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The control of charge-ordering-insulating (COI) phase in epitaxial La$_{1-x}$Ca$_x$MnO$_3$/NdGaO$_3$ (001) ($x=0.30–0.45$) thin films with essentially the ferromagnetic metal ground state as observed for the bulk counterparts has been realized via the anisotropic strain relaxation. This epitaxial system is special in that there is a negligible average lattice mismatch but a large anisotropic strain in between the film and the substrate. By changing the film thickness, postannealing temperature, along with the doping level for strain relaxation, the COI phase in the films can be tuned to either melt completely under 1 T, producing a huge low-field magnetoresistance (MR) in a wide temperature range (e.g., for the 20 nm film with $x=0.33$ and annealed at 780 °C, the MR can be over 70% at 0.2 T and 97% at 0.5 T in 10–200 K), or survive under a high magnetic field of 6 T. The results demonstrate the crucial role of anisotropic strain relaxation in inducing the inhomogeneity in manganites films, thus providing a forward understanding of the strain field in manganite physics.

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I. INTRODUCTION

The formation of charge-ordering-insulating (COI) phase in doped perovskite manganites has been considered as a collective outcome of electron-phonon coupling and the Coulomb interaction. The difference in manganite ionic valences (e.g., Mn$^{3+}$ and Mn$^{4+}$, albeit highly debatable) can be created by localization of $e_g$ itinerant electrons on specific Mn sites via the electron-phonon coupling, of which one well-known example is the Jahn-Teller distortion on Mn$^{3+}$. In order to lower the electrostatic potential energy from Coulomb repulsion of various ions, COI phase characterized by the periodic arrangements of different Mn ions appears, and the atomic stripes have been further confirmed by more detailed scanning tunneling microscope (STM) images on distorted and alternately undistorted MnO$_6$ octahedrons in COI phases. Apart from the inhomogeneity at nanoscale, the autarchy of COI phase as a ground state is often inhibited by the microscale inhomogeneity in manganites, resulting in phase coexistence of ferromagnetic metallic (FMM) or paramagnetic insulating (PMI) with the COI in the phase separation (PS) scenario. Recently, both theoretical and experimental studies have strongly suggested that the strain field, along with the electron-phonon coupling, plays a crucial role in determining the inhomogeneities at various length scales, and to get a COI ground state in epitaxial manganite films the anisotropic strain should be introduced. These mean that the phase-separated texture or COI phase in manganites can be controlled by engineering the strain field.

In this paper, we demonstrate an anisotropic-strain-relaxation mediated COI phase or PS in prototype La$_{1-x}$Ca$_x$MnO$_3$/NdGaO$_3$ (001) [NGO(001)] ($x=0.30–0.45$) thin films, contrary to bulk counterparts showing only the FMM ground state in this doping range. The films grown on orthorhombic NGO(001) substrates, albeit with a negligible average lattice mismatch in between, suffer from a large anisotropic strain in the film inplane, and this strain effect is so remarkable that after annealing a huge low-field magnetoresistance (LFMR) can be induced in the epitaxial system. The LFMR that occurred in a wide temperature range makes the approach very distinct from the isotropic strain effect and promising for device applications.

II. EXPERIMENTS

La$_{1-x}$Ca$_x$MnO$_3$ ($x=0.30, 0.33, 0.37$, and 0.45) films with various thicknesses (8–24 nm) were grown on NGO(001) substrates ($5 \times 3 \times 0.5$ mm$^3$) by pulsed laser deposition method using a 248 nm KrF excimer laser. The ceramic targets were prepared by standard solid state reactions. For all samples, during deposition the temperature and oxygen pressure were kept at 735 °C and 45 Pa, while the laser energy density and repetition rate were set at 2 J/cm$^2$ and 5 Hz, resulting in a growth rate of 6 nm/min. In order to improve the oxygen content and facilitate the strain relaxation, the films were postannealed in flowing O$_2$ for 3 h at a temperature chosen carefully based on the film thickness as well as the doping level, as will be described in detail in Sec. III. For each film the temperature-dependent resistivity ($\rho$-$T$) was measured using the four-probe method on a superconducting quantum interference device (SQUID) magnetometer.
(Quantum Design, MPMS). The magnetic properties of the films were measured on SQUID and also probed using electron spin resonance (ESR) (Brucker, ER200D) at 9.6 GHz and in the temperature range from 300 to 110 K, where the magnetic field was applied perpendicularly to the film plane. The structure of the films was characterized by high-resolution x-ray diffractions (XRDs) using Cu $K\alpha_1$ ($\lambda = 1.5406$ Å) radiation (Philips, X’pert), and the surface morphology of the films was analyzed by the atomic force microscopy (AFM) (SII NanoTechnology, Inc., Nanonavi Probe Station).

III. RESULTS AND DISCUSSION

We first select La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) to grow on the orthorhombic NGO(001) substrates, since this compound in both the bulk and thin-film forms is well studied and the doping is safe in the FMM ground state. The in-plane lattice sketch with the orthorhombic lattice constants for relaxed LCMO (green) and the substrate (purple) as denoted has been illustrated in the upper right of Fig. 1(a), indicating that the coherent LCMO films should suffer an anisotropic strain from the (001)-cut NGO substrates, although in pseudocubic notation the average lattice mismatch in between is quite small (<0.15%). In fact, for Nd$_{0.5}$Sr$_{0.5}$MnO$_3$, Pr$_{0.5}$Sr$_{0.5}$MnO$_3$, and (Bi, Ca)MnO$_3$ with the COI ground state, the anisotropic strain has been demonstrated to be essential to promote the electron localization, thus facilitating the COI transition in the epitaxial thin films. Bulk LCMO shows only a PMI-FMM transition near 260 K and keeps the FMM ground state down to lower temperatures, while STM images from the LCMO films exhibit inhomogeneity and PS at microscale. Considering the narrow bandwidth of LCMO, we suppose that if the anisotropic strain in between LCMO and NGO(001) can work as in the other systems mentioned above, the COI phase might be induced in the films, and the resultant PS could be modulated artificially through the control of strain relaxation.

In Fig. 1(a), well-regulated $\rho$-$T$ curves have been displayed in terms of the film thickness and post annealing temperature, both of them being commonly acknowledged as factors for tailoring the strain state relaxation. All the as-grown films from 24 to 8 nm thick show only bulklike $\rho$-$T$ behaviors with the PMI-FMM transition temperature $T_P$ decreasing fast for the ultrathin films, and there is no difference in $\rho$-$T$ during the cooling and warming over the whole temperature range. After postannealing, however, the films can give the COI phase related resistivity with a large thermal hysteresis during cooling and warming, suggesting that a first-order phase transition or PS between FMM and COI phases has been induced in the films. The results manifest that the anisotropic strain alone cannot induce the COI
phase, and the strain relaxation through postannealing seems indispensable. The COI phase transition occurs at a high temperature with a sharp change in resistivity, as guided by the dashed lines, approaching $T_p$ of the LCMO bulk. Furthermore, the thinner films can easily get COI phase transition than the thicker ones. For example, after being annealed at 800 °C the film at 24 nm shows only slight thermal hysteresis with overall lower resistivities, while the one at 16 nm displays a clear COI transition with large thermal hysteresis at lower temperatures. Specifically, for films at 12 or 16 nm, it is seen that with increasing annealing temperature the $\rho$-$T$ behaviors change gradually from FMM to COI ground state. For the 8 nm films, however, after annealing in the same temperature range, the change is too abrupt to show all the states. Then, we annealed the 8 nm samples at lower temperatures from 500 to 700 °C, respectively, with the results summarized in Fig. 1(b). The films postannealed at 500 °C show only bulklike $\rho$-$T$, and at 600 °C they have weak COI phase competing with FMM, as reflected by the thermal hysteresis. After annealing at 650 °C the COI phase is strengthened, while the samples annealed at 700 °C show only COI with the thermal hysteresis hardly discernible. Hence, the thickness or annealing temperature evolution of COI phase in the PS background can be extracted, giving a phase diagram as illustrated in Fig. 1(c). This sketch can be divided into three areas: the thinner films annealed at higher temperatures prefer the COI phase, while the thicker films annealed at lower temperatures favor the FMM phase, and in between the films show phase coexistence and competition, leading to various thermally hysteretic transport behaviors.

In Fig. 1, the most striking feature is that the anisotropic strain relaxation during the postannealing can induce COI phase in the FMM matrix. The charge-orbital ordering is usually accompanied with the regular arrangements of distorted and undistorted MnO$_6$ octahedrons, which can also be viewed as a strain relaxation for minimal elastic energy. We speculate that the annealing may provide necessary energy to activate the in-plane anisotropic-strain relaxation, possibly leading to inhomogeneity even at the atomic scale. Since part of the coherently strained orthorhombic unit cells of LCMO may be relaxed more easily by just rotating themselves to match the diagonal with the orthorhombic NGO(001) substrate, the films are hard to relax uniformly in the film plane. This structural inhomogeneity induced by the shear strain relaxation will cause the PS in this peculiar epitaxial system, although the films are doped for a FMM ground state. However, the thicker films have generally more defects such as twin boundaries that may enhance FMM phase and at the same time destroy the PS related strain field as described before. In this scenario, the inhomogeneity at various length scale depends sensitively on the anisotropic strain states over which the control should provide possible approaches for patterning the magnetic and electronic states in epitaxial manganite thin films.

Surely, it is interesting to investigate the magnetoresistance (MR) behaviors of LCMO films with various PS characteristics. In Fig. 2, $\rho$-$T$ of the 8 nm samples annealed at different temperatures was measured under various magnetic fields [Figs. 2(a)–2(c)], and the MR denoted by $[\rho(H) - \rho(0)]/\rho(0)$ is shown in Figs. 2(d)–2(f), correspondingly. For those annealed at 600 °C, the FMM state dominates with lower resistivities, resulting in a MR peaked at 185 K (93%, 1 T). The 650 °C annealed samples may have comparable volume fractions of the COI and FMM phases, producing a large MR in the whole temperature range below 185 K (89%, 1 T). However, for those annealed at 700 °C the COI phase is so robust that it can only be melted completely into FMM under a magnetic field higher than 3 T, and upon cooling a comparable MR at 1 T can only be reached at much lower temperatures. According to Fig. 2, it can be concluded that the COI state controlled by the anisotropic strain states is critical to the MR effect, and the films with two competing phases evenly distributed may give rise to a larger MR and in a wider temperature range.

Along this line, we annealed the LCMO films 20 nm thick at 780 °C in order to get a state with more intensive phase competition. In Fig. 3(a), an overshoot of resistivity during warming was observed in the thermal hysteresis, and as a reflection of phase coexistence between the COI and FMM states, it has been explained by the different growing size and distribution of FMM during the cooling and warming processes. More strikingly, the phase-separated texture in 20 nm films is more competitive, since a LFMR has been achieved for the films. The MR denoted by $[\rho(H) - \rho(0)]/\rho(0)$ or $[\rho(0) - \rho(H)]/\rho(H)$ was shown in Figs. 3(b) and 3(c), respectively. It can be over 70% (260%) at only 0.2 T and 97% (6000%) at 0.5 T in the whole range of 10–200
K. Compared with the 8 nm films, the thicker films annealed at higher temperature can give larger LFMR and in a wider temperature range, suggesting that the LFMR could be further improved by carefully adjusting the film thickness and the annealing temperature so as to change the strain-state-controlled PS nature consistent with our supposing model.

In order to get more understanding on PS in the LCMO/NGO(001) thin films, their magnetic properties were probed. The sample at 24 nm and annealed at 750 °C with only the FMM ground state and the one at 20 nm annealed at 780 °C showing the most intensive phase competition were chosen for comparison. First, the temperature-dependent magnetization ($M-T$) of the films was measured, as shown in Fig. 4(a), where the magnetization is normalized [$M(T)/M(320 \, K)$] with the presence of strong paramagnetic background from the NGO substrates. For the film at 24 nm, the $M-T$ shows clearly a paramagnetism-ferromagnetism (PM-FM) transition at about 260 K, consistent with its $\rho-T$ behavior. For the film at 20 nm, however, it shows only a PM signal in the whole temperature range, and due to the strong PM from the substrate, which makes the magnetization of the films hard to be quantified, the PS related changes in magnetization cannot be defined. Then, to explore the micromagnetism of the films, we measured the ESR at various temperatures, as shown in Figs. 4(b) and 4(c). For the 24 nm film, the PM-FM transition around 260 K can also be observed clearly, consistent with the bulk samples, and with decreasing temperature the FM signal shifts to lower fields, indicating a dominant FMM state at lower temperatures. In contrast, the 20 nm film performs in a totally different way below 260 K. Instead of the sharp PM-FM transition as observed for the 24 nm film, the sample at 20 nm gives several signals from 260 to 110 K. According to previous ESR studies on PS in manganites, the complex may arise from the FM, PM, and antiferromagnetic (AFM) components in the film, and the AFM signal moves to higher fields and becomes more inten-

**FIG. 3.** (Color online) (a) $\rho-T$ curves measured under various magnetic fields from the film 20 nm thick and annealed at 780 °C, and the corresponding MR denoted by [$\rho(H)-\rho(0)\]/\rho(0)$ and [$\rho(0)-\rho(H)\]/\rho(H)$ is shown in (b) and (c), respectively.

**FIG. 4.** (Color online) (a) $M-T$ curves measured from the films at 24 nm and annealed at 750 °C and at 20 nm annealed at 780 °C. In (b) and (c), ESR spectra from the two samples were measured at 300–110 K.
sive at still lower temperatures. Although it cannot be clearly indexed at this moment, considering the ρ-T behaviors, the ESR spectra could be a signature of spin relaxation induced by the phase coexistence and competition in the films.

LFMR materials have the potential for applications in many areas including the data storage, but traditionally manganites with LFMR employ structural discontinuities such as natural or artificial boundaries that may be inappropriate for the vertical junctions, and the LFMR effect is usually observed at much lower temperatures. Considering the much prominent LFMR due to PS, as has been demonstrated, it is necessary to check the structure and surface quality of the films. Figure 5(a) shows the XRD linear scans on (002) reflections from the as-grown (green) and 780 °C annealed (red) 20 nm films. The clear interference fringes in the curves imply a uniform thickness and smooth surface of the films. The shift and deformation of the reflections and fringes can also be a signature of oxygen uptake and the strain relaxation during postannealing, although the details on microstructure are still lacking. The smooth surface of the films was further confirmed by AFM images shown in Figs. 5(b) and 5(c), respectively. After annealing, the changes in morphology are hardly discernible. Hence, the LCMO/NGO(001) films are very suitable for fabricating heterostructures with the LFMR effect incorporated.

We have shown that the COI phase in LCMO (x=0.33) films is strongly affected by the film thickness and annealing temperature, the factors that are relevant to the control of strain states. In addition to carrier concentration, the doping levels can also modify the crystal structure, therefore, the strain states and electron-phonon coupling in the films. In Fig. 6, various ρ-T curves were measured from the La1−xCaxMnO3/NGO(001) (x=0.30, 0.37, and 0.45) films annealed simultaneously at 770 °C. Aside from the COI phase observed for the films in the wide doping range with noticeable thickness effect, more strikingly, with the increasing of Ca content, the COI phase becomes more and more stable. Similar to bulk counterparts, the overdoping of Ca enhances the electron-phonon coupling, and as a result, the COI phase can dominate more easily over the FMM ground state, leading to a weak thermal hysteresis and a large melting field, and this is starkly observed for La0.55Ca0.45MnO3 films, where the COI phase is robust even at 20 nm and can hardly be suppressed at a high magnetic field of 6 T.

IV. SUMMARY

In summary, we make use of the in-plane anisotropic-strain relaxation to induce COI phase in epitaxial La1−xCaxMnO3/NGO(001) (x=0.30, 0.33, 0.37, and 0.45) films, where the COI phase is robust even at 20 nm and can hardly be suppressed at a high magnetic field of 6 T.
films with essentially the FMM ground state as observed for the bulk counterparts. By controlling the doping level, film thickness, and especially the postannealing temperature, the COI phase can be modulated to either melt completely under a small field, producing a huge LFMR in a wide temperature range, or survive under a high magnetic field of 6 T. The results strongly suggest that the PS nature or inhomogeneity in manganites can be intrinsically determined by the strain fields, as emphasized theoretically in the last several years. The huge LFMRs induced in the epitaxial systems also make the approach very promising for novel manganite devices.

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