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Memory Effect in Thin Thermocycling-modified $La_{0.67}Ca_{0.33}MnO_3$ Films

Fiodoras ANISIMOVAS, Steponas AŠMONTAS, Jonas GRADAUSKAS, Oleg KIPRIJANOVIČ [*], Bonifacas VENGALIS

Center for Physical Sciences and Technology, A. Goštauto 11, LT-01108 Vilnius, Lithuania

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Nonhomogeneous thin $La_{0.67}Ca_{0.33}MnO_3$ films, having T_m in 180 K – 200 K temperature range, were thermocycled between 80 K and 210 K using liquid nitrogen. After the thermocycling it was confirmed formation of highly resistive state with additional low temperature peak of resistance with maximum at 115 K when measuring *R-T* plots. Measurements of electroresistive effect in this state using low dc of different values and performed in cooling run reveal discontinuities of *R-T* plots. It is proposed formation of two different high resistive states: at low temperatures and at vicinity of T_m. The discontinuities disclose switching between these two states initiated by substrate-induced long-range strain and by manifestation of memory effect. This interpretation of experimental results explains appearing of low temperature peak based on influence of the long-range strains on formation of high resistive interlayers in the film during the thermocycling. We argue that the interlayers acquire memory properties after being modified by martensitic-type transformations.

Keywords: manganite thin films, thermocycling, highly resistive states, martensitic-type transformations, memory effect.

INTRODUCTION

In advanced technologies temperature changes are often significant in obtaining of nanostructural materials. It is known method of intensive plastic deformation of metals and alloys, led by temperature increase, which allows to change their structure on nanoscale and mesoscopic levels and accordingly to obtain novel unusual properties [1]. Method, in which metallic materials heated up to melt, followed by superfast cooling, allows obtain multilevel structured media, including nanostructures [2]. Repeating heating and cooling temperature cycles play an important role on multilevel structural changes in case of materials having phase transitions, for example having strongly correlated electron system. It may be noted temperature cycling of magnetic materials near Curie temperature T_C [3] and of manganite films in temperature range 77 K – 300 K, where the phase transitions are present [4, 5]. Efficiency of thermocycling procedure depends on existing of polycrystalline structure, when properties of grain boundaries, mainly coefficient of thermal expansion, are differ from those that grains have.

Structural transformations induced by cooperative movement of atoms are inherent to hole doped perovskite manganites [6]. The transformations caused by an internal stress in the films and by substrate-induced long-range strain are crucial for the manganite film property changes [7], even demonstrating memory effects [8]. Absence of atom diffusion in such martensitic-type transformations gives possibility to modify rapidly thin film properties. Materials modified by the transformations and demonstrating memory effects are also of interest for practical application, especially now.

$La_{0.67}Ca_{0.33}MnO_3$ manganite undergoes a phase transition from the paramagnetic (PM) to the ferromagnetic (FM) state during its cooling. The resistance on temperature dependence (*R-T* plot) has a peak at temperature T_m, close to Curie temperature T_C, pointing to this transition [5].

In paper [9] thermocycling procedure, using liquid nitrogen (LN-thermocycling), was performed for the nonhomogeneous $La_{0.67}Ca_{0.33}MnO_3$ thin films. Each cycle of the procedure consisted of quick cooling followed by slow heating during the evaporation of nitrogen. After 6 – 8 cycles between 80 K and 200 K highly resistive states (HR states) were formed in the film. In such case resistance peak was registered at lower temperatures along with resistance increase in the vicinity of T_m. The low temperature resistance peak (LT-peak) was very sensitive to applied low dc and magnetic field [9]. It is worth noting on papers [4, 10] where formation of states with LT-peaks was described and martensitic-type transformations are involved in formation of these peaks in our opinion.

The aim of this work is further experimental investigation of HR states' properties in thin nonhomogeneous $La_{0.67}Ca_{0.33}MnO_3$ films. The results of additional experiment for generation of two-peak HR states using LN-thermocycling are included. Attention is paid to explanation of experimental results indicating presence of memory effect and finally to give an interpretation of this effect.

EXPERIMENTAL

Thin $La_{0.67}Ca_{0.33}MnO_3$ films were prepared by pulsed laser deposition (PLD) technique on cleaved MgO substrate at 650 °C. Before the deposition the substrates were investigated using atomic force microscope. There were revealed terrace-like structures with a step height typically from 5 nm to 25 nm. The films were deposited under fixed oxygen pressure of 25 Pa using ceramic target.

[*]Corresponding author. Tel.: +370-5-2619759; fax: +370-5-2627123.
E-mail address: *kipriol@pfi.lt* (O. Kiprijanovič)

Oxygen pressure was increased up to 1 atmosphere after deposition. The last stage of film preparation was slow reduction (3 hs) of substrate temperature from 650 °C to room temperature.

The fabricated films of average thickness 300 nm – 400 nm had the resistance maximum T_m ranging from 180 K to 200 K which is lower than that of the bulk samples. This is due to 9 % mismatch of lattice constants of a pseudo cubic single phased $La_{0.67}Ca_{0.33}MnO_3$ and MgO (100) face. Due to this and to the substrate, relatively wide reflexes of (100) type are seen in the X-ray diffraction scans, measured for the films, certifying growth of the material with slightly missoriented grains.

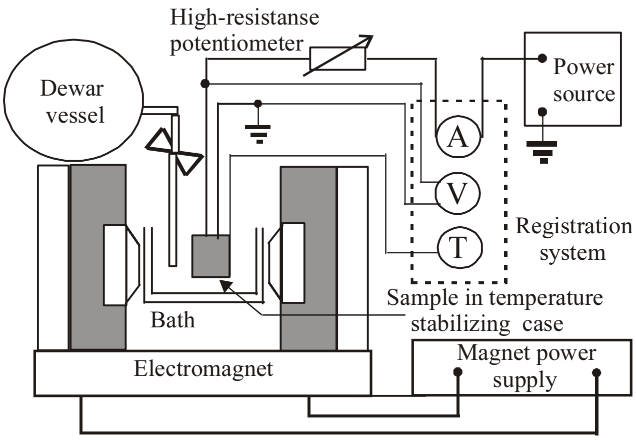

Fig. 1. Schematic diagram of the experimental set-up for HR state formation in $La_{0.67}Ca_{0.33}MnO_3$ films by LN-thermocycling and for investigation of their electrical properties

To prepare the samples Ag coatings of 0.8 mm – 1 mm in width and up to 3 mm in length were magnetron sputtered onto the films to form a couple of planar electrodes. Distance between them varied from 200 μm to 650 μm.

Schematic of experimental set-up for providing both a LN-thermocycling in bath and measurement of *R-T* plots using small dc is shown in Fig. 1. High voltage power source and high-resistance potentiometers connected in series with the sample are used to provide stabilized dc during huge resistance changes of the sample. The bath is placed between the poles of an electromagnet with possibility to perform measurements in magnetic field as it was done in [9]. *R-T* plots measurements are performed during slow temperature changes and data is collected by registration system. The sample was protected from direct contact with the liquid nitrogen by few layers of teflon ribbon, providing temperature stabilization, and was placed vertically. It can be also placed horizontally to regulate rapidity of cooling. Thermocycles (6 – 8 cycles in 80 K – 200 K range) were provided by relatively quick injection of the nitrogen from Dewar vessel (rapid cooling) and slower temperature growth during the nitrogen evaporation (slower heating). After this procedure generated HR states were detected using probe currents as small as 1 μA.

The sample has the gap of 600 μm, its resistance at 300 K is 7.66 kΩ in initial state and is 10.66 kΩ in HR state. In Fig. 2 are presented four *R-T* plots normalized to room temperature. Two of them are of initial states and another two are of HR states, which were generated by the thermocycling, measured in heating run. One pair of plots was presented in [9] and indicated by filled symbols and another has been obtained during the repeated experiment. The newly obtained plots also indicate on the appearance of the HR state with the LT-peak. As it is seen from Fig. 2 the peaks are at different temperatures for the different samples.

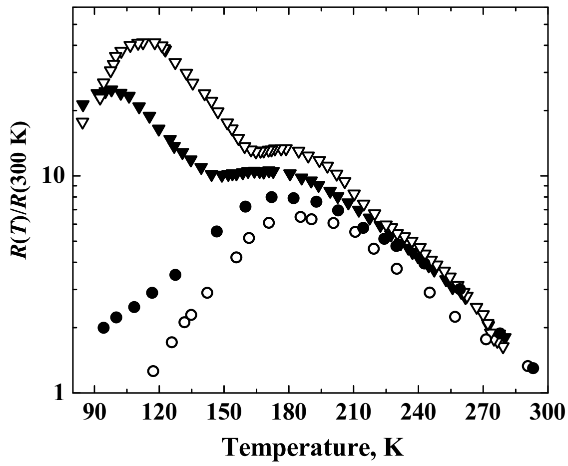

Fig. 2. Normalized to room temperature *R-T* plots of old and new $La_{0.67}Ca_{0.33}MnO_3$ samples (filled and open symbols, respectively). The circles indicate the initial states and the triangles indicate the HR states

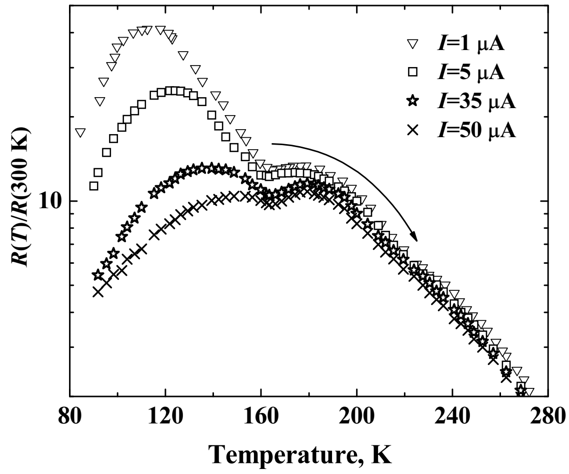

Fig. 3. Normalized to room temperature *R-T* plots of the $La_{0.67}Ca_{0.33}MnO_3$ sample in the HR state after the LN thermocycling. Measurements were done in warming run using dc of different values

The obtained in warming run using dc of different values *R-T* plots of HR state are presented in Fig. 3. It is obvious essential resistance drop of LT-peak under low flowing current (so called current-induced electroresistance). Fig. 4 shows the same experiment provided in cooling run.

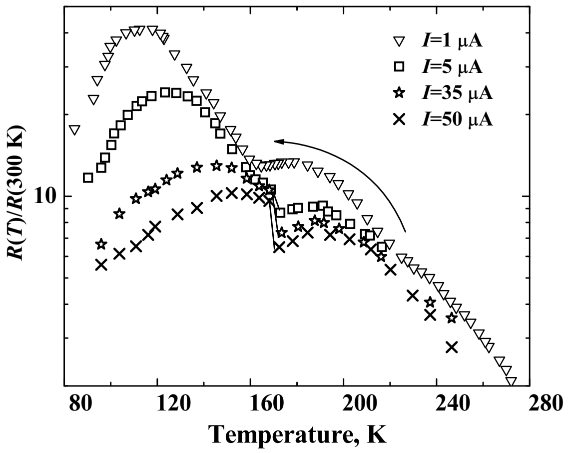

Fig. 4. Normalized R-T plots of the $La_{0.67}Ca_{0.33}MnO_3$ sample in the HR state after the LN thermocycling. Measurements were done in cooling run using dc of different values. Resistance jumps around 170 K indicate on switching to memorized LT peak

Discontinuities of the plots at 170 K are to be noted. This peculiarity we had detected previously in [9] for a sample, HR state of which is shown in Fig. 2 by filled symbols. However amplitudes of the jumps in the repeated experiment are smaller.

DISCUSSION

Results of the repeated experiment confirm formation of HR state, characterized by LT-peak, in the films. Differences in the HR state R-T plots after LN-thermocycling of the samples (see Fig. 2) we associate with a new cleaved substrate and with insufficient control of cooling rapidity during temperature cycles in both cases. Some grains and nonhomogeneities are present in the films fabricated by PLD due to the specifics of the technology.

Let us return to the interpretation of experimental results presented in [9] to remind main phases of HR state formation. Under the thermocycling the film temperature changes from 80 K to 200 K so that FM phase interchanges with condition in which FM and PM phases are separated. It was proposed that during the thermocycling encapsulation of FM regions by resistive boundaries occurs firstly (formation of polycrystalline-like structure). This means that the film at 80 K is no longer in homogeneous FM phase. Then, accommodation-like strain transforms FM regions to high resistive media by means of martensitic-type transformation. Such interpretation explains high resistivity of LT-peak, but now we came to conclusion that the explanation relied almost solely on martensitic- and even martensit-martensitic- type transformations in the film. Not enough attention was paid to consequences of long range strains induced by the substrate [6]. Another flaw was that phenomenon responsible for discontinuities in R-T plots was attributed to memory effect without any explanation.

Improving on that interpretation we revise the process of HR state formation in the film via LN-thermocycling. Existing film nonhomogenities are the first places to transit in PM phase during heating. Cooling phase of the thermocycling is rapid and does not facilitate homogeneous FM state formation. In the result of the thermocycling nonhomogenities enlarge on account of adjacent areas of distorted lattice and form interfacial layers (interlayers). At relatively slow heating recrystallization process lengthens the interlayers, which also change direction of growth. In the result of the thermocycling FM regions become framed by highly resistive interlayers. Charge localization in the interlayers and therefore resistance strongly depend on Mn-O-Mn bonds angle and Mn-O length, which are altered by internal strain as it was considered in [9].

So indeed a certain polycrystalline-like structure did form. In the current model however the FM regions framed by interfacial layers do not disappear after LN-thermocycling at lower temperatures. The lack of percolation transition between FM regions determines high resistivity of LT-peak.

Let us regard substrate influence on the film in described process. The long-range strains induced by substrate act as external strain on the film because both the film and the substrate are affected by temperature changes. High resolution experiments using X-ray absorption and diffraction techniques confirmed about importance of strain-induced distorted lattice on structural changes and ferromagnetism in manganites [11]. Appearance of strains and tensions during the changes induces martensitic-type transformations, imparting interfacial layers with unique transformational properties such as mutual switching of mesoscopic objects and different phenomena related to structural memory [12]. Therefore due to occurrence of martensitic-type transformations highly resistive interlayers can demonstrate properties of memory.

Results of strong ER effect at LT-peak here (see Fig. 3 and in [9]) and of magnetoresistance [9] show that at lower temperatures we have non-linear conduction that arises in the multistructured films due to presence of a large number of interfacial layers. They act as Schottky barriers or tunneling junctions, so called intrinsic tunneling [13], and can strongly reduce the film resistance under locally applied voltage.

During warming run to the phase separated region the number of FM inclusions significantly decreases. But interlayers induced through the LN-thermocycling increase the film resistance also causing dispersion of T_C in the sample. We adhere to the position of a current flow in network of filaments in media with metallic and insulating clusters. Filaments contain many FM and PM parts. Under applied electric field junctions between them most probably serve as tunnel junctions. Increasing the field increases conductivity of the junctions in turn, demonstrating ER effect, but now it is much less in value than of LT-peak (see Fig. 3). So, in the vicinity of T_m it is formed HR state, higher resistivity of which is defined by changes at low temperature.

Fig. 4 presented R-T plots of slow cooling (after warming) demonstrating sharp jumps to higher resistance values. These measurements disclose the temperature at which resistive state with LT-peak is restored. We conclude that HR state consists of two states. These states, having different properties, are formed at T_m and at low temperatures.

The resistance jumps in R-T plots can be observed during temperature runs if during manifestation of phase separation volume of one of the phases abruptly increases or decreases [14]. In our case this event does not take place as it is seen from the discussion. Most probably in our case the jumps indicate transition between two states induced by long-range strain during temperature decrease. After the transition LT-peak is restored. Research using high resolution technique, including small-angle X-ray and neutron diffraction [15], should be done to investigate LT-peak internal structure and properties to make more valid conclusions on the switching between the states.

CONCLUSIONS

During repeated experiments on LN-thermocycling of thin nonhomogeneous $La_{0.67}Ca_{0.33}MnO_3$ films it was confirmed both HR state formation and appearing of high resistive LT-peak.

Improved interpretation of the experimental results includes:

a) that long-range strain induced by substrate strongly influences on formation of the state with LT-peak during LN-thermocycling;

b) interlayers induced through the LN-thermocycling increase the film resistance in the vicinity of T_m creating HR state with the properties, which differ from HR state with LT-peak;

c) created interlayers are imparted with memory properties by means of martensitic type transformations, which appear due to influence of strains, including the long-range ones, and of tensions appearing in nonhomogeneous film during LN-thermocycling.

LT-peak is restored due to memory effect after the transition between two states, which occurs during slow temperature decrease and is initiated by the long-range strain.

Obtained results could be useful for further investigation of imparting memory properties to manganite thin films fabricated by different technologies.

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