Giant resistance switching effect in nano-scale twinned La$_{0.65}$Ca$_{0.35}$MnO$_3$ film

V. G. Prokhorov, G. G. Kaminsky, and V. A. Komashko

Institute of Metal Physics, National Academy of Sciences of Ukraine
36 Vernadsky Str., Kiev, 03142, Ukraine
E-mail: pvg@imp.kiev.ua

Y. P. Lee

Department of Physics, Hanyang University, Seoul, 133-791 Korea

A. I. Tovstolytkin and A. N. Pogorily

Institute of Magnetism, National Academy of Sciences of Ukraine, Kiev, 03142, Ukraine

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The magnetic and transport properties of a 20 nm-scale twinned La$_{0.65}$Ca$_{0.35}$MnO$_3$ film are investigated in a temperature range of 77–300 K. The coexistence of ferromagnetic metallic and charge-ordered insulating phases is suggested by analyzing the temperature and current dependences of the resistance at low temperatures. It is shown that thermocycling leads to the formation of a nonequilibrium state in the ensemble of charge-ordered domains and to the appearance of a giant switching in resistance of up to 100%. The experimental results are discussed on the basis of phase separation.

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The hole-doped perovskite manganites are of great current interest not only for fundamental science in connection with the discovery of colossal magnetoresistance (CMR), but also for their potential applications to new devices such as magnetic reading heads, field sensors, and memories. Recently evidence was presented for the coexistence of ferromagnetic metallic (FM) and charge-ordered insulating (COI) phases in La$_{0.67}$Ca$_{0.33}$MnO$_3$ films at low temperatures governed by the lattice strains accumulated during the deposition [1,2]. This defies the common knowledge that the phenomenon of charge ordering (CO) is observed only in compounds with a small average A-site cation radius, $\langle r_A \rangle \leq 0.118$ nm. However, in view of the very similar energies of the COI and FM states in these compounds [3] one might expect the appearance of the COI region in the compound with a larger $\langle r_A \rangle$ induced by a structural distortion away from the ideal cubic perovskite lattice [2]. Charge ordering controlled by lattice strains was observed previously in Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ films [4].

In this paper we report experimental results for the magnetic and transport properties of a La$_{0.65}$Ca$_{0.35}$MnO$_3$ film prepared by rf magnetron sputtering using a so-called «soft» (or powder) target [5]. The substrate was a LaAlO$_3$ (001) twinned crystal with a lattice parameter $a$ of 0.379 nm for the pseudocubic symmetry. The substrate temperature during deposition was 750 °C. The thickness $d$ of the film was about 50 nm. In contrast to the two-step cooling of the chamber, with a hold at 400 °C for 1 h, which is usual for the preparation of films with perfect crystal structure, here one-step cooling was employed to enhance the lattice strains. The $\theta - 2\theta$ x-ray diffraction (XRD) patterns were obtained using a Rigaku diffractometer with CuK$_{\alpha1}$ radiation. The lattice parameters evaluated directly from the XRD data were plotted against cos$^2$ $\theta$/sin $\theta$. With straight-line extrapolation to cos$^2$ $\theta$/sin $\theta$ = 0, a more precise determination of
the lattice parameter is obtained. The resistance measurements were carried out by using the four-point-probe method in a temperature range of 77–300 K and a magnetic field up to 1.5 T. The magnetization curves in a field up to 100 Oe were taken with a Quantum Design SQUID magnetometer in a temperature range of 50–300 K.

Figure 1. $\theta$–2$\theta$ XRD scan of the La$_{0.65}$Ca$_{0.35}$MnO$_3$ film. The (003) diffraction peaks of the film $a$ and substrate $c$ for the cubic symmetry.

Figure 2. Temperature dependence of the resistance of a La$_{0.65}$Ca$_{0.35}$MnO$_3$ film at different applied magnetic fields. The inset displays the temperature dependence of the field-cooled (FC) and zero-field-cooled (ZFC) magnetization.

Figure 1. $\theta$–2$\theta$ XRD scan of the La$_{0.65}$Ca$_{0.35}$MnO$_3$ film. The (003) diffraction peaks of the film $b$ and substrate $c$ for the cubic symmetry.
rized tunneling of carriers between ferromagnetic grains through an insulating grain boundary leads to the formation of a peak on the $R(T)$ curve at a low temperature, which must be very sensitive to a low applied magnetic field [8]. However, in our case the resistance has a weak dependence on magnetic field near $T_p$, and the magnitude of the negative magnetoresistance in this temperature range is much smaller than that observed for manganites films with artificially grown GB [11,12]. Our results are coincident with the $T - H$ phase diagram for a nonuniformly strained La $\text{Ca MnO}_0.67$ $\text{CaO}_0.33$ $\text{MnO}_3$ thin film, which predicts this type of behavior of the resistance in the COI state [2]. On the other hand, Fig. 3 shows that the second peak disappears at a low electric field. A similar effect was observed recently in epitaxial films of charge-ordered rare-earth manganites and it was shown that the COI state is destroyed by applying a small electrical current [13,14]. Therefore, we might conclude that the nano-scale twinned La $\text{Ca MnO}_0.65$ $\text{CaO}_0.35$ $\text{MnO}_3$ film becomes phase-separated below the Curie temperature and includes both FM and COI regions simultaneously. There are reasons for a nonuniform distribution of magnetic moments in the film and the unusual behavior of $M(T)$. The absence of saturation on the FC $M(T)$ curve at low temperatures and the very large difference between the ZFC and FC values of the magnetization attest to a spin-glass-like (or cluster-glass-like) magnetic state in the film below $T_C$. In this case the FM clusters are randomly distributed in the antiferromagnetic insulating matrix, and the long-range exchange interaction between them is essentially suppressed.

Figure 4 displays the influence of thermocycling on the shape of the $R(T)$ curve for the prepared La $\text{Ca MnO}_0.65$ $\text{CaO}_0.35$ $\text{MnO}_3$ film. In the first cycle (1) the film was cooled down to 77 K and the $R(T)$ curve was recorded with increasing temperature. The third cycle (2) means that the film was heated to 300 K twice before the measurement. It is seen that the third cycle invokes a large oscillation in the resistance (or voltage). The resistance switching appears strictly between the two peaks on the $R(T)$ curve and vanishes at both high ($T \geq T_{p1}$) and low ($T \leq T_{p2}$) temperatures. Further repetition of thermocycling does not change the $R(T)$ shape obtained after the third cycle (Fig. 4, curve 2). The measurements of the resistance at fixed temperature as a function of time did not manifest voltage oscillations of such giant amplitude. Moreover, the stopping in thermocycling and relaxation of the film during half an hour at 77 K or room temperature leads to disappearance of the resistance switching effect and the $R(T)$ behavior becomes similar to that after the first thermocycle (Fig. 4, curve 1).
Consequently, the observed oscillations of the resistance cannot be explained by telegraph noise or dynamic fluctuation of the resistivity [15,16].

Figure 4 (curve 2) shows that the resistance switching takes place between two limited high- and low-resistance states. The temperature dependence of the maximum resistance values in Fig. 4 (curve 3) can be described by expression of $R(T) = R_0 + \alpha T \exp(T_0/T)$ with the following fitting parameters: $R_0 = 2.6 \, \text{k}\Omega$, $\alpha = 0.11 \, \text{k}\Omega/\text{K}$ and $T_0 = 620 \, \text{K}$. Such thermally activated behavior of the conductivity is typical for the La$_{0.65}$Ca$_{0.35}$MnO$_3$ compound in the insulating state above the Curie point. The $R(T)$ curve enveloping the minimum resistance values in Fig. 4 (curve 4) displays metal-like behavior and can be described by $R(T) = R_0 + \beta T^2$ with the following fitting parameters: $R_0 = 1.4 \, \text{k}\Omega$, $\beta = 0.023 \, \text{k}\Omega/\text{K}^2$. Therefore, one can conclude that the nano-scale twinned La$_{0.65}$Ca$_{0.35}$MnO$_3$ film really consists of COI (high-resistance) and FM (low-resistance) regions with a different behavior of $R(T)$. The thermocycling, owing to the structural transformations in the ensemble of COI domains [17,18], results in nonequilibrium phase separation of the film and the appearance of resistance switching between the COI and FM states. The disappearance of the switching below $T_{p2}$ can be attributed to freezing of the COI domains, as indicated by Mori et al. [19].

In summary, we present evidence for the coexistence of FM and COI phases in a nano-scale twinned La$_{0.65}$Ca$_{0.35}$MnO$_3$ film, which has been confirmed by magnetic and transport measurements. Thermocycling leads to a giant switching in resistance, up to 100%, between the COI and FM states. This is explained by the structural perturbation of the COI domains.

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