Lithuanian Journal of Physics, Vol. **48**, No. 1, pp. 85–90 (2008) doi:10.3952/lithjphys.48111

MAGNETORESISTANCE AND CURRENT-INDUCED ELECTRORESISTANCE OF THE Ag / $La_{0.67}Ca_{0.33}MnO_3$ INTERFACE

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Received 10 December 2007; revised 20 February 2008; accepted 22 February 2008

Electrical properties of highly resistive Ag / $La_{0.67}Ca_{0.33}MnO_3$ interface were changed at 80 K by applying nanosecond electrical pulses to a couple of planar Ag electrodes magnetron sputtered onto $La_{0.67}Ca_{0.33}MnO_3$ thin films. The properties of the metal / manganite interface were investigated in a wide temperature range ($T = 80$–295 K) using various dc current values (1, 5, 10, 30, and 50 μA). We point out formation of highly resistive metastable states of the Ag / $La_{0.67}Ca_{0.33}MnO_3$ interface being sensitive to a weak current and demonstrating magnetoresistance and electroresistance phenomena, and also a presence of electrical memory effect. The investigations showed that combining properties of the interface and manganite film may have potential applications for creating new electronic devices.

Keywords: manganite thin films, magnetoresistance, electroresistance, metal/thin film interface, resistance switching

PACS: 73.63.Bd, 73.50.Fq, 75.47.Lx, 75.47.Gk

1. Introduction

Thin films of rare earth manganites have been intensively investigated during the last decade due to a number of interesting properties such as phase transition from high resistance paramagnetic (PM) to low resistance ferromagnetic (FM) state at the Curie temperature T_c (100–350 K), colossal magnetoresistance (CMR), and phase separation phenomena indicated in the vicinity of T_c. Characteristic resistivity peak temperature T_m of the films is just below T_c. Recently new additional effects such as electroresistance (ER) [1], formation of high resistive metastable states [2], resistance switching [3, 4], and resistance switching at a metal / manganite interface [5] have been reported for the manganite films. Recent progress in film preparation and nanotechnology development revealed new ideas for creating novel electronic devices. It was found that new effects are present in the films with embedded nanoparticles [6] and now the effects at the metal electrode / manganite film interface are considered equally important as effects in the film [7].

Electrical properties of oxygen-saturated thin films of $La_{0.67}Ca_{0.33}MnO_3$ / MgO with relatively high T_m values (up to 250 K) and Ag electrodes fabricated by magnetron sputtering have been investigated in [8]. These films demonstrated the ER effect in a wide temperature range (from 90 to 250 K), while no resistance switching to a highly resistive state has been indicated for the films by applying either dc current or short electrical pulses. It is important to note that certain resistance switching phenomenon has been only reported for the $La_{0.67}Ca_{0.33}MnO_3$ / MgO films with reduced oxygen content and lowered T_m values (of about 140 K) [3].

In this work we focus on Ag / $La_{0.67}Ca_{0.33}MnO_3$ interface resistance switching phenomenon. Thin films of $La_{0.67}Ca_{0.33}MnO_3$ saturated by oxygen have been fabricated for the investigations. Electrical properties of the Ag / $La_{0.67}Ca_{0.33}MnO_3$ (Ag / LCMO) interface were modified at low temperature ($T \approx 80$ K) by applying nanosecond electrical pulses.

2. Samples

The $La_{0.67}Ca_{0.33}MnO_3$ thin films were fabricated on cleaved (100) faces of MgO crystals by applying pulsed laser deposition technique. During film deposition, the substrates were held at $T = 650\,^{\circ}$C under a fixed oxygen pressure ($p_{O_2} \cong 25$ Pa). Just after the deposition, oxygen pressure in the vacuum chamber was increased up to 10^5 Pa and the films were cooled down to a room temperature during 3 hours.

ISSN 1648-8504

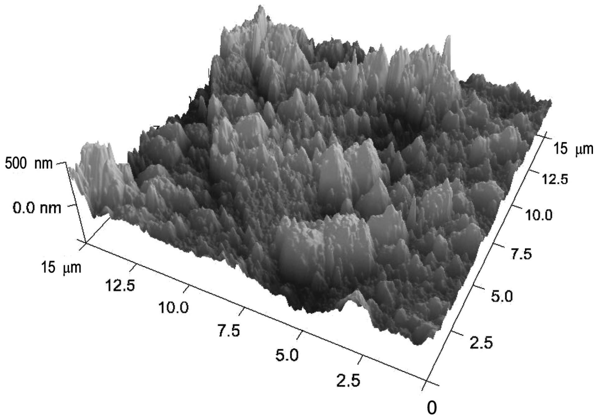

Fig. 1. AFM image of the $La_{0.67}Ca_{0.33}MnO_3$ / MgO film. Scale of z axis is different from that of x and y.

θ–2θ X-ray diffraction (XRD) scans measured for the films revealed single-phase material with preferential (100)-texture. Relatively wide reflexes of (100) type seen in the XRD spectra certified growth of the material with slightly misoriented grains. Typical AFM surface image of the film (d = 250–300 nm) is shown in Fig. 1. Significant surface roughness seen from the figure may be understood assuming relatively large mismatch (9%) of MgO and $La_{0.67}Ca_{0.33}MnO_3$ lattices and presence of terrace-like structures on cleaved MgO surface [3]. One can expect that significant surface roughness may facilitate formation of a highly resistive interfacial layer. The Ag coatings of 0.8–1.25 mm width (w) and 4 mm in length were magnetron sputtered onto the tape-like films to prepare a couple of planar electrodes. Distance d between the neighbouring Ag electrodes varied from 260 to 630 μm.

Ag electrodes with reduced dimensions (down to 0.2 mm) were prepared to investigate electrical properties of the Ag / manganite interface. The area of this electrode was ~90 times smaller compared to that of the other one. Highly resistive Ag / LCMO interface was formed at this small area electrode due to a local heating (up to 250–300 °C) by applied strong electrical pulse.

3. Experiment

3.1. Modification of highly resistive Ag / LCMO interface properties by short electrical pulses

Samples with highly resistive Ag / LCMO interface were placed into a break of a microstrip transmission line. Flexible transmission line with 50 Ω resistance was used for connection of the microstrip line to the experimental technique. Schematic diagram of the experimental technique used for the investigation of voltage–current characteristics in a nanosecond time scale was described earlier [3].

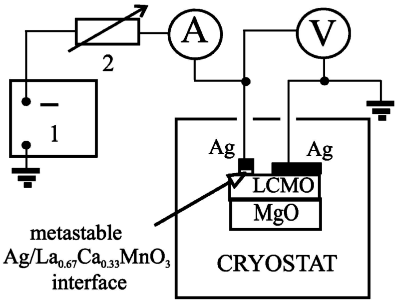

Fig. 2. Schematic diagram of the experimental set-up used for sample resistance measurements. *1* stabilized power source, *2* high-resistance potentiometer.

Nanosecond electrical pulse generator used in this work consisted of power source with charged line and high voltage mercury relay. Amplitude of short electrical pulses was tuned by the regulated power source and power attenuators. Sampling oscilloscope with inputs protected by thin film attenuators was used to measure electrical parameters of the samples in a nanosecond time scale.

The Ag / LCMO interface was modified by applying series of electrical pulses (repetition rate 100–150 Hz) at $T \approx 80$ K. Pulse duration τ was tuned from 10 to 300 ns by varying the length of a charged line. Pulsed electric current I through the sample in this case exceeded 40 mA.

3.2. Electrical properties of the modified Ag / LCMO interface

Schematic diagram of the experimental set-up used in this work for electrical measurements is shown in Fig. 2. Resistance versus temperature (R–T) plots measured for the sample (d = 260 μm, R(300 K) = 2.2 kΩ) in the initial state (*1*), after formation of highly resistive Ag / LCMO interface (*2*), and after a series of 100 ns pulses (*3*) are presented in Fig. 3. Curve *3* in the figure demonstrates metastable state of Ag / LCMO interface formed at $T = 80$ K by applying a series of nanosecond electrical pulses ($I \approx 40$ mA).

4. Main results

Figure 4 shows resistance versus temperature (at different dc values) of the sample with modified (metastable) Ag / LCMO interface measured just after sample heating up to a room temperature.

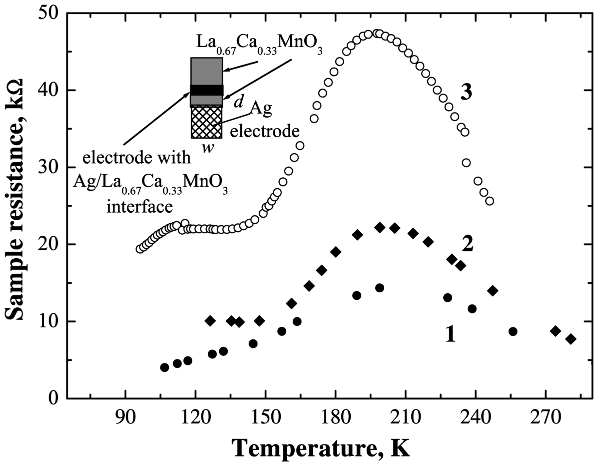

Fig. 3. R–T plots of the sample measured in the initial state (*1*), after formation of highly resistive $Ag/La_{0.67}Ca_{0.33}MnO_3$ interface (*2*), and in a metastable state of $Ag/La_{0.67}Ca_{0.33}MnO_3$ interface (*3*); $I = 1$ μA. The top view of the sample is shown.

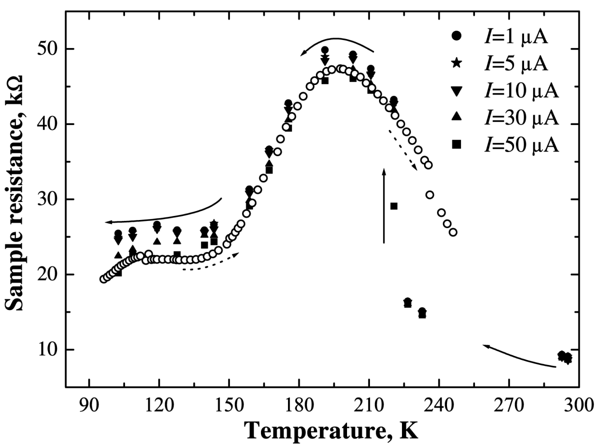

Fig. 4. R–T plots of the sample with $Ag/La_{0.67}Ca_{0.33}MnO_3$ interface modified by $I = 40$ mA. Open circles – after modification ($I = 1$ μA), filled marks – at different dc values. Arrows show course of temperature during the measurements.

The Ag / LCMO interface with higher resistance values was created at higher electric current values ($I \geq$ 45 mA). The corresponding R–T plots in a case of different dc values are plotted in Fig. 5 by open circles and filled marks.

Open circles in Fig. 6 demonstrate the R–T plots of the same sample obtained by applying series of negative electrical pulses ($I = 73$ mA, $\tau = 100$ ns). It can be seen from the figure that the applied negative electrical pulses (at $T \approx 80$ K) resulted in additional resistance increase rather than switching of the sample resistance from high resistance state to the initial low resistive state. Growth of the sample resistance in this case may be associated with growth of Ag / LCMO interface resistance rather than with film resistance increase. Certainly, our additional investi-

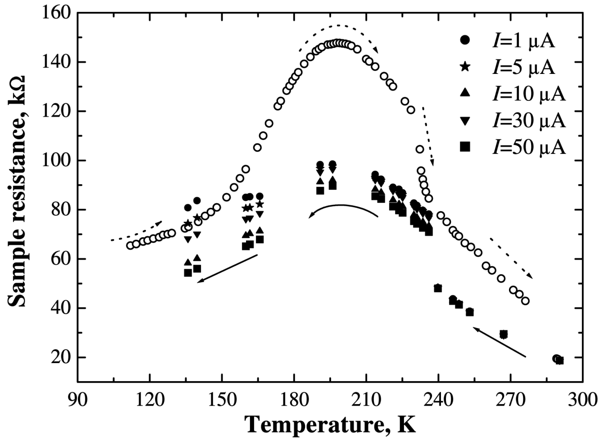

Fig. 5. R–T plots of the sample in a new metastable state of $Ag/La_{0.67}Ca_{0.33}MnO_3$ interface. Open circles – after modification ($I = 1$ μA), filled marks – at different dc values. Arrows show course of temperature during the measurements.

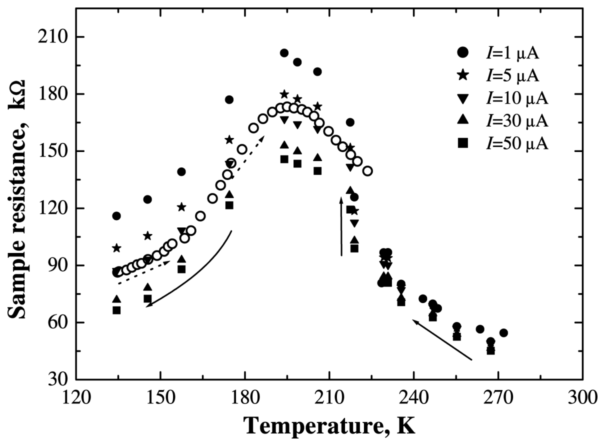

Fig. 6. R–T plots of the sample in a metastable state of $Ag/La_{0.67}Ca_{0.33}MnO_3$ interface after a series of negative pulses. Open circles – after modification ($I = 10$ μA), filled marks – at different dc values. Arrows show course of temperature during the measurements.

gations of $La_{0.67}Ca_{0.33}MnO_3$ film with large area low resistance Ag electrodes showed only negligible resistance change by applying electrical pulses ($I \approx 70$ mA) of different polarity. Typical R–T plots of the sample ($d = 265$ μm, R(300 K) $= 3.125$ kΩ) corresponding to various current and magnetic field values are presented in Fig. 7. Highly resistive metastable state of the interface was induced in the sample by passing positive current pulses ($I = 45$ mA). Open marks in Fig. 7 demonstrate the R–T plots of the sample at different dc values while filled marks show the R–T plots with applied magnetic field $B = 0.4$ T.

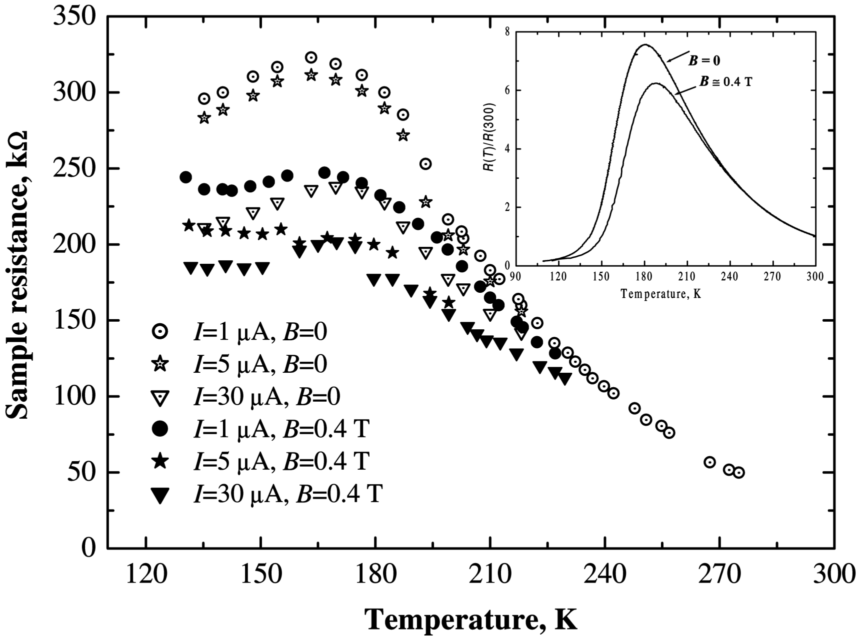

Fig. 7. Typical R–T plots of the Ag / $La_{0.67}Ca_{0.33}MnO_3$ interface in a metastable state corresponding to different current values; $B = 0$ and 0.4 T. Inset shows R–T plots of the $La_{0.67}Ca_{0.33}MnO_3$ film.

5. Discussion of the results

Resistance switching phenomenon observed by us earlier in ultrathin $La_{0.67}Ca_{0.33}MnO_3$ films [3] has been explained assuming presence of electrical nonhomogeneities in a bulk of the manganite film. We believe that relatively thick $La_{0.67}Ca_{0.33}MnO_3$ films ($d = 250$–300 nm) used in this work should be electrically more uniform. However, we suppose that electrical nonhomogeneities in this case may appear in the vicinity of a metal–manganite interface. So, we believe that the model we have used earlier to explain formation of highly resistive metastable states in a bulk of nonuniform thin $La_{0.67}Ca_{0.33}MnO_3$ films [3] could be suitable to explain formation of highly resistive metastable states of the Ag / LCMO interface. Certainly, electrical nonhomogeneity at the Ag / LCMO interface may occur due to a possible temperature gradient as well as temperature-dependent hopping or tunnelling of carriers in the interface region. Nonhomogeneities may also be caused by relatively rough film surface at the interface. We suppose that in a case of nonhomogeneities, local electric field values at the Ag / manganite interface may significantly exceed the averaged E value ($\sim$20 kV/cm). Mean electric field strength $E = V/d$, where V is voltage drop across the sample. Highly resistive Ag / LCMO interface could be formed due to a possible migration of oxygen atoms at the interface. Formation of metastable states of the Ag / LCMO interface may be understood assuming possible changes of Mn^{+4}/Mn^{+3} ratio and Mn–O–Mn bond geometry at the interface due to extraction of weakly bound oxygen ions from the manganite by strong electrical field [9].

The ER values (defined as $[R(I) - R(1\mu\text{A})]/R(1\mu\text{A}))$ corresponding to a gradual interface resistance decrease were calculated for dc current increasing from 1 to 50 μA. An increase of the ER values with temperature lowering can be seen either from Fig. 5 or 6. Contribution of ER effect induced by the film was eliminated in our calculations. Note that the observed increase of ER values with temperature decreasing at $T < T_m$ corresponds to a significant decrease of voltage drop at the interface. Certainly, stronger E should cause higher ER value. However, similar resistance changes observed earlier for the manganite films [10–12] have been associated with flowing dc current, i. e. the effect has been interpreted as current-induced ER effect.

The observed current-induced ER effect of the interface at $T < T_m$ may be explained assuming injection of spin-polarized curriers into a highly resistive Ag / $La_{0.67}Ca_{0.33}MnO_3$ interface region from low resistance FM regions. The role of injected spin-polarized carriers in such a case is to reduce effective thickness of highly resistive regions resulting in reduced resistance of the interface. Both the observed increase of ER values and the corresponding decrease of voltage drop at the interface with temperature decreasing at $T < T_m$ may be understood taking into account the increase of FM phase volume with cooling below T_m.

The absence of reversible resistance switching effect under applied negative electrical pulses (see Fig. 6) indicates that the observed resistance increase (either by positive or negative electrical pulses) is not related to Ag ion migration or possible carrier trapping at the Ag / LCMO interface.

The MR values (defined as $[R(H, I) - R(1\mu\text{A})]/R(1\mu\text{A}))$ corresponding to a metastable highly resistive interface were calculated for applied magnetic field of 0.4 T and dc current increasing from 1 to 30 μA (see Fig. 7). Contribution of ER and MR effects induced by the film was eliminated in our calculations. It can be seen from Fig. 7 that the maximal magnetoresistance values for the metal–manganite interface can be estimated at $T \approx 165$ K and the maximal magnetoresistance value for the film is at the same temperature. Therefore it is convenient to estimate the influence of magnetic field at the temperature $T = 165$ K. It is also worth noting the strengthening of the ER effect with current growth: -5.1% (5 μA) and -27.5% (30 μA). Only negligible variation of the R–T plots (at $B = 0.4$ T) has been indicated with current increase at the temperature $T \approx 165$ K. The MR values of -35.3% (0.4 T, 1 μA), -31.9% (0.4 T, 5 μA), and -12.9% (0.4 T, 30 μA) have been estimated for this sample. The resultant interface resistance decrease caused by the ER and MR effects can be estimated as -35.3, -37, and -40.4 percent for $I = 1$, 5, and 30 μA, respectively. These results, in our opinion, show magnetic origin of current-induced ER effect.

Significant resistance jumps seen in R–T plots at $T \sim 215$ K (see Figs. 4 and 6) and at $T \sim 240$ K (see Fig. 5) demonstrate presence of electrical memory effect of the Ag / LCMO interface. It can be seen from Fig. 5 that after heating to a room temperature and the following cooling down there was only a partial recovery ($T \sim 240$ K) of the initial highly resistive state of the Ag / LCMO interface, while it follows from Fig. 6 that a series of negative pulses resulted in almost full recovery ($T \sim 215$ K) of the initial highly resistive Ag / LCMO interface.

Though in our experiments we have not observed resistance switching at Ag / $La_{0.67}Ca_{0.33}MnO_3$ interface of the $La_{0.67}Ca_{0.33}MnO_3$ films, now it is clear that combining the film and Ag / LCMO interface properties gives interesting results that may have potential application.

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MAGNETOVARŽA IR SROVĖS SUKURTAS ELEKTROVARŽINIS REIŠKINYS Ag / $La_{0,67}Ca_{0,33}MnO_3$ KONTAKTO SRITYJE

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Santrauka

Didelės ominės varžos Ag / $La_{0,67}Ca_{0,33}MnO_3$ kontakto srities elektrinės savybės buvo keičiamos, pridedant galingus nanosekundinės trukmės elektrinius impulsus tarp poros plokštuminių elektrodų esant 80 K temperatūrai. Ag elektrodai buvo užgarinti magnetroninio garinimo būdu ant $La_{0,67}Ca_{0,33}MnO_3$ plono sluoksnio. Sidabro / manganito priekontakčių elektrinės savybės buvo nagrinėjamos leidžiant fiksuotos 1, 5, 10, 30 ir 50 μA vertės nuolatinę srovę plačiame temperatūros intervale (T = 80–295 K). Didelės ominės varžos metastabilios būsenos, kurios yra labai jautrios tekančiai silpnai srovei, buvo aptiktos Ag / $La_{0,67}Ca_{0,33}MnO_3$ kontakto srityje. Ag / $La_{0,67}Ca_{0,33}MnO_3$ priekontakčio varža mažėjo, didėjant nuolatinei srovei (srovės sukurtas elektrovaržinis reiškinys). Taip pat buvo stebimi magnetovarža ir elektrinės atminties reiškiniai, didinant ir mažinant priekontakčio temperatūrą. Ag / $La_{0,67}Ca_{0,33}MnO_3$ kontakto srityje suformuotų metastabilių būsenų tyrimas parodė, kad kontakto srities ir sluoksnio savybių integravimas potencialiai gali būti pritaikytas kuriant naujus elektronikos prietaisus.