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Research Article

Tuning of Transport and Magnetic Properties in Epitaxial $LaMnO_{3+\delta}$ Thin Films

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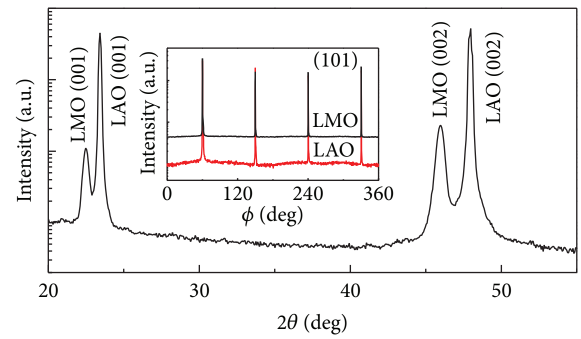
The effect of compressive strain on the transport and magnetic properties of epitaxial $LaMnO_{3+\delta}$ thin films has been investigated. It is found that the transport and magnetic properties of the $LaMnO_{3+\delta}$ thin films grown on the $LaAlO_3$ substrates can be tuned by the compressive strain through varying film thickness. And the insulator-metal transition, charge/orbital ordering transition, and paramagnetic-ferromagnetic transition are suppressed by the compressive strain. Consequently, the related electronic and magnetic transition temperatures decrease with an increase in the compressive strain. The present results can be explained by the strain-controlled lattice deformation and the consequent orbital occupation. It indicates that the lattice degree of freedom is crucial for understanding the transport and magnetic properties of the strongly correlated $LaMnO_{3+\delta}$.

1. Introduction

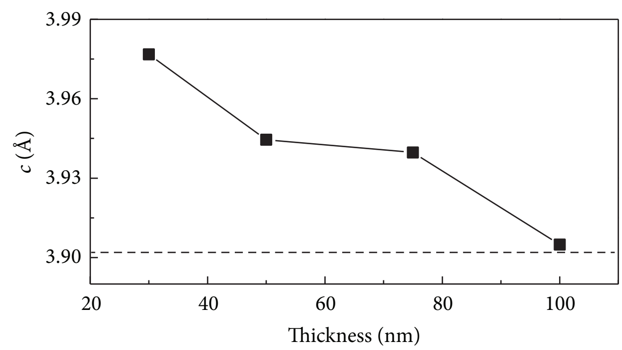
Perovskite manganese oxides $La_{1-x}A_xMnO_3$ (A = alkaline earth) have attracted a great deal of attention due to their interesting properties such as colossal magnetoresistance (CMR), charge/orbital ordering (COO), and insulator-metal transition (IMT) [1–3]. The interesting properties originate from the strong correlation of charge, orbital, spin, and lattice degrees of freedom. In this family, the substitution of divalent A for La introduces hole carriers in the Mn 3D band and oxidizes Mn^{3+} to Mn^{4+}, which results in the ferromagnetic metal (FMM) state in terms of double exchange (DE) interaction [4]. In particular, even if without chemical substitution, the $LaMnO_3$ compound also exhibits a wide range of oxygen nonstoichiometry, which involves the oxidation of some Mn^{3+} to Mn^{4+} in samples of global composition $LaMnO_{3+\delta}$. However, the insertion of excess oxygen is impossible in the perovskite structure as there is no straightforward way of accommodating any extra oxygen in the close-packed structure. The oxygen nonstoichiometry in $LaMnO_{3+\delta}$ is incorporated via cation vacancies on both A and B sites [5]. Therefore, the actual crystallographic formula of such compositions should be written as $La_{1-x}Mn_{1-x}O_3$, with $x = \delta/(3+\delta)$ [6].

The structure, transport, and magnetic properties of $LaMnO_{3+\delta}$ highly depend on the value of δ [7–9]. As $0 \leq \delta \leq 0.04$, the crystallographic structure of $LaMnO_{3+\delta}$ is orthorhombic structure (Pbmn, $c/\sqrt{2} < a < b$) and is strongly Jahn-Teller (JT) distorted; with the δ increasing, the structure changes to the slightly JT distorted orthorhombic structure (Pbmn, $a \leq c/\sqrt{2} < b$); when the $\delta > 0.1$, it falls into the rhombohedral structure. Ritter et al. reported that a small fraction of FMM phase appears in $LaMnO_{3.07}$ due to the local Mn^{3+}–O–Mn^{4+} DE interaction [10]. Furthermore, the COO phase emerges at low temperatures below ~110 K, which is far below the FM transition temperature (~150 K) for the $\delta = 0.07$ and 0.1 samples. The magnetization measurement results of the samples ($0.085 \leq \delta \leq 0.125$) show a step-like jump at T_C and T_{COO} [11]. Meanwhile Choi et al. reported that a giant softening by 30 cm^{-1} of the 490 and 620 cm^{-1} JT and breathing optical phonon modes had been observed by Raman spectroscopy below T_C in the $LaMnO_{3+\delta}$ ($0.085 \leq \delta \leq 0.125$) compounds [12]. The results indicate the importance of the electron-phonon coupling in the appearance of COO phase. For these $LaMnO_{3+\delta}$ ($0.085 \le \delta \le 0.125$) compounds, with decreasing temperature these samples exhibit transition from a paramagnetic insulator (PMI) to FMM at T_C, where the resistivity starts to decrease. At low temperatures, the samples undergo transition from FMM state to COO state at T_{COO}, while the resistivity shows an upturn. This COO phase coexists with the isotropic three-dimensional FM state in spite of the insulating behavior. The overall behaviors of $LaMnO_{3+\delta}$ ($0.085 \le \delta \le 0.125$) compounds are quite similar to those of the lightly doped $La_{1-x}Sr_xMnO_3$ ($0.11 < x < 0.15$) [13, 14].

The study on the lightly doped $La_{1-x}Sr_xMnO_3$, the counterpart of the $LaMnO_{3+\delta}$, has verified the essential role of lattice deformation in the formation of COO phase. Chen et al. succeeded in realizing the COO phase in the $La_{7/8}Sr_{1/8}MnO_3$ thin films induced by the anisotropic strains on (011) $SrTiO_3$ substrates [15]. Wang et al. uncovered that the in-plane tensile strain in the $La_{7/8}Sr_{1/8}MnO_3$ thin film grown on the 0.7Pb $(Mg_{1/3}Nb_{2/3})O_3$–$0.3PbTiO_3$ substrate can induce COO [16]. However, few works have been reported on the strain effect on the properties of nonstoichiometric $LaMnO_{3+\delta}$ thin films. Zheng et al. found that the JT distortion of MnO_6 reduces the charge coupling of the $LaMnO_{3+\delta}$ thin film under an in-plane tensile strain on $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.3PbTiO_3$ substrate [17, 18]. In this letter, the epitaxial $LaMnO_{3+\delta}$ thin films have been fabricated on (001)-oriented $LaAlO_3$ substrate, and in-plane compressive strains have been modified by varying the thickness of thin film. The effect of compressive strain on COO transition and FM transition of the films has been systematically investigated.



(a)



(b)

Figure 1: (a) XRD pattern of the 50 nm $LaMnO_{3+\delta}$/LAO. The inset shows the XRD ϕ scans on the LAO (101) and $LaMnO_{3+\delta}$(101) reflections, respectively. (b) Film thickness dependence of out-of-plane lattice parameter. The dashed line represents the c values of bulk $LaMnO_{3+\delta}$.

2. Experimental

The $LaMnO_{3+\delta}$ thin films were grown on single crystal substrates by dc magnetron sputtering. We chose (001)-oriented $LaAlO_3$ (LAO) and (001)-oriented $SrTiO_3$ (STO) as substrates, and the lattice parameters of the substrates are a_{LAO} = 3.792 Å and a_{STO} = 3.905 Å. The deposition temperature is 700°C and there are 10 Pa oxygen-argon mixed gases flowing during deposition. After deposition, the films were *in situ* cooled to room temperature in the deposition atmosphere. The thickness of the films was controlled by the deposition time. The degree of orientation and crystallographic characterization of the $LaMnO_{3+\delta}$ thin films were measured on X-Pert-PRO system using Cu Kα radiation. The superconducting quantum interference device (SQUID) magnetometer was used to measure the magnetic properties of the $LaMnO_{3+\delta}$ thin films and electrical properties were performed by four-electrode method in a physical property measurement (PPMS) system.

3. Results and Discussion

Figure 1(a) shows the XRD θ–2θ scan for the $LaMnO_{3+\delta}$/LAO thin film of thickness ~50 nm. The $LaMnO_{3+\delta}$ thin films are c-axis oriented and there are no secondary phases. The inset shows the XRD ϕ scans on the $LaMnO_{3+\delta}$ (101) and LAO (101) reflections. Fourfold symmetry is clearly seen for both $LaMnO_{3+\delta}$ thin film and LAO substrate, which is an indication of cubic-on-cubic epitaxial growth of the $LaMnO_{3+\delta}$ thin films on the LAO substrates. The out-of-plane lattice parameter c of 50 nm $LaMnO_{3+\delta}$/LAO was calculated to be 3.9445 Å. As mentioned above, the lattice constants of the $LaMnO_{3+\delta}$ bulk materials vary with δ. By comparing the T_C and T_{COO} of the $LaMnO_{3+\delta}$ thin films with those of $LaMnO_{3+\delta}$ bulk materials, it is estimated that the δ of the $LaMnO_{3+\delta}$ thin films is ~0.09. For δ ~0.09, the lattice constant of the $LaMnO_{3+\delta}$ bulk materials is ~3.903 Å [10, 12]. This value is smaller than that of the 50 nm $LaMnO_{3+\delta}$/LAO, indicating that the films are subjected to in-plane compressive and out-of-plane tensile strain. Figure 1(b) shows the out-of-plane lattice parameters of the $LaMnO_{3+\delta}$/LAO depending on the film thickness. Clearly, for the 30 nm $LaMnO_{3+\delta}$/LAO thin film, the out-of-plane lattice parameter is larger than that of the bulk material, which indicates that there exists in-plane compressive strain in the $LaMnO_{3+\delta}$/LAO thin film. With the increasing of film thickness, the out-of-plane lattice parameter decreases and approaches the value of the bulk material. The results show that the in-plane compressive strain of the $LaMnO_{3+\delta}$/LAO exhibits a relaxation with the increase of film thickness.

Figure 2(a) shows the temperature-dependent resistivity of the $LaMnO_{3+\delta}$/LAO. The $LaMnO_{3+\delta}$/LAO presents a large variation of electrical transport properties with the increase of film thickness. For the 30 nm $LaMnO_{3+\delta}$/LAO, it exhibits insulating behavior in the whole temperature range. For the 50 nm, 75 nm, and 100 nm $LaMnO_{3+\delta}$/LAO, with lowering temperature these films exhibit IMT at T_{IMT}, where the resistivity starts to decrease. The FMM state undergoes a transition to COO state at T_{COO}, while the resistivity shows an upturn. The $T_{IMT}(T_{COO})$ of the 50 nm, 75 nm, and 100 nm $LaMnO_{3+\delta}$/LAO are 182 (94) K, 186 (139) K, and 194 (141) K, respectively. Furthermore, both transition temperatures $T_{IMT}$and T_{COO} of the $LaMnO_{3+\delta}$/LAO can be enhanced by an external magnetic field. As shown by the dashed line in Figure 2(a), the magnetic field of 5 T increases the T_{IMT} and T_{COO} of 50 nm $LaMnO_{3+\delta}$/LAO to 208 K and 110 K, respectively. The results indicate that the magnetic field could stabilize the COO phase in $LaMnO_{3+\delta}$ thin films, which is similar to the reported in the lightly doped $La_{1-x}Sr_xMnO_3$ $(0.11 < x < 0.15)$ [19]. Figure 2(b) presents the temperature dependence of resistivity of the $LaMnO_{3+\delta}$/STO thin film. The electrical transport properties of $LaMnO_{3+\delta}$/STO are almost independent of the film thickness, in contrast to those of $LaMnO_{3+\delta}$/LAO. The 30 and 100 nm $LaMnO_{3+\delta}$/STO exhibit two successive transitions upon cooling: high-temperature PMI phase to intermediate FMM phase and then to low-temperature COO phase at T_{COO}. The $T_{IMT}(T_{COO})$ of the 30 nm and 100 nm $LaMnO_{3+\delta}$/LAO are 125 (206) K and 134 (205) K, respectively.

Figure 3 shows the temperature dependence of the field-cooled (FC) magnetization under a field of 0.1 T for the $LaMnO_{3+\delta}$/LAO. The FM transition temperature T_C is defined as the inflection point in the M–T curves. Similar to the transport properties, the magnetic properties of $LaMnO_{3+\delta}$/LAO are strongly dependent on the film thickness as well. The 30, 50, 75, and 100 nm $LaMnO_{3+\delta}$/LAO exhibit the T_C of 203, 205, 210, and 220 K. The T_C values of the $LaMnO_{3+\delta}$/LAO increase with the increase of the film thickness.

The variation of the transport and magnetic properties of the $LaMnO_{3+\delta}$/LAO with the film thickness suggests the essential role of the lattice degree of freedom. In $LaMnO_{3+\delta}$/LAO under large compressive strain, the MnO_6 octahedra are stretched at the out-of-plane direction and compressed in the in-plane. The lattice distortion can make electrons tend to occupy the $d_{3z^2-r^2}$ orbital and the in-plane transfer integral for the FM-DE decreases, leading to a lower T_C and the insulating transport behavior [20]. With the decrease of the compressive strain, the $d_{3z^2-r^2}$ orbital occupation is weakened and the T_C is increased with the film thickness. Another important feature is the evolution of the COO transition of $LaMnO_{3+\delta}$/LAO with the compressive strain. For the 30 nm $LaMnO_{3+\delta}$/LAO, the COO transition is quenched and the film exhibits insulating behavior in the whole temperature range. Furthermore, the T_{COO} increases with the decrease (increase) of in-plane compressive strain (film thickness). It is well known that the occurrence of COO transition in bulk material of $LaMnO_{3+\delta}$ is intimately correlated with structural anomalies that c-axis increases and a-, b-axes decrease [10]. The lattice deformation associated with the structural anomalies would prefer an occupation of special orbital arrangements that are characteristic of COO

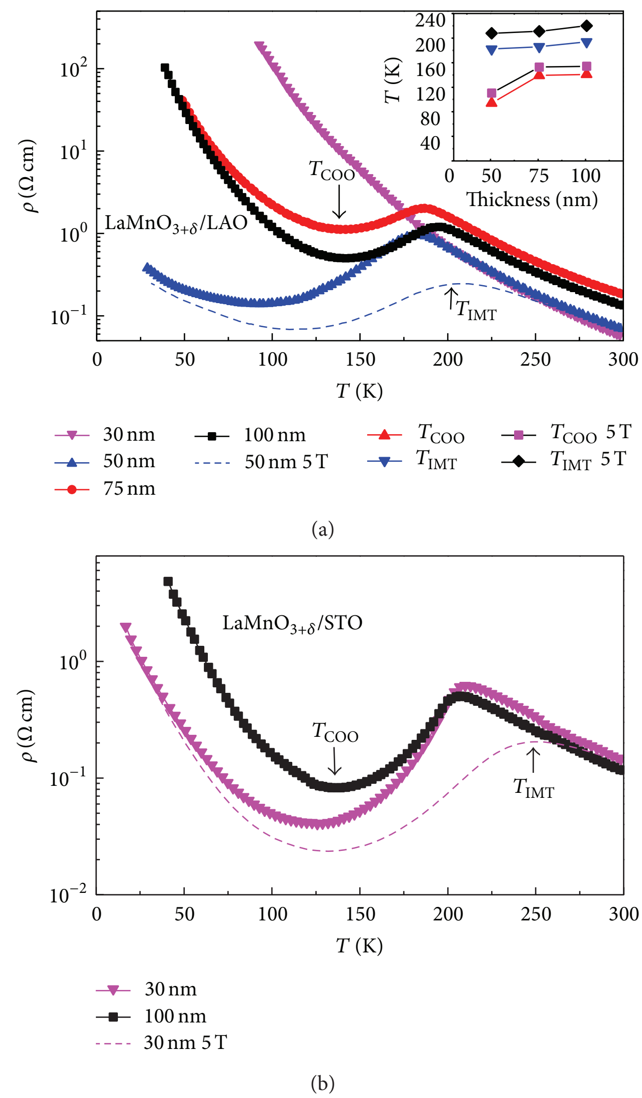


Figure 2: Temperature dependence of resistivity for (a) $LaMnO_{3+\delta}$/LAO and (b) $LaMnO_{3+\delta}$/STO film. In (a) solid lines with symbol are zero field results and dashed lines are results of the 50 nm $LaMnO_{3+\delta}$/LAO thin film under 5 T applied field; the inset shows the thickness dependence of the T_{COO} (T_{IMT}) at zero field and the T_{COO} (T_{IMT}) at 5 T field. In (b) solid lines with symbol are zero field results and dashed lines are results of the 30 nm $LaMnO_{3+\delta}$/LAO thin film with 5 T applied field.

[19, 21, 22]. For the $LaMnO_{3+\delta}$ thin films, the epitaxial strain provided by the substrate would clamp the in-plane lattice of the film. As a result, the lattice deformation associated with structural anomalies of $LaMnO_{3+\delta}$ thin films would be largely diminished by the epitaxial strain. For the thinnest 30 nm $LaMnO_{3+\delta}$/LAO, the in-plane lattice constants are fixed to that of LAO substrate and the out-of-plane lattice parameter is elongated due to the large compressive strain. Consequently, no COO transition is observed. As shown in Figure 1(b), the compressive strain and the clamp effect decrease with the increase of the film thickness. Then the presence of COO phase at low temperatures is expected to

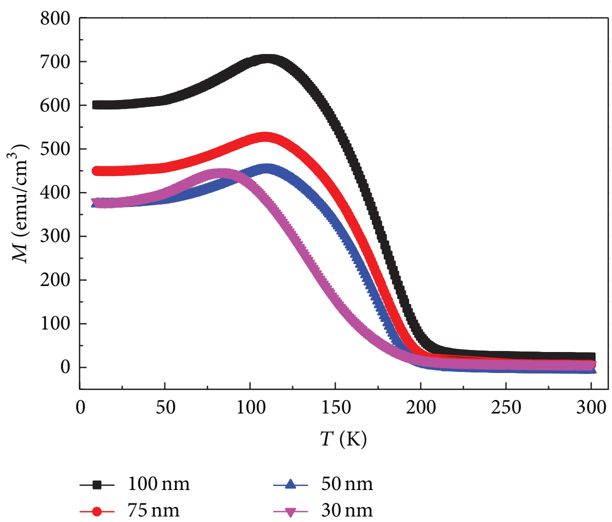


FIGURE 3: FC temperature-dependent magnetization under a field of 0.1 T for $LaMnO_{3+\delta}$/LAO.

appear in thicker films and T_{COO} increases with the increase of film thickness. For the $LaMnO_{3+\delta}$/STO with negligible compressive strain, the suppression of lattice deformation and the associated structural anomalies by the STO substrate can be neglected. Consequently, the $LaMnO_{3+\delta}$/STO films with different thickness show bulk-like behavior and the COO transitions are independent of the film thickness, as shown in Figure 2(b). These results verify that the transport and magnetic properties of the $LaMnO_{3+\delta}$ thin film can be tuned by the epitaxial compressive strain and confirm the importance of the lattice degree of freedom in the $LaMnO_{3+\delta}$ compound.

4. Conclusion

In summary, the effect of compressive strain induced by substrate on the transport and magnetic properties of $LaMnO_{3+\delta}$ thin films has been investigated. It was found that the transport and magnetic properties of $LaMnO_{3+\delta}$ thin films could be tuned by the compressive strain. We demonstrated that the T_{IMT}, T_{COO}, and T_C increase with the decrease of the compressive strain. These results indicate the vital role of lattice degree of freedom and the importance of coupling among charge, orbital, spin, and lattice in $LaMnO_{3+\delta}$.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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