Modification of Electrical Properties of Thin $La_{0.67}Ca_{0.33}MnO_3$ Films by Pulsed Thermocycling

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Highly resistive states were formed in nonhomogeneous thin $La_{0.67}Ca_{0.33}MnO_3$ films at 80 K temperature after resistance switching induced by the pulsed thermocycling. Heating up to room temperature does not destroy the resistive states. They demonstrate high values of electroresistance at applied pulsed electric field. It was registered formation of novel highly resistive state by resistance switching at 130 K in T_m region. We suppose that local temperature increase in the film is responsible for the formation of the resistive states in both cases and present a plausible explanation of the obtained results. The method of cyclic nanosecond temperature increase and decrease can be useful for modification of material properties having strongly correlated electron system and of ferroelectrics. Questions of practical realization of proposed method are discussed.

Keywords: manganite thin films, high pulsed electric fields, pulsed thermocycling, resistance switching, highly resistive states.

INTRODUCTION

Significant place amongst novel materials belongs to materials with properties modified at nanostructural and mesoscopic levels by fast intensive energy influence. That influence could be realized by power laser illumination [1], high voltage electric pulses [2] and shock waves [3].

Materials with strong correlated electron system such as perovskite compounds based on transition metal oxides – including high-temperature superconductors and doped manganese oxides – are intensively studied objects in contemporary physics. $La_{0.67}Ca_{0.33}MnO_3$ manganite undergoes a phase transition from the paramagnetic (PM) to the ferromagnetic (FM) state during its cooling and has a resistance peak at the specific temperature T_m which is close to Curie temperature T_C. This manganite is intensively studied due to colossal magnetoresistance (CMR), that is, huge resistance drop induced by the applied magnetic field [4, 5]. CMR effect manifests itself in the vicinity of T_m where the phases are separated.

Investigation of manganites and manganite thin films revealed a resistance decrease induced by an electric field or a direct current. This effect was called electroresistance (ER). The drop of resistance was observed in highly resistive (HR) states: charge ordered [6], structurally distorted due to oxygen deficiency [7] and caused by strains due to lattice mismatch [8]. Further investigations show that structural distortion of lattice or/and mesoscopic structural nonhomogeneities should be present in manganite samples for ER effect to manifest itself. In contrast to CMR manifestation ER effect could lead to irreversible resistance changes or even to transitions between states of different resistance – resistance switching [9, 10]. In the thin films fabricated by PLD some nonhomogeneities are present due to the specifics of the technology [11]. Defects and local strains appearing within the PLD grown films serve as nucleation points for further expansion of the deformed structures.

Investigations of the nonhomogeneous $La_{0.67}Ca_{0.33}MnO_3$ thin films grown by PLD on cleaved MgO substrates have shown that high voltage nanosecond pulses applied to the films at 80 K temperature can irreversibly change the film resistance, causing appearance of HR states (comparing with initial state) [2]. The effect of local film heating induced by the series of the pulses which create high electric field strength was interpreted as a pulsed thermocycling.

During fast nanosecond heating diffusionless martensitic-type transformations are possible, as well as formation of inclusions having boundaries and changed lattice parameters [3]. Fast cooling to ambient temperature also plays an important role in retaining of structural nonhomogeneities in thin films. Experimental results representing resistance switching, induced by pulsed thermocycling are presented in [12]. It was found that the duration of pulse in the series and temperatures runs during measurements plays an significant role on the results. On the other hand, it is clear that the questions important for practical application are stability of HR states at relatively low fields and formation of HR states with predictable properties.

In this work we concentrate on investigation of ER effect in $La_{0.67}Ca_{0.33}MnO_3$/MgO using the series of relatively low voltage pulses after HR states formation. A plausible explanation of the obtained results is presented. We suppose that besides $La_{0.67}Ca_{0.33}MnO_3$ the method could be useful for changing properties of manganites of other doping levels of divalent ions and ferroelectric materials.

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EXPERIMENTAL

Thin $La_{0.67}Ca_{0.33}MnO_3$ films were prepared by pulsed laser deposition technique. The films with average thickness 0.1 μm – 0.2 μm were deposited on cleaved MgO substrates under the oxygen pressure 20 Pa – 25 Pa using a ceramic target. The substrate temperature during the deposition was 750 °C. The oxygen pressure was increased up to 1 atmosphere after deposition. The last stage of film preparation was slow reduction (3 hrs) of substrate temperature from 750 °C to the room temperature.

The fabricated films had the resistance maximum T_m ranging from 135 K to 150 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. The surface of the cleaved substrates was investigated by atomic force microscopy [2]. Terrace-like structures with a step height typically from 5 nm to 25 nm were revealed. But nonhomogeneities formed in the films during PLD on the substrates only slightly widened reflexes of (100) type seen in the X-ray diffraction scans measured for the films.

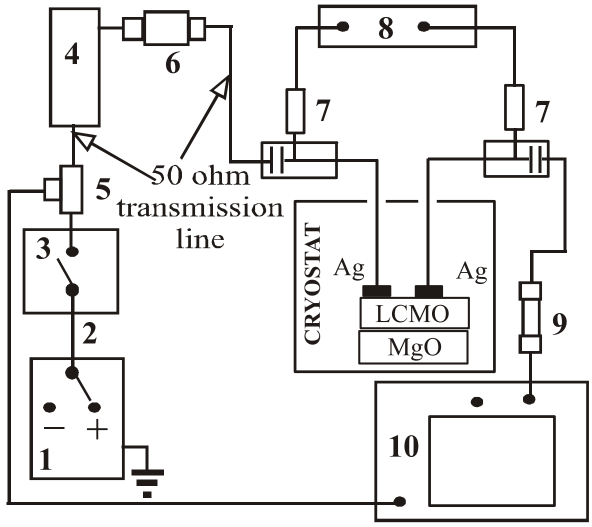

Fig. 1. Schematic diagram of the experimental set-up used for HR state formation in $La_{0.67}Ca_{0.33}MnO_3$ films and for investigation of their electrical properties. 1 – high voltage power source, 2 – pulse forming line, 3 – relay pulse generator, 4 – delay line, 5 – synchronization tee, 6 – power attenuator, 7 – dc tee, 8 – dc measurement system, 9 – attenuator, 10 – memorized sampling oscilloscope

For the investigation, we used $La_{0.67}Ca_{0.33}MnO_3$ planar samples 0.5 mm – 0.75 mm in width with the gap d between the Ag electrodes ranging from 10 μm to 50 μm. The samples were mounted in the break of a microstrip transmission line and were placed in cryostat or Dewar vessel. The schematic diagram of the experimental set-up is shown in Fig. 1. High voltage power source (1) is used to charge pulse forming line (2). Mercury relay is used as switch to generate fast rising pulses launched by series. Pulse duration in the series depends on the forming line length. Through the delay line (5) and power attenuator (6) pulses are transmitted to cryostat (Dewar vessel) where the sample is placed. From the cryostat the pulses are feed to memorized oscilloscope (10) attenuated by attenuator (9) which also protect the input of the sampling oscilloscope from high voltage pulse action. The set-up also allows to measure sample resistance using conventional ohmmeter with high input resistance (8).

Using this technique the pulsed thermocycling was performed at 80 K temperature using series of 1500 – 2000 electrical pulses of 20 ns in duration and of 100 Hz repetition rate. Voltage of the pulses is chosen to create electric field strength above 20 kV/cm through the sample. The technique allows changing pulse length up to 500 ns, repetition rate from 50 Hz to 200 Hz and length of the series.

The technique used for measurement of the *I–V* dependences using nanosecond duration pulses was outlined earlier [2]. For measuring the *I–V* dependences, and therefore sample resistance at ns time scale, additional measurements of falling pulse amplitude must be made. The extended variant including relaxation phenomena measurements, e. g., after applied pulsed electric field, is introducing in [13]. Estimation of the measurement error also presented in [13] and is about 7 % at high fields above 50 kV/cm.

EXPERIMENTAL RESULTS

A sample with the gap d of 30 μm and an average thickness of 100 nm has resistance R_{300} of 1.1 kΩ at room temperature in the initial state (see Fig. 2). After the pulsed thermocycling at 80 K with applied electric field of 25 kV/cm (the average electric field is found by $E = V/d$, where V is the applied voltage) HR state was formed by resistance switching as indicated by an arrow. The series pulse duration was 20 ns. After the procedure the sample was heated up to the room temperature. The dependences of the resistance of the sample on temperature (*R–T* plots) during investigation of ER effect are presented in Fig. 2. ER effect in the HR state was investigated in cooling run using pulse series with 100 ns pulse duration. During the run the field strength was gradually increased up to 12 kV/cm. No irreversible resistance changes were observed up to these field values.

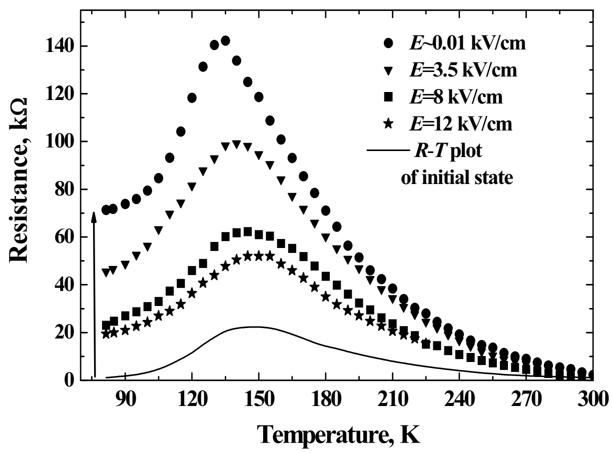

Fig. 2. *R–T* plots of the $La_{0.67}Ca_{0.33}MnO_3$ sample. ER effect at applied electric field of different strengths in HR state. Formation of HR state from initial state (line) is indicated by an arrow

Value of ER effect is determined as $ER(E) = [R(E) - R(0)] / R(0)$ at fixed temperatures. It is followed from Fig. 2 at 130 K ER (3.5) = –33.8 %, ER (8) = –60.1 %, ER (12) = –68.7 %.

Sample with the gap d of 10 μm and an average thickness of 150 nm have R_{300} of 0.81 kΩ in initial state (see Fig. 3). HR state was formed by the pulsed thermocycling at 80 K after electric field strength reach 22 kV/cm and is denoted by open symbols in Fig. 3. The investigation of ER effect in this HR state by the pulses of 100 ns shows results similar to that presented in Fig. 2. The obtained plots are not shown. ER effect values of the HR state at 120 K and 140 K are ER(1.5) = –24 %, –20 %; ER(4) = –41.6 %, –38.2 %; ER(8) = –54.2 %, –51.7 % correspondingly. During measurements at the field strength of 12.5 kV/cm at 130 K (ER(12.5) = –61.4 %) we detected switching to higher resistance (indicated by an arrow), and formation of novel HR state at phase separated region was registered during heating up to room temperature.

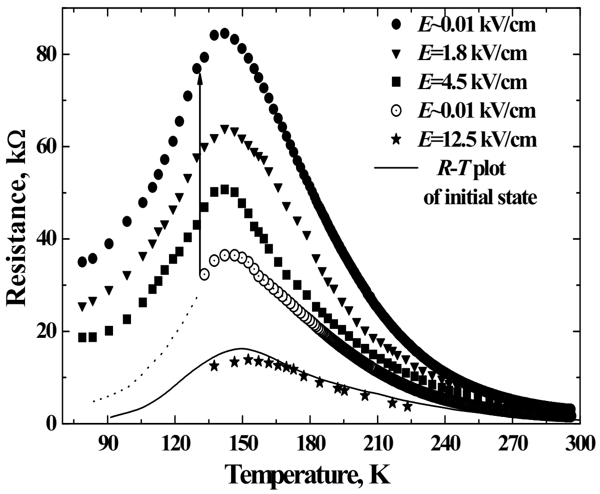

Fig. 3. R–T plots of the $La_{0.67}Ca_{0.33}MnO_3$ sample in novel HR state. ER effect at applied electric field of different strengths. Open symbols is primary HR state. Formation of novel HR state is indicated by an arrow. Line is the plot of initial state

Investigation of ER effect was provided by the pulses of 100 ns duration using similar series. This novel HR state also demonstrates high ER values and up to fields 4.5 kV/cm does not exhibit resistance switching.

DISCUSSION

Fabrication of the nonhomogeneous thin film begins with deposition on substrate having terrace-like structures. This increases nonhomogeneity of our films on the nanoscale level during the fabrication. During the post-deposition annealing the number of strained areas and structural defects is increasing. Supposedly, this may cause a shift of the film's T_m to lower temperatures with respect to the bulk material. But the measured film's X-ray diffraction scans reveal only small widening of (100) type reflexes.

At the ambient 80 K temperature the film is in the conducting FM state. Existing strained areas and nonhomogeneities formed during PLD allow us to exploit a concept of current flow in network of filaments. Filament paths include local places of higher resistance, like the thinner strained places between the grains, the defects at conducting FM channels and the boundaries between FM regions.

During the series action local voltage drop on these nonhomogeneities can be much higher than the average one. They undergo local heating during the application of pulses. Such local heating of thin film processed by dc was already described in [14]. Extending these results, we assume that in our case at strong fields thermal breakdown of the FM state occurs in the vicinity of the locally heated places when the local temperature exceeds the T_m values.

Accordingly, each pulse of the thermocycling procedure forms local large temperature gradients around heated points. Strains and structural lattice changes appear within the sample simultaneously with local FM-PM transition. Rapid cooling after the pulse action to ambient liquid nitrogen temperature does not assist in complete restoration of the FM state. Thus, the pulsed thermocycling creates inclusions of nonhomogenous media rich with interfacial layers (boundaries between phases with adjacent areas having a distorted lattice) causing irreversible resistance increase – resistance switching. High resistivity remains during heating up to room temperature, indicating on HR state formation.

Investigation of thin manganite films using single high voltage pulses until their irreversible damage is presented in [15]. This paper shows that at first entire the sample is fast heated to higher temperatures. Then irreversible damage of the films occurs, leaving traces of local damage. Also it was established that due to locality of heating the film is damaged in times of 10 ns order. Thus this experiment partly confirms the proposed mechanism of HR state formation at 80 K.

Measurements of ER effect are performed in cooling run. They show that HR states do not erase by heating to room temperature. As we can see from Fig. 2 gradual increase of pulse voltage induces growing resistance decrease during the pulse action. At phase separated region we adhere to the position of a current flow in network of filaments in media with metallic and insulating clusters. Theory of such conduction in "lattice disordered" thin films and crystals with content x = 1/3 at low electric fields are developed in [16]. The resistive peak broadening is also representative for our HR states. 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.

At 80 K the interfaces in the inclusions are formed as FM metallic-non-metallic junctions and very thin nonmetallic (oxygen depleted) interfaces between FM regions. They also act as Schottky barriers or tunneling junctions – the so called intrinsic tunneling [17] – and can reduce the film resistance under an applied voltage. But the spintronic aspect of the ER effect is also very attractive. It works as follows: at low temperatures when the polarized current from the FM regions is pumped into neighboring nonmetallic region and keeping its polarization. Thus, the non-metallic region is polarized at certain depth, leading to increasing of FM region and therefore resistance decrease.

At higher temperatures, in the vicinity of T_m, the double exchange mechanism could be used to explain ER effect. There is strong interaction between carrier spins of Mn^{+3} and localized spins. The carriers' spins are forced to become parallel to localized spins on the same site due to a strong Hund's rule coupling. The hopping rate of carriers gets higher if the localized spins on the nearest neighbors are parallel. Under applied electric field the carriers are forced to move irrespectively of their spin being parallel or not to localized spins. However the spin-exchange coupling will force the localized spins to be parallel. Alignment of localized spins would reduce the spin scattering of carriers. Therefore the hopping rate of the carriers increases with increasing of magnetic coupling among Mn ions, and as consequence, the resistance will decrease. Such films demonstrating ER effect could be used for example in high voltage pulse limiters or protectors against electromagnetic pulse action at different temperatures [18].

In the end let us consider resistance switching in the phase-separated region. In our case this transition shown in Fig. 3 by an arrow. Beginning stage of explanation of the switching near T_m was presented in [12]. Extending these results we suppose that when the fields reach 10 kV/cm local heating of PM parts becomes apparent. Resistance switching is possibly realized due to abrupt appearing of strains that increase volume of PM phase. Our experiment partly confirms results of paper [19] where it is stated that resistance switching is not dominated by a detailed electronic structure of each sample, but is of a more general origin, which are the processes at crystalline defects initiated by electric field.

However, detailed investigations of the film microstructure before and after switching similar to [20, 21] should be done for strict explanations of observed results.

Finally some remarks on possible practical applications of this method. Serial manufacturing of nonhomogeneous films cannot rely on cleaved substrates. Patterned substrates with profile heights of several nm should be used instead. On the other hand, films having artificial nonhomogeneities can be created using methods of nanotechnology. Application of the pulsed thermocycling technique to such films improves stability of resistance switching and ability to obtain desired properties.

It is possible to apply pulsed thermocycling to manganite thin films fabricated by other methods, for instance, synthesized using sol-gel method. Such films sintered at different temperatures and, as a result they are structured and have nanograins ranged in size depending on sintering temperature [22]. They therefore have a network of grain boundaries, which can serve as locally heated places and the series of high voltage pulses could also be used to change properties of the nanophasic manganite thin films. Another application possibility follows from work [6] when applied over voltage to manganite in HR insulating state induces collapse of the HR state thus causing an insulator-to-metal transition. Therefore the series of high voltage pulses could be used to change properties of phase separated manganites with another concentration of divalent alkaline earth ions (x = 0.2, x = 0.5) or even of ferroelectric crystals and films.

Modified in such ways manganites and ferroelectrics could be used for creating of devices demonstrating stable reproducible resistance switching.

CONCLUSIONS

1. Resistance switching in nonhomogeneous $La_{0.67}Ca_{0.33}MnO_3$ thin films was induced at 80 K when high voltage nanosecond pulse series created electric field through the samples above 20 kV/cm.

2. After the switching the film was heated up to room temperature and measurements show appearance of HR state in this temperature range. The HR state is not erased at 300 K.

3. The films in HR state demonstrate high values of ER effect under applied pulsed electric field lower than 20 kV/cm both at low temperatures (~ –50 % at 8 kV/cm) and in the vicinity of T_m (~ –70 % at 12 kV/cm).

4. It was registered resistance switching of HR state occurring at T_m region (130 K) with formation of novel HR state of higher resistance.

5. We propose that the local film heating caused by pulse due to existing nonhomogeneities is responsible for resistance switching both at 80 K and at 130 K.

6. We suppose that the pulse, which creates the local heating in our films, could also create local over voltage in manganite films with other x contents and in ferroelectric samples and thus could be used to change their properties.

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