impact of substrate induced tensile strain on the magnetic and transport properties of LSMO both statically and dynamically.

The thin film of LSMO was grown on the (001)-oriented single-crystal substrates of PMN-PT using pulsed laser deposition. For comparison, a LSMO film with the same thickness (~10 nm) was also deposited on the (001)-oriented STO substrate, which has very small lattice mismatch (~0.2% for in-plane). Both substrates were placed adjacently in the center of the sample plate and the films were grown synchronously to ensure identical growth conditions. The deposition took place at an oxygen pressure of 1 mbar and a substrate temperature of 700 °C. The films were cooled to room temperature in a pure oxygen atmosphere of 1 atm after deposition. 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 COO, a static bias field up to 20 kV/cm was applied across the PMN-PT substrate [see inset of Fig. 1(b)]. 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 1 shows typical θ-2θ XRD patterns for the LSMO/PMN-PT and LSMO/STO structures, which indicates the single pseudocubic phase and high crystallinity for both films. For the pattern of LSMO/STO, the reflections from the film were found to overlap with those from STO substrate, indicating a nearly pseudomorphic growth and a small strain induced by substrate taking into account the small misfit between them. As for LSMO/PMN-PT, a LSMO(002) reflection appears at the right side of the PMN-PT(002) reflection [shown in the inset of Fig. 1(a)], whose signal is weak due to the thin film thickness of 10 nm. The out-of-plane lattice parameter c of LSMO/PMN-PT was determined

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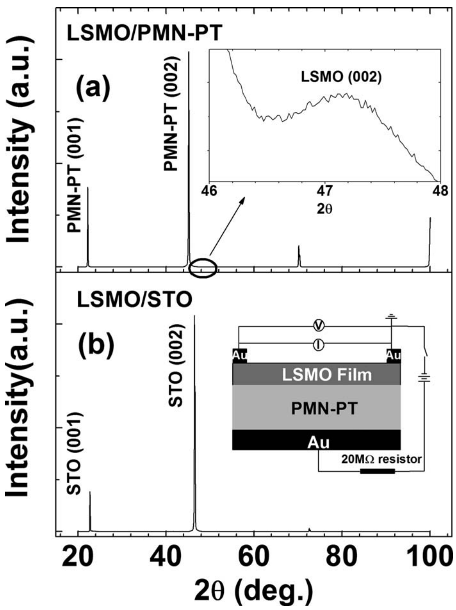

FIG. 1. X-ray diffraction patterns of (a) the LSMO/PMN-PT and (b) LSMO/STO structures. Inset of (a) shows the expanded view of the pattern of LSMO (002). Inset of (b) shows a schematic diagram of the LSMO/PMN-PT structure and the circuit for electrical measurements.

to be 3.851 Å, indicating an out-of-plane compressive strain $[\varepsilon_{zz}=(c_{film}\text{-}c_{bulk})/c_{bulk}=-1.15\%]$ existing in the film. An in-plane tensile strain could be calculated as 1.59% by Poisson relation $\varepsilon_{xx}=-2\nu/(1-\nu)\varepsilon_{zz}$ using $\nu=0.41$.[14]

Figure 2(a) presents the temperature dependent magnetization under a field of 0.05 T for LSMO/STO and LSMO/PMN-PT. The PM-FM transition temperature T_C for both films has been determined from the curves as follows: ~290 K for LSMO/STO and ~220 K for LSMO/PMN-PT. 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

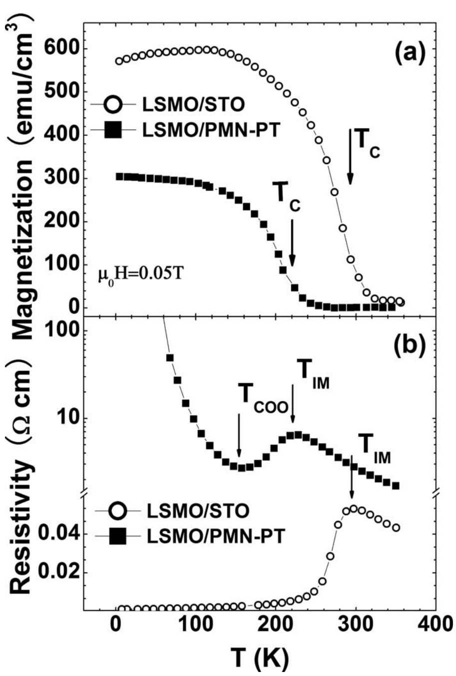

FIG. 2. (a) The temperature dependent magnetization under a field of 0.05 T for LSMO/STO and LSMO/PMN-PT. (b) The temperature dependent resistivity of LSMO films grown on (001) STO and (001) PMN-PT substrates.

in-plane transfer integral for the FM double exchange significantly decreases, resulting in a lower T_C. On the other hand, the competing JT coupling is enhanced by the compressive octahedral distortion, leading to an increase in the formation energy of JT distortion, hence, the decrease in T_C. Since the film of LSMO on PMN-PT experiences a large tensile strain while the one on STO undergoes a much small compressive strain, it is reasonable that the T_C of the sample LSMO/PMN-PT is much lower than that of LSMO/STO.

Figure 2(b) displays the temperature dependent resistivity of LSMO films grown on (001) STO and PMN-PT substrates on cooling. One could find that both films experience an insulator-metal transition around their respective PM-FM transition temperature. The LSMO/STO film exhibits a FM and metallic behavior below T_C/T_{IM}, in agreement with previous reports.[6,15,16] Previous researches have shown that the tetragonal lattice stability by the substrates will suppress the JT distortion and thus the COO in (001) oriented manganites films at low temperature.[4–8] The pseudomorphic strain from the substrate of (001) STO limits the freedom of in-plane lattice deformation and increases the JT stabilization energy. In addition, in-plane isotropic strain and strong clamp effect in (001)-oriented LSMO films induce tetragonal lattice distortion and diminish the orthorhombicity inherent in the COO state. In contrast to the film of LSMO/STO, LSMO/PMN-PT shows a clear metal-insulator transition around 150 K (T_{MI}/T_{COO}), similar to bulk materials. Our further experiments indicated that additional post annealing under oxygen atmosphere cannot cause any change of the T_{MI} transition around 150 K. It means that the appearance of the transition around T_{MI}/T_{COO} does not relate to nonstoichiometry of oxygen but is a natural result of the formation of COO, caused by an extremely large tensile strain. The large tensile strain leads to an enhanced JT distortion and tends to trap the carriers in a local lattice distortion.[17] With the assistance of the enhanced distortion, the hole could be frozen on the lattice site (Mn^{4+} site) and a polaron ordering would be constructed.[18–20] Due to the freeze of hole site, the mobilization of carriers between lattice is suppressed upon cooling, resulting in the upturn of resistivity at low temperature.

Previous investigations indicated that anisotropy strain is a crucial parameter in controlling the COO transition in (110)-oriented films. Our results show that besides the anisotropy strain, a large in-plane tensile strain could also induce a clear COO transition by enhancing the JT distortion. The large in-plane lattice mismatch between LSMO and PMN-PT reaches ~−2.6%, which causes a quite strong in-plane tensile strain in thin LSMO film. Such tensile strain would lead to a large compression of the MnO_6 octahedrons in the out-of-plane direction with simultaneous elongation in the in-plane directions. In such a situation, the concurrent JT distortion might provide a freedom for the occurrence of COO, thus the transition between COO and non-COO phases may be allowed in present (001)-oriented LSMO on PMN-PT. To fully understand the mechanism of the large tensile strain acting on the JT distortion and COO formation, detailed information about the strain state and its impact on electron-phonon coupling is required and the related investigations are in process.

Since the extremely large tensile strain plays a dominant role in the occurrence of COO transition in LSMO/PMN-PT, any alteration of the strain state would lead to a change of

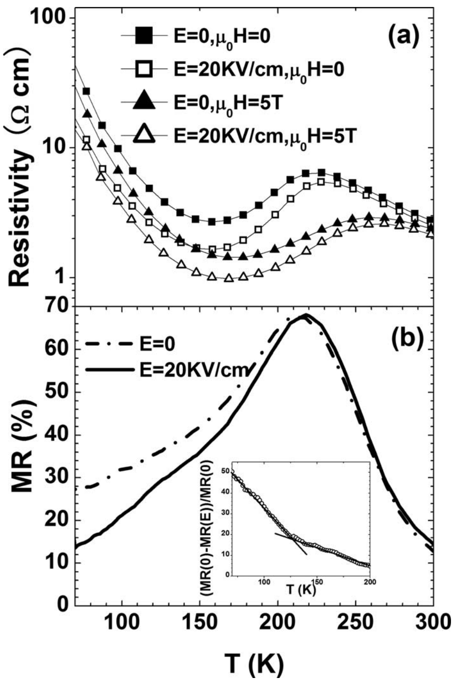

FIG. 3. For LSMO/PMN-PT, (a) the temperature dependent resistivity with magnetic field μ_0H=0, 5 T and bias field E=0, 20 kV/cm and (b) the temperature dependent MR under 5 T for the LSMO film with bias field E=0 (dashed dotted line) and 20 kV/cm (solid line). Inset of (b) shows the temperature dependent reduction ratio of MR due to a small reduction in tensile strain caused by a bias field of 20 kV/cm. Lines shown to guide the eye.

COO state. It is known that an in-plane contraction strain, in the PMN-PT substrate, could be induced and controlled by an external static electric field due to the converse piezoelectric effect. Such compressive strain could be transferred to the film grown on the PMN-PT and modify its strain state.[10–12] Taking advantage of this characteristic, we investigated the dynamical impact of the strain on the magnetotransport behavior in LSMO/PMN-PT film. Figure 3(a) shows the temperature dependent resistivity under 5 T and a static bias electric field of 20 kV/cm that leads to a reduction in the tensile strain in the film of LSMO [$\delta\varepsilon_{xx}=\varepsilon_{xx}(E)-\varepsilon_{xx}(0)\approx-0.16\%$ at 20 kV/cm, assuming the compressive strain in substrate is fully transferred to the film].[10,11] In addition, the resistivity without any external disturbance was also plotted in Fig. 3(a) for comparison. First of all, one could find that the reduction in tensile strain induced by bias field causes a reduction in the resistivity in the whole measured temperature range with the COO transition remained. The reduction in tensile strain under a bias field leads to a decrease in the JT distortion to some extent and delocalizes the charge carriers somewhat, behaving a reduction in resistivity. However, the nearly unchanged transition temperatures indicate that the JT polaron formation energy does not have a big change due to the small reduction in tensile strain, −0.16%. Different from the effect of external bias field, the magnetic field of 5 T shifts the COO transition temperature T_{COO}/T_{MI} to a higher temperature in addition to a reduction in resistivity. Such an increase in T_{COO} due to external magnetic field had been also observed in the bulk LSMO materials,[21] which was ascribed to the decrease in the JT distortion and the corresponding energy gain in the FM metallic phase. Figure 3(b) plots the temperature dependent magnetoresistance (MR) under 5 T, defined as [R(0)—R(5 T)]/R(0), for the LSMO film with the bias field applying on PMN-PT substrate or not. The results demonstrate that the reduction in tensile strain caused by a bias field makes MR decrease at the temperatures below T_C/T_{IM}. Especially, the reduction rate of MR experiences a substantial enhancement around COO transition with decreasing temperature [see the slope change in the inset of Fig. 3(b)]. Similar variation tendency of MR around the transition was observed with varying the bias field, though the reduction rate increases linearly with increasing the bias field at specific temperatures. It was found that the reduction ratio of MR, defined as [MR(0)-MR(E)]/MR(0), due to bias fields of 15 kV/cm and 20 kV/cm reaches 12% and 50% at 70 K, respectively. Such behaviors indicate that the COO insulating state is more sensitive to the strain modification than the charge/orbital disordering state. This result provides a collateral evidence for the tensile strain origin of the COO transition.

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