Electroresistance of La–Ca–MnO Thin Films

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Epitaxial, textured, and polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ films, having about 150 nm thickness, were prepared by pulsed laser deposition techniques onto (110) $NdGaO_3$, MgO and lucalox substrates and investigated using 10 ns duration, 0.5 ns rise time electrical pulses having amplitude up to 500 V. Electroresistance of the films $[R(E)-R(0)]/R(0)$ was investigated up to 80 kV/cm electric field strengths in temperatures ranging from 300 K to 4.2 K. Strong (up to 93%) negative electroresistance was obtained in polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ films prepared on MgO and lucalox substrates. The epitaxial films grown on $NdGaO_3$ substrate demonstrated only a small resistance change due to Joule heating induced by a current pulse. It was concluded that electroresistance manifests itself in strongly inhomogeneous manganites films exhibiting a large number of structural imperfections producing ferromagnetic tunnel junction nets.

PACS numbers: 73.50.Gr, 73.50.Lw, 73.63.Bd

1. Introduction

It has been observed that manganites exhibiting colossal magnetoresistance (CMR) phenomenon are also sensitive to electric fields that induce strong decreases in the electrical resistance of these materials. This effect was named electroresistance (ER) and was studied in $Pr_{0.7}Ca_{0.3}MnO_3$ [1–3], $Nd_{0.7}Sr_{0.3}MnO_3$ [4], and $La_{1-x}Ca_xMnO_3$ system. The ER was detected in bulk polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ [5], single crystals of $La_{0.82}Ca_{0.18}MnO_3$ [6], and epitaxial

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La$_{0.7}$Ca$_{0.3}$MnO$_3$ films [7]. The effect of short pulsed electric fields on the resistance of thin La$_{0.67}$Ca$_{0.33}$MnO$_3$ films was investigated in [8, 9]. As a result, a fast fault current limiter with subnanosecond time turn on time was suggested [10, 11]. However, the reasons for the origin of ER are still unclear, thus making difficult the further development of this device and wider application of the ER phenomenon for other field effect devices. Moreover, it seems that the nature of ER is different in bulk ceramics, single crystals, and thin films of manganites. According to [5], the strong decrease in resistance that occurs with the increase of electric field is due to the Frenkel–Poole effect in the interfacial regions of the manganite ceramic. The ER in single crystal samples was explained as electric field induced CMR [6] which takes place in narrow channels of the crystal because of current percolation in medium consisting of two phases with different electronic densities. The explanation of ER in epitaxial films was also based on a two-phase system containing high conductivity ferromagnetic regions (FM) and low conductivity charge ordering (CO) regions [7]. However, in this case, it was suggested that the electric field modifies the volume fractions of the FM and CO components. It has to be noted that the effect of experimental conditions, i.e. dc or pulsed current at which ER appears, was not taken into consideration.

In this paper, we report on an experimental study of short electrical pulse induced ER in La$_{0.67}$Ca$_{0.33}$MnO$_3$ films containing different imperfection densities and demonstrating that the very large (up to 93%) ER effect is caused by effects of strong electric fields on the resistance of these imperfections.

2. Sample preparation

The films were grown onto (110) NdGaO$_3$ (NGO), MgO (MGO), and lucalox substrates by on-axis pulsed laser deposition using La$_{0.67}$Ca$_{0.33}$MnO$_3$ target synthesized by a solid state reaction technique. A Nd^{3+}:YAG laser, operated in a doubled frequency mode ($\lambda = 532$ nm), was used for this deposition. Laser pulse energy was chosen to be 50 mJ. During the deposition, the temperature of the substrate was kept at 750°C. The growth was followed by annealing in 1 atm. pressure oxygen at 750°C for 30 min. After this, the film was cooled down to room temperature for 3 hours. The thickness of the La$_{0.67}$Ca$_{0.33}$MnO$_3$ films was about 140 nm. NdGaO$_3$ and MgO substrates were single crystals with orthorhombic and cubic unit cell structures, respectively. The difference between the plane lattice constants of the NdGaO$_3$ and MgO substrates and the bulk La$_{0.67}$Ca$_{0.33}$MnO$_3$ were 1% and 9%, respectively. Lucalox substrate was a polycrystalline structure.

The samples, having a length of 5 mm, were designed in a co-planar shape with the width ranging from 1.5 mm to 3 mm. Four Ag tapes having 1 mm width and spaced by 50 μm gap were deposited onto the film by thermal evaporation at 200°C. After this, the films were annealed for 1 hour at 1 atm. pressure in argon gas at 400°C. The resistance of the samples for low value dc currents was measured

by a standard four-probe method. In order to investigate the ER of the samples exposed to strong pulsed electric fields, the samples were connected in series to a 50 Ω impedance high frequency (18 GHz) transmission line and pulsed by 5–10 ns duration, 0.5 ns rise time rectangular shape electrical pulses [9]. The amplitude of these pulses was changed from 10 V to 500 V. Measurements of dc resistivity and ER were performed at temperatures ranging from 4.2 K to 300 K, using a closed cycle helium gas cryocooler.

3. Results

3.1. DC resistivity measurements

Figure 1 shows a typical electrical resistivity (ρ) vs. temperature (T) dependence for $La_{0.67}Ca_{0.33}MnO_3$ films prepared on different substrates. Films deposited on NGO substrate was investigated using a 0.86 mA excitation current. In the case of films deposited on MGO and lucalox substrates, this current was 0.1 mA. It is evident that $\rho = f(T)$ for all the investigated films exhibits a maximum at a certain critical temperatures T_m. For films grown on NGO, MGO, and lucalox
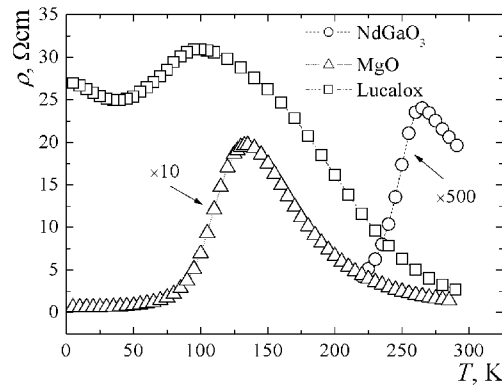

Fig. 1. Resistivity vs. temperature dependence for $La_{0.67}Ca_{0.33}MnO_3$ films prepared on different substrates.

substrates, this temperature is 265 K, 135 K, and 100 K, respectively. At temperatures below T_m, the resistivity of the films deposited on NGO and MGO substrates decreases with temperature, while for films prepared on lucalox substrate, the $\rho = f(T)$ dependence has a minimum at $T = 35$ K. At this temperature, the metallic-like resistivity behavior changes to a semiconductor state. Figure 1 also demonstrates that an increase in T_m is always accompanied with a significant decrease in the resistivity of the film. The largest resistivity ($\rho_{max} = 30.9 \ \Omega$ cm) corresponds to the lowest $T_m = 100$ K obtained for films prepared on lucalox substrate. In the case of MGO and NGO, the ρ_{max} was 1.97 Ω cm and 50 mΩ cm, respectively.

3.2. Electroresistance induced by pulsed electric field

The ER using short electric pulses was investigated at temperatures ranging from 4.2 K to 300 K. We defined the value of the electroresistance (ER) as follows:

$$ER = \frac{R(E) - R(0)}{R(0)} \times 100\%, \tag{1}$$

where $R(E)$ is the resistance of the sample effected by pulsed strong electric fields and $R(0)$ is the resistance of the sample effected by pulsed electric fields, the value of which does not exceed 0.5 kV/cm. It was found that $R(0)$ is the same as that measured using dc current.

Figure 2 depicts the ER effect in $La_{0.67}Ca_{0.33}MnO_3$ films deposited on NGO substrate. The resistance change was measured 2 ns after the start of the pulse. As can be seen below, if the temperature is approximately equal to 260 K, the ER is positive if electric field strength does not exceed 25 kV/cm, however at higher temperatures it is very small (less than 10%) and negative. The positive ER vs. E dependence increase is higher at low temperatures and becomes less abrupt at temperatures close to T_m. At these temperatures, this dependence exhibits a maximum at electric field strengths of 20 kV/cm.
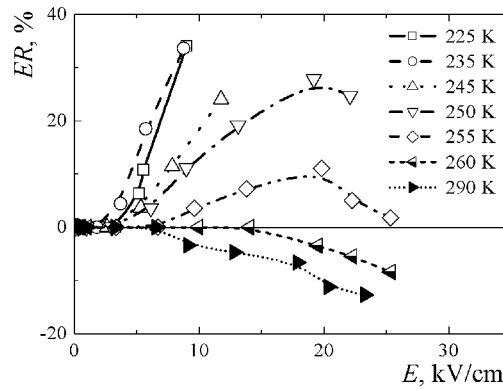

Fig. 2.   Electroresistance vs. electric field strength dependence for $La_{0.67}Ca_{0.33}MnO_3$ films deposited on $NdGaO_3$ substrate.

The ER vs. electric field strength behavior of films grown on MGO substrates strongly differs from that obtained for films on NGO substrate. The highest negative ER was obtained at temperatures around T_m. Decrease or increase in temperature from T_m has a smaller effect on the ER. A typical ER vs. E dependence of negative ER effects slightly below T_m demonstrates the decrease in ER with an increase in E. This increase at high electric field strength tends to saturate. The saturation becomes more noticeable at lower temperatures and at critical fields at which the saturation starts to decrease as the temperature decreases. Starting from temperatures at around 80 K, the ER vs. E dependence

exhibits a minimum. In this case, the ER value increases only up to a certain critical electric field; for higher fields the ER value decreases with an increase in E. This increase becomes so strong at 60 K that the ER changes its sign from negative to positive (see Fig. 3a). The increase in temperature above T_m also makes the ER vs. E dependence less abrupt. However, in this case, the saturation of the ER vs. E dependence at higher electric fields disappears. At high temperatures, this dependence is very similar to that obtained in films prepared on NGO substrates (see Fig. 3b).
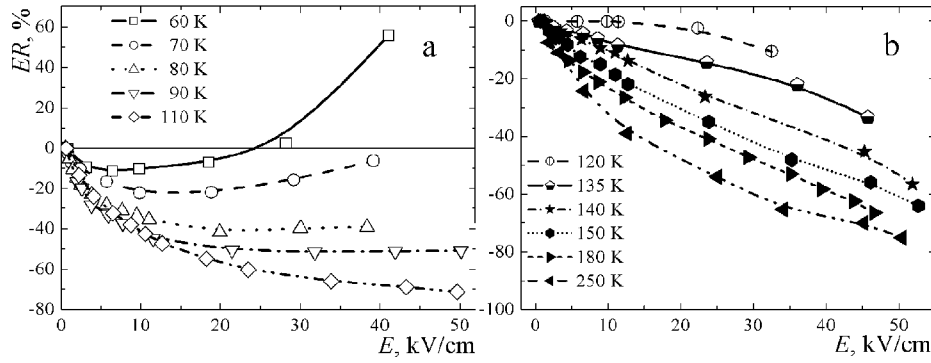

Fig. 3. (a, b) Electroresistance vs. electric field strength dependence for $La_{0.67}Ca_{0.33}MnO_3$ films deposited on MgO substrate.
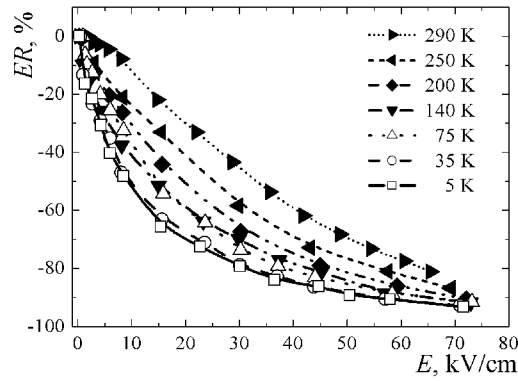

Fig. 4. Electroresis tance vs. electric field strength dependence for $La_{0.67}Ca_{0.33}MnO_3$ films deposited on lucalox substrate.

The results of ER effect investigation in films grown on lucalox substrate is presented in Fig. 4. It is evident that only negative electroresistance appears in this case over the entire investigated temperature range. The value of ER increases with the increase in electric field strength and with the decrease in film temperature. The highest value of ER (93%) was obtained at 5 K. In this case, the shape of the ER vs. E curve is similar to that obtained in films prepared on

MGO substrate and kept at temperatures around T_m. The changes in the shape of the ER vs. E curves with the increase in temperature are also similar to films deposited on MGO substrate, if the temperature increases above T_m.

4. Discussion

Before discussing possible reasons for the origin of electroresistance in the investigated films, it is necessary to discuss the results of the resistance vs. temperature dependence investigated for the dc current regime. It was found that films prepared on NGO substrate had low resistance and a high critical temperature $T_m = 265$ K. Such behavior is typical of epitaxial film grown on a substrate with a small mismatch of lattice parameters between substrate and film (a lattice parameter difference between bulk LCMO and NGO is only 1%). In the case of the MGO substrate, this mismatch is significant (9%) and a large number of dislocations producing grain boundaries (GBs) necessary to absorb the misfits are formed [12]. The film grown on polycrystalline lucalox substrate has to contain more imperfections than that prepared on MGO substrate, because in addition to the lattice mismatch, the lucalox substrate is of granular structure. Thus, if the lattice mismatch generates GB in the same direction as the orientated crystallites, like in the MGO case, the lucalox substrate creates additional GBs between the disorientated crystallites [13]. A higher resistivity and strong differences between the $R(T)$ dependence for the films prepared on lucalox and MGO substrates confirm this assumption.

Small values of ER and ER vs. E dependence in films grown on NGO substrate can be explained by current induced heating of the film due to a strong electric field pulse action. Positive and negative ER obtained below and above T_m, respectively, show that Joule heating could be the main reason of this effect. Let us suppose that $R(T)$ is the same for all electric field strength values, heating is adiabatic and the film resistance dependence on temperature is linear. It is almost true for relatively narrow temperature ranges and short electrical pulse durations. In this case, the temperature increase of the film during the electrical pulse action can be obtained from the following formula:

$$\Delta T = \frac{U^2 t}{R_a cm}, \tag{2}$$

where U is the voltage, t is the time of current flow, and c and m are the heat capacity and mass of the film, respectively. R_a is the average resistance of the sample. Figure 5 (triangular dots) shows the temperature increase calculated when $t = 2$ ns and when the electric field strength was 20 kV/cm. The circular dots are experimental data points (see Fig. 1) and demonstrate how much the temperature has to increase in order to get a corresponding electric field induced resistance change (see Fig. 2). As can be seen, experimental data and calculations are in relatively good agreement at temperatures below T_m. However, the difference at $T > T_m$ demonstrates that in addition to Joule heating, there is a non-thermal
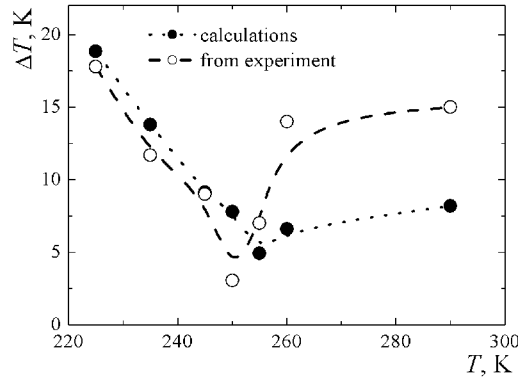
Fig. 5. Calculated (solid dots) electric pulse induced temperature increase of
$La_{0.67}Ca_{0.33}MnO_3$ film deposited on $NdGaO_3$ substrate (applied electric field
20 kV/cm). Circular dots show temperature increase obtained from the resistance vs.
temperature dependence.

origin of the strong electric field effect, such as field assisted hopping [14], which
manifests itself when the film is transformed to semiconductor-like behavior.

As it is shown in Fig. 1, films prepared on MGO substrates have a signifi-
cantly lower $T_m = 135$ K and 50 times higher resistivity than films deposited on
NGO. In this case, the main reason for the electroresistance phenomenon (negative
and positive) at $T \gg T_m$ and $T \ll T_m$ is also Joule heating, while a large negative
electroresistance nearby T_m is of pure electronic origin and probably is determined
by charge carriers tunneling across high resistivity grain boundaries [13]. Most
probably, the same or similar effect is responsible for ER phenomenon in high re-
sistivity films fabricated using polycrystalline lucalox substrate. In this case grain
boundaries formed between disoriented manganite crystals could play a significant
role in determining the film's electrical properties. The main voltage drop in this
case is concentrated at these imperfections, where the resistivity is less sensitive to
magnetic ordering. For this reason, only a strong negative electroresistance phe-
nomenon was observed for the investigated temperature range from 5 K to 300 K.

5. Summary

The electroresistance effect caused by nanosecond duration electrical pulses
in high quality $La_{0.67}Ca_{0.33}MnO_3$ films grown onto (110) NGO substrate and
having a small number of imperfections for the investigated temperature range is
mostly due to Joule heating. However, the resistance changes close to and above T_m
is the result of both Joule heating and non-thermal strong electric field effects.
The films prepared on MGO substrates have significantly lower $T_m = 135$ K
and 50 times higher resistivity than films deposited on NGO. Most probably, this
is caused by grain boundaries formed due to the misfit between the film and

substrate lattice constants. In this case, the main reason for the ER phenomenon (negative and positive) at $T \gg T_{\mathrm{m}}$ and $T \ll T_{\mathrm{m}}$ is also Joule heating, while large negative ER values near T_{m} is of pure electronic origin and probably is determined by charge carrier tunnelling across high resistivity grain boundaries. The ER phenomenon in films fabricated using polycrystalline lucalox substrate is also associated with strong electric fields on the GB, which, most probably, are formed between disoriented manganite crystals. For this reason, only a strong negative ER phenomenon was observed over the investigated temperature range from 5 K to 300 K.

Acknowledgments

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