Correlation of structural phase transition and electrical transport properties of manganite films on $SrTiO_3$

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Magnetic phase transition in the manganite films has been found to be induced by the structural phase transition of the $SrTiO_3$ substrate at $T_s=105$ K [Vlasko-Vlasov *et al.*, Phys. Rev. Lett. **84**, 2239 (2000) and Ziese *et al.*, New J. Phys. **10**, 063024 (2008)]. However, no change in the electrical transport properties has been detected at this temperature. Here we report the observation of the satellite peaks in the temperature dependence of the temperature coefficient of resistivity (TCR) at temperatures around 105 K in the ultrathin manganite films grown on $SrTiO_3$ substrates, triggered by the cubic-to-tetragonal structural phase transition in $SrTiO_3$. The TCR peak's magnitude decreases with an increasing thickness of the manganite film and with an increasing applied magnetic field. Our results demonstrate the strong coupling between the structural and transport properties in the manganite films.

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The physical properties of manganite thin films are dramatically different from those of bulk manganite samples since the film's properties can be very sensitive to the lattice strain that results from the mismatch of the lattice constants between the film and its substrate. For example, the epitaxial strain effects have been observed in manganite thin films, which dramatically affect the primary magnetotransport properties such as the ferromagnetic transition temperature or the metallic conductivity.[1,2] Manganite thin films are often deposited on oriented single-crystal substrates such as $SrTiO_3$ (STO).[3] STO is known to have a cubic perovskite structure at room temperature, but at a temperature $T_s \approx 105$ K, it undergoes an antiferrodisplacive soft-mode structural second-order phase transition to a tetragonal phase.[4] Magneto-optical imaging performed by Vlasko-Vlasov *et al.*[5] revealed that when a 150-nm thick film of $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) is deposited on a STO substrate, twin boundaries are formed in the film at temperatures below T_s.[5] The formation of twins is a hallmark of a martensitic phase transformation occurring in the film at T_s, below which the symmetry of the film is lowered from tetragonal to orthorhombic.[6] Note that such a transition has not been observed in bulk $La_{2/3}Ca_{1/3}MnO_3$. Hence, there is strong evidence that the structural changes in the STO substrate induce a structural transition in the film. Ziese *et al.*[7] have studied the effects of the structural phase transition at T_s in the STO substrate on the magnetic properties of $La_{0.7}Sr_{0.3}MnO_3$ films. They found a clear magnetic transition at T_s in these films, associated with the formation of three differently oriented crystallographic domains. This interpretation is different from that provided by Vlasko-Vlasov *et al.*[5] for the LCMO case. Although the structural changes are clearly occurring in the films, no structural phase-transition-induced anomaly has been reported in the temperature dependence of the electrical transport.

Here we report careful measurements of the temperature dependence of the resistivity of the manganite films grown on the STO substrate. The temperature dependence of resistivity has been measured for the *c*-axis-oriented $La_{0.65}Ca_{0.35}MnO_3$ (LCMO), $Nd_{0.55}Sr_{0.45}MnO_3$ (NSMO), and $La_{0.8}Sr_{0.2}MnO_3$ (LSMO) films of thickness between 9 and 150 nm. The lattice mismatch between these films and the (100)-oriented STO substrate at room temperature is +0.60%, +(0.30–0.90)%, and +0.40%, respectively, producing tensile strain in the films.[8–11] We found that the structural phase transition in the manganite films (caused by the antiferrodisplacive phase transition in the STO substrate at T_s) produces a peak in the temperature dependence of the temperature coefficient of resistivity at temperatures around 105 K. The magnitude of the peak decreases with an increasing thickness of the film and with an increasing magnetic field. In films thicker than 150 nm, the peak is smeared out probably because there is partial relaxation of the substrate-induced strain.

The *c*-axis-oriented LCMO, NSMO, and LSMO films were deposited in a dc magnetron sputtering system using 50-W power and an argon-oxygen mixture (of partial pressures 100 and 20 mTorr of oxygen and argon, respectively) at 750 °C on (100)-oriented STO substrates. After deposition the chamber was filled with oxygen at atmospheric pressure in order to ensure that the films gained the optimum oxygen content and hence the maximum T_c. The films were cooled down from 750 to 650 °C with a rate of 10 °C/min, followed by annealing at 650 °C for 2 h and subsequent cooling down to room temperature with a rate of about 15 °C/min.[12] Such an annealing process is essential for producing films with the lowest possible residual resistivity (ρ_0). We note that there appears to be a correlation between the sharpness of the temperature coefficient of resistivity (TCR) peak and the residual resistivity ratio of the sample; in particular, the structural phase transition in STO does not appear to produce a noticeable peak in films with large ρ_0. The films used in this study were patterned in the form of 3×10 mm^2 strips. Four silver dots (diameter 0.5 mm) were deposited on each film using rf magnetron sputtering at 50 W. Immediately after the Ag deposition, leads were attached to the four dots with indium.[13]

The temperature dependence of resistivity ρ and magnetoresistivity $\mathrm{MR}(H)=[\rho(0)-\rho(H)/\rho(H)]$, where $\rho(0)$ and $\rho(H)$ are resistivities in a zero magnetic field and a finite

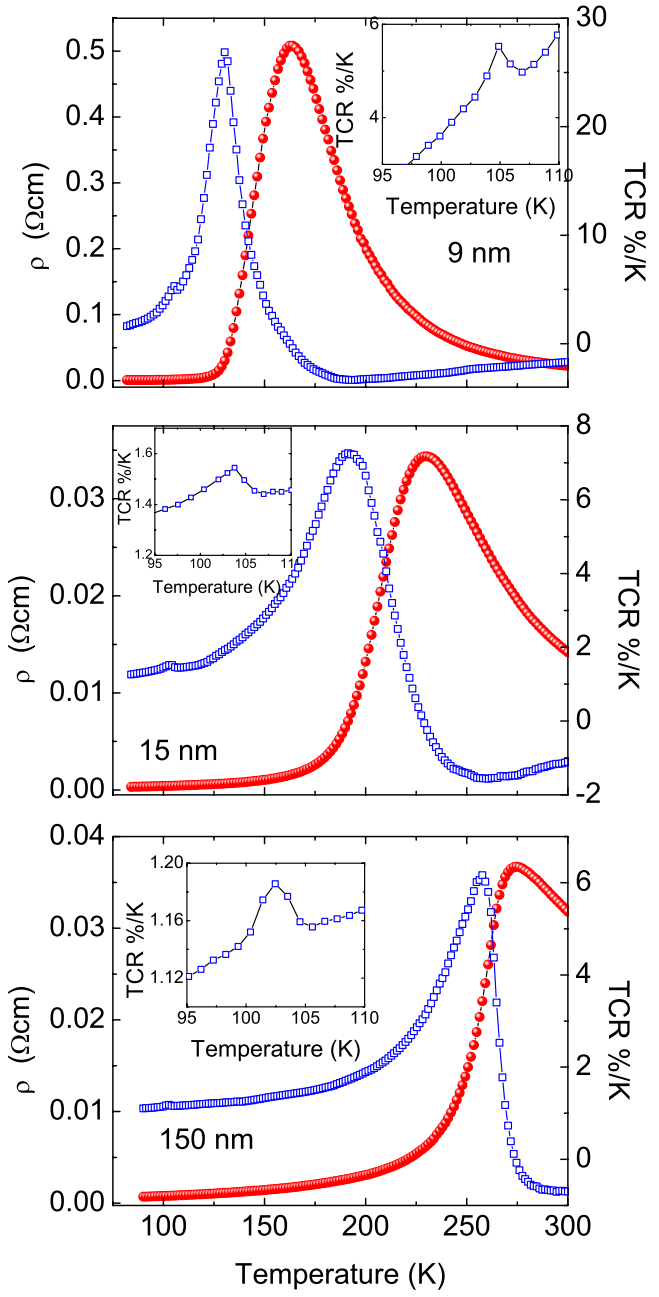

FIG. 1. (Color online) Temperature dependence of ρ measured in a zero magnetic field and that of TCR for 9-, 15-, and 150-nm thick LCMO/STO films. The insets show the change in TCR at $T_s \approx 102-105$ K.

field, respectively, has been measured in LCMO, NSMO, and LSMO films over a temperature range between 80 and 300 K and in magnetic fields up to 0.7 T. The results for the LCMO films of different thickness are shown in Fig. 1. As the thickness of the film is reduced the metal-insulator transition temperature decreases, and the magnitude of the resistivity increases dramatically due to an increased epitaxial strain (see Table I). This is in agreement with the theoretical analysis of the strain effects in manganite films, which predicts an increase in the resistivity with the tensile strain in very thin manganite films.[14]

In order to detect the very small changes in the resistivity

TABLE I. Properties of the LCMO, NSMO, and LSMO films. The ΔTCR denotes the change in the TCR at T_s. The MR_{max} indicates the maximum value of the magnetoresistivity in a field of 0.68 T. T_p and ρ_p are the temperature and the resistivity of the resistivity peak at the metal-insulator transition.

Film	Thickness (nm)	T_p (K)	ρ_p (Ω cm)	MR_{max} (%)	ΔTCR (%/K)
LCMO-1	9	163	0.510	300	0.90
LCMO-2	15	230	0.034	60	0.10
LCMO-3	150	275	0.036	30	0.04
LSMO	10	320	0.016	8	0.05
NSMO	150	199	0.100	96	0.20

of these films at T_s we calculated $TCR = (1/\rho)(d\rho/dT)$ for the LCMO films (see Fig. 1). The temperature dependence of the TCR clearly exhibits two peaks, a prominent one at the metal-insulator transition temperature of the LCMO films, and a small sharp peak at T_s. The amplitude of the peak at $T_s \approx 102-105$ K increases as the LCMO film is made thinner. In Fig. 2 we have plotted ΔTCR at T_s. ΔTCR was obtained by subtracting the background from the temperature

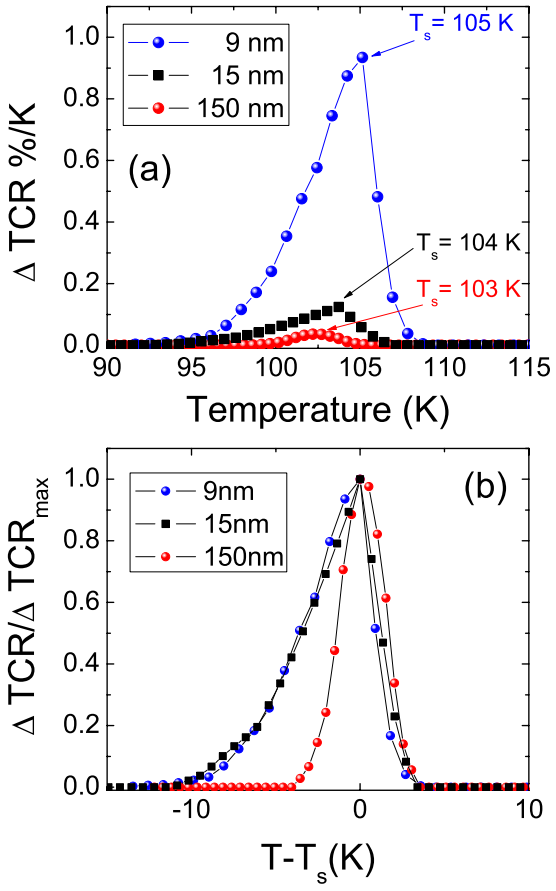

FIG. 2. (Color online) (a) Temperature dependence of ΔTCR of LCMO films obtained by subtracting the background from the temperature dependence of TCR shown in Fig. 1. (b) Temperature dependence of ΔTCR normalized to its maximum value. The lines are guides for the eye.

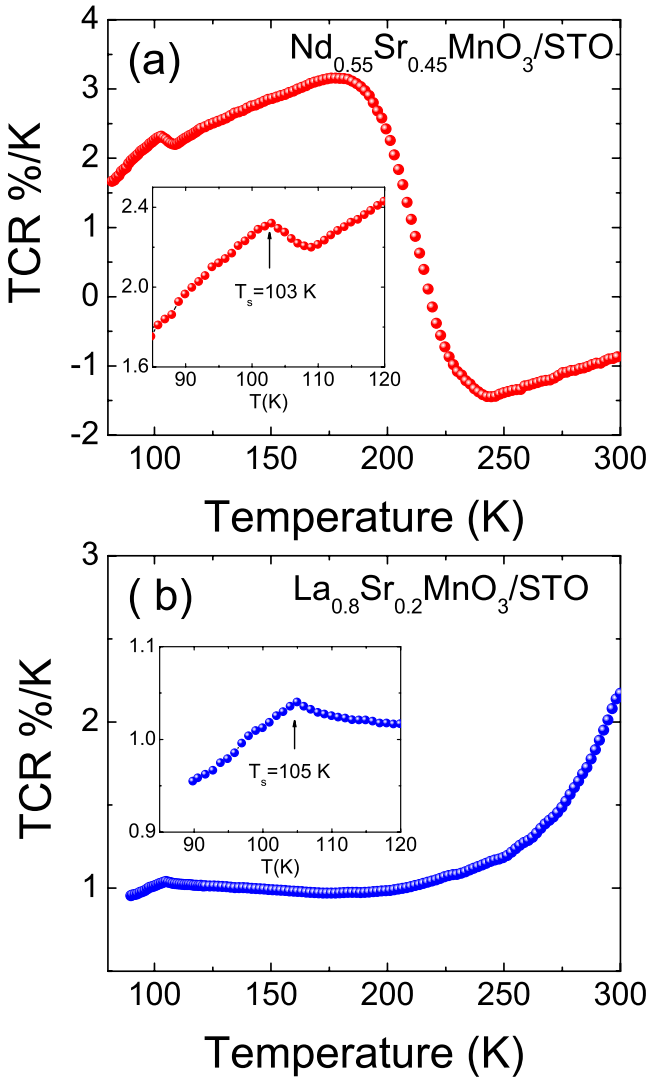

FIG. 3. (Color online) (a) and (b) Temperature dependence of TCR of a 150-nm thick NSMO/STO film and a 10-nm thick LSMO/STO film, respectively. The insets show the peak in TCR at $T_s \approx 103-105$ K.

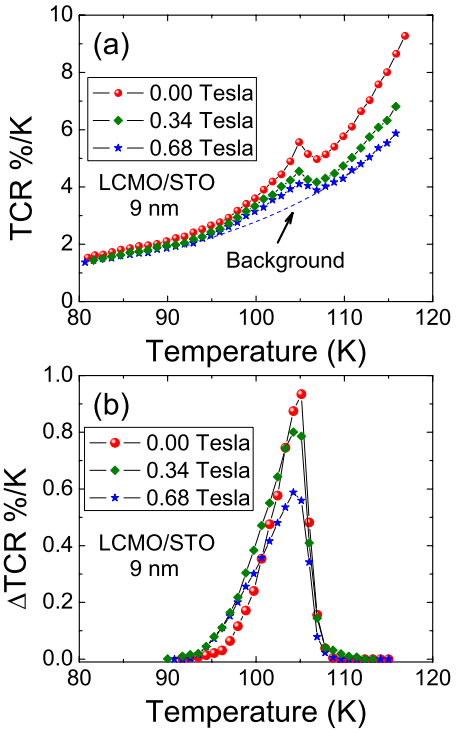

FIG. 4. (Color online) (a) Temperature dependence of TCR of a 9-nm thick LCMO/STO film measured in a zero magnetic field, and 0.34 and 0.68 T in-plane magnetic fields. (b) Temperature dependence of ΔTCR obtained by subtracting the background from the temperature dependence of TCR shown in (a) for this film.

dependence of the TCR shown in Fig. 1 for these films. Figure 2(a) shows an increase in the ΔTCR with a decreasing thickness of the film. ΔTCR peaks normalized to their maximum value reveal that the ultrathin films exhibit a broader transition at T_s [see Fig. 2(b)]. Peaks in the temperature dependence of the TCR at 103–105 K were also observed for NSMO and LSMO manganite films deposited on STO substrates (see Fig. 3), further confirming that they are induced by the structural phase transition in the $SrTiO_3$. Figure 4(a) shows the temperature dependence of the TCR measured in different magnetic fields in the vicinity of T_s for a 9-nm thick LCMO film. Figure 4(b) shows the temperature dependence of the ΔTCR obtained by subtracting the background from the temperature dependence of the TCR shown in Fig. 4(a) for this film. The magnetic field reduces the magnitude and increases the width of the TCR peak at T_s.

The main effect of the structural phase transition in STO on the transport properties of manganite films is the formation of the satellite peaks in the TCR of LCMO, NSMO, and LSMO films. We have found that the effect does not depend on the direction of the current. These peaks reveal the presence of a change in the slope of the temperature dependence of the resistivity at temperatures around T_s. It has been shown before that the very thin LCMO films of thickness less than 25 nm grown on STO substrates are coherent, i.e., they have the same in-plane lattice parameters as the substrates.[8] These films, therefore, exhibit very large tensile strain. In general, the physical properties of the ultrathin manganite films are more sensitive to the substrate-induced strain than those of thicker films (that are structurally very similar to the bulk material) in which the lattice strain is partly relaxed. As seen in Fig. 2, a decreasing thickness of the LCMO film leads to both an increase in the magnitude of the TCR peak and its broadening. The lattice constants of the cubic phase of the STO decrease with temperature by about 0.2% over a temperature range between 300 and 105 K.[15] On the other hand the in-plane lattice constants of LCMO decrease with temperature also by about 0.2% between 300 and 100 K,[16] suggesting that the in-plane elastic misfit between the LCMO film and the STO substrate remains almost independent of temperature at temperatures above T_s. In the tetragonal phase of the STO, i.e., below T_s, a defect structure consisting of tetragonal domains is formed.[17] The in-plane a-axis lattice constant decreases with temperature, while the out-of-plane c-axis lattice constant increases slightly with a decreasing temperature. This can produce large internal stresses in the LCMO film. As discussed earlier a twin defect structure has been observed to form in the LCMO film at

temperatures below T_s.[5] On the other hand, in LSMO films differently oriented crystallographic domains are created at these temperatures.[7]

The question is: What is the mechanism that leads to the peak of the TCR (the resistivity change) at T_s in the manganite films? The contributions to the resistivity could arise from both the scattering of the charge carriers by the structural defects, such as twin boundaries and the strain-induced modifications of the in-plane and out-of-plane electron hopping amplitudes due to the substrate-induced distortions of the film's unit cell.[14] Large internal stresses due to the changes in the lattice constants at the martensitic phase transformation are usually reduced by the formation of twin boundaries.[5] Therefore, it seems reasonable to suggest that a significant contribution to the resistivity at T_s is from charge or spin scattering at the (possibly magnetic) boundaries.

The response of the TCR to the in-plane magnetic field in LCMO is shown in Fig. 4. The TCR drops with increasing field below and above T_s, a phenomenon that is expected in manganites because of the field-induced smearing out of the resistive transition.[18] The magnitude of the ΔTCR peak decreases and its width increases slightly with an increasing magnetic field at around T_s. It is widely accepted that the low-field and low-temperature MR observed in manganites containing structural defects, such as grain boundaries, is the result of the spin-polarized transport across these defects.[19] Since it appears that below T_s twins are formed, it may be possible that magnetic-field-enhanced spin-polarized tunneling of the charge carriers across these defects is responsible for the observed changes in ΔTCR.

In summary we have shown that the structural phase transition in the $SrTiO_3$ substrate affects the transport properties, and in particular the temperature dependence of resistivity of thin manganite films that have been grown on it. This suggests the presence of a coupling between the structural and the electrical transport properties of manganite films deposited on the $SrTiO_3$ substrates. The results of these studies should stimulate renewed interest in the strain-induced changes in the temperature dependence of the magnetotransport properties of the manganite films.

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