ELECTRIC-FIELD EFFECT IN MANGANITE FILMS ON FERROELECTRIC SUBSTRATES

A.I. TOVSTOLYTKIN, A.M. POGORILY, S.A. SOLOPAN[1], O.I. V'YUNOV[1], L.L. KOVALENKO[1], A.G. BELOUS[1]

Institute of Magnetism, Nat. Acad. of Sci of Ukraine
(36b, Academician Vernadsky Blvd., Kyiv 03142, Ukraine, e-mail: atov@imag.kiev.ua),

[1]**Vernadsky Institute of General and Inorganic Chemistry, Nat. Acad. of Sci of Ukraine**
(32/34, Academician Palladin Pr., Kyiv 03680, Ukraine)

UDC 537.6;538.212

The paper concentrates on the investigation of electric and magnetoresistive properties of perovskite heterostructures "substituted lanthanum manganite – doped barium titanate". It is shown that the character of the temperature dependences of the electric resistance and magnetoresistance is strongly dependent on the structure and chemical composition of substrates. The possibility to tune the resistance and magnetoresistance of the films by means of a change of the voltage applied to a substrate is demonstrated experimentally.

1. Introduction

In recent years, a great deal of attention has been paid to the materials and artificial structures, whose properties can be controlled by application of electric and magnetic fields [1, 2]. They provide ample opportunities for the potential application as multifunctional devices such as electrically/magnetically tuned filters, transducers, actuators, and sensors [1–3].

One of the perspective directions to achieve the controllability of electric and magnetic fields is the development of multilayer film composites on the basis of manganese and titanium oxides having the perovskite structure [2–4]. An advantage of such composite systems is the possibility to combine different kinds of orderings within one structural type: doped manganites on the base of $LaMnO_3$ are ferromagnetic [4], whereas doped titanates on the base of $BaTiO_3$ are ferroelectrics [3, 5].

In this paper, we describe the electric and magnetoresistive properties of $La_{1-x}Sr_xMnO_3$ ($x = 0.225$) films produced by the screen printing technique [6, 7] on the substrates of barium–titanate-based ceramics, whose properties can be controlled by applying an electric field.

2. Experimental Results and Discussion

The $La_{0.775}Sr_{0.225}MnO_3$ (LSMO) films of 10 μm in thickness were deposited on 200-μm-thick substrates by screen printing [7] followed by heat treatment at 1170 °C for 2 h. Four types of barium–titanate-based ceramics were used as substrates. The $BaTi_{0.85}Zr_{0.11}Sn_{0.04}O_3$ material has nonlinear dielectric properties, i.e. the nonlinear variation of the dielectric permittivity with an applied electric field [5]. Materials based on $Ba_{0.996}Y_{0.004}TiO_3$, $Ba_{0.996}Y_{0.004}TiO_3$+0.04% Mn, and $Ba_{0.996}Y_{0.004}Ti_{0.65}Sn_{0.35}O_3$ are ferroelectrics which display a positive temperature coefficient of resistance (PTCR) and differ from each other in the room-temperature resistivity and the phase-transition temperature [3, 5]. It should be noted that, for all the specimens studied, the substrate resistivity was more than 3 orders of magnitude higher than the maximum resistivity of the films. As a reference substrate, we used α-Al_2O_3, a nonconductive material which does not have nonlinear properties.

The electric resistance of the films was measured by the four-probe technique in the temperature range from 77 to 350 K. Silver contacts were deposited by magnetron sputtering. Magnetoresistance (MR) was calculated as $(R_0 - R_H)/R_0 \times 100\%$, where R_0 is the zero-field resistance and R_H is the resistance in a magnetic field H.

Figure 1 compares the temperature dependence of the normalized resistance for a bulk $La_{0.775}Sr_{0.225}MnO_3$ sample with those for the films of the same nominal composition deposited on various substrates. For all the films, the maximal value of resistance is between 100 and 600 Ohms. The peak-resistance temperature T_{max} for the film on the alumina substrate (curve *2*) is lower than that for bulk LSMO (curve *1*). At the same time, the maximum in the resistance for the films on the $BaTi_{0.85}Zr_{0.11}Sn_{0.04}O_3$, $Ba_{0.996}Y_{0.004}TiO_3$+0.04% Mn, and $Ba_{0.996}Y_{0.004}Ti_{0.65}Sn_{0.35}O_3$ substrates is shifted to

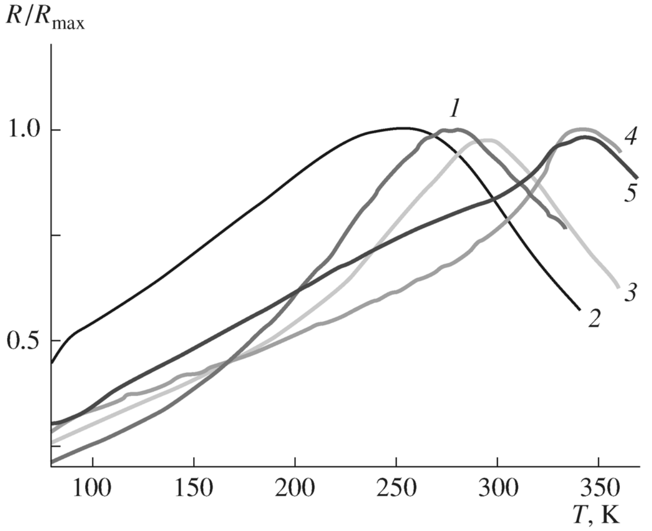

Fig. 1. Temperature dependences of the normalized resistance for a bulk $La_{0.775}Sr_{0.225}MnO_3$ sample (1) and LSMO films on α-Al_2O_3 (2), $Ba_{0.996}Y_{0.004}Ti_{0.65}Sn_{0.35}O_3$ (3), $BaTi_{0.85}Zr_{0.11}Sn_{0.04}O_3$ (4), and $Ba_{0.996}Y_{0.004}TiO_3$+0.04% Mn (5) substrates

higher temperatures in comparison with the ceramic sample (curves *3–5*).

As was shown in works [2, 4, 8], the principal effect, which gives rise to a shift of T_{max} in manganite films, originates from a substrate-induced strain. It should also be taken into account that the inhomogeneity in the elastic strain distribution in manganite films increases the scatter in the effective manganese–oxygen bond length, which also contributes to changes in $T_{\max}$ [2, 4]. In addition, the resistance of the films is affected by the characteristics of grains, in particular by a degree of structural and magnetic disorder, and also by deviations of the chemical composition from the nominal one at grain boundaries [9].

Figure 2 shows the temperature dependence of the magnetoresistance in an applied field $H=$ 15 kOe for the bulk polycrystalline and thin-film LSMO samples. According to earlier results [4, 10, 11], the magnetoresistance of single crystalline manganites displays a maximum near their Curie temperature T_C, a transition point from the semiconducting paramagnetic to metallic ferromagnetic state. In polycrystalline samples, there is an additional contribution to MR at low temperatures ($T < T_C$), which rises steadily with decrease in the temperature. This contribution was attributed to the spin-dependent scattering of charge carriers at grain boundaries [10] or to the spin-polarized grain-boundary tunneling [9]. Both in bulk LSMO and in the films on doped barium titanate substrates, two contributions to the magnetoresistance are significant (see Fig. 2), which allows the T_C of these samples to be evaluated as the peak temperature in the MR(T) curve. The temperature variation of MR for a film on the alumina substrate is typical of materials with a broadened phase transition, as is usually observed in inhomogeneous or strained manganites [2, 8, 12]. Thus, the present results demonstrate that the films deposited on alumina and doped barium titanate substrates differ in the transition temperature, which can be originated from a high sensitivity of exchange interactions to interatomic distances and, thus, to the deformations induced by a substrate [8, 13].

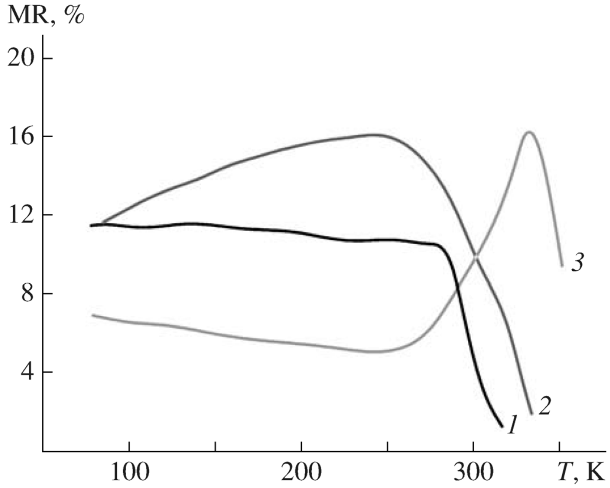

Fig. 2. Temperature dependences of the magnetoresistance for a bulk $La_{0.775}Sr_{0.225}MnO_3$ sample (*1*) and LSMO films on α-Al_2O_3 (*2*) and $BaTi_{0.85}Zr_{0.11}Sn_{0.04}O_3$ (*3*) substrates

K. Dörr [2] discussed the potential of composite films such as substituted lanthanum manganites/ doped barium titanates for the use in devices, whose magnetic or magnetoresistive properties can be tuned by an applied electric field. The proposed mechanism of such a coupling includes the inverse piezoelectric effect in titanate-based substrate and its action on properties of the magnetic layer through the creation of mechanical deformations [2, 5]. To ascertain whether such an effect takes place in structures under investigation, we studied the electric-field effect on properties of doped lanthanum manganite films.

Figure 3 schematically illustrates the film–substrate geometry we used to study the influence of the nonlinear properties of $BaTi_{0.85}Zr_{0.11}Sn_{0.04}O_3$ substrates and the properties of PTCR ferroelectric substrates ($Ba_{0.996}Y_{0.004}TiO_3$, $Ba_{0.996}Y_{0.004}TiO_3$+0.04% Mn,

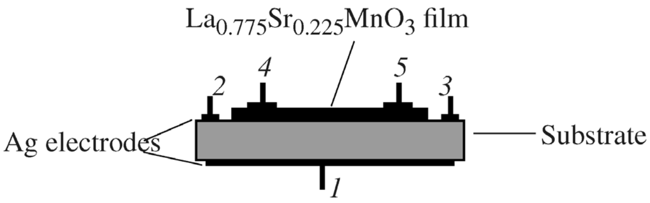

Fig. 3 The geometry of measurement electrodes for LSMO films on various substrates: (*1–3*) electrodes to the substrate, (*4* and *5*) electrodes to the film

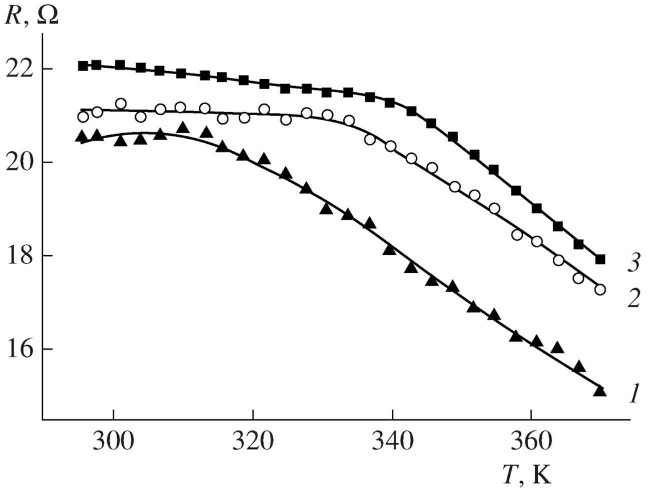

Fig. 4. Resistance as a function of the temperature for the LSMO film on a $Ba_{0.996}Y_{0.004}TiO_3$+0.04% Mn substrate at a 30-V voltage applied: (*1*) between electrodes *1* and *2*; (*2*) between electrodes *2* and *3*; (*3*) at the zero voltage

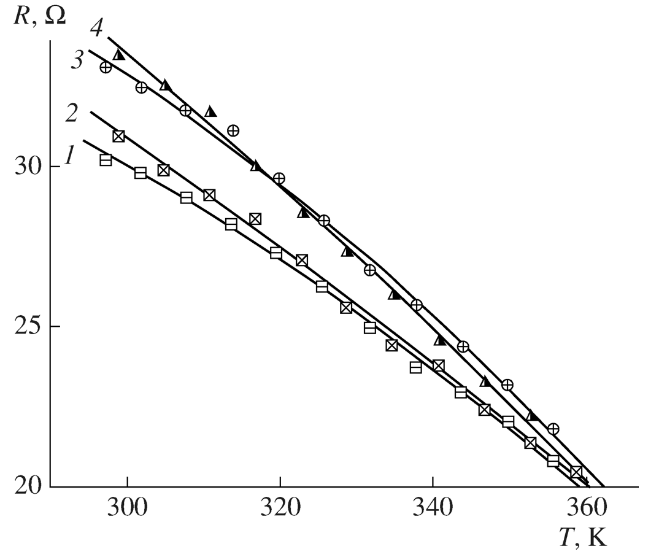

Fig. 5. Resistance as a function of the temperature for the LSMO film on a $Ba_{0.996}Y_{0.004}Ti_{0.65}Sn_{0.35}O_3$ substrate in applied electric and magnetic fields: (*1*) $H = 15$ kOe, $V = 0$; (*2*) $H = 15$ kOe, $V = 20$ V between electrodes *1* and *2*; (*3*) $H = 0$, $V = 0$; (*4*) $H = 0$, $V = 20$ V between electrodes *1* and *2*

and $Ba_{0.996}Y_{0.004}Ti_{0.65}Sn_{0.35}O_3$) on the properties of manganite films. The electric resistance and magnetoresistance of the films was determined using electrodes *4* and *5*. The measurements were made in an applied magnetic and/or electric field or without field.

As an example, Fig. 4 shows the temperature dependence of the electric resistance for the LSMO film on a $Ba_{0.996}Y_{0.004}TiO_3$+0.04% Mn substrate at different applied electric fields. Here, we recall that the doped manganite compounds are characterized by a tight interrelation between the electric conductance and the magnetic state and, thus, the behavior of the electric resistance can provide information about the magnetic state [2, 4, 12]. At the zero voltage or a voltage applied between electrodes *2* and *3*, the slope of the $R(T)$ curve changes sharply near the phase transition (curves *2* and *3*). A voltage applied between electrodes *1* and *2* (curve *1*) shifts the temperature of the resistivity kink and reduces the resistance of the film. This behavior can be accounted for by the sensitivity of the doped barium titanate to an external electric field and by the coupling between the layers via the mechanism described above. The greater effect of the electric field for curve *1* as compared with that for curve *2* is believed to be due to the higher electric field applied to the substrate: $E = V/d$, where d is the electrode separation. However, it should be noted that, for the measured configurations described above, the distribution of the electric field within the substrate is highly non-uniform, and the effect of this non-uniformity needs to be studied further.

Figure 5 shows the temperature dependence of the resistance for the LSMO film on $Ba_{0.996}Y_{0.004}Ti_{0.65}Sn_{0.35}O_3$ substrate in applied electric and magnetic fields. An electric field applied to the substrate is seen to have little effect on the resistance of the film, whereas an applied magnetic field reduces it (curves *1* and *2*), which is characteristic of manganites [4,7]. The weaker electric-field effect on properties of the system under investigation seems to be associated with a weaker sensitivity of the properties of $Ba_{0.996}Y_{0.004}Ti_{0.65}Sn_{0.35}O_3$ ceramics to electric fields.

3. Conclusions

The above-presented results demonstrate that the screen printing is a viable approach for the preparation of

$La_{1-x}Sr_xMnO_3$ manganite films on ceramic substrates of various compositions. The use of the doped-titanate-based substrates of different compositions makes it possible to control the phase transition temperature of manganite films. An appropriate choice of the substrate composition enables the synthesis of substituted lanthanum manganite/doped barium titanate structures, whose magnetoresistive properties can be tuned by applying an electric field, which provide opportunities for the potential application as multifunctional devices.

The work is partly supported by the Science and Technological Center in Ukraine, project N 4137.

1. C.-W. Nan, M.I. Bichurin, S. Dong, D. Biehland, and G. Srinivasan, J. Appl. Phys. **103**, 031101 (2008).
2. K.Dörr, J. Phys. D: Appl. Phys. **39**, 125 (2006).
3. S.A. Solopan, O.I. V'yunov, L.L. Kovalenko, and A.G. Belous, Ukr. Khim. Zh. **72**, 28 (2006).
4. A.I. Tovstolytkin, A.M. Pogorily, A.I. Matviyenko, A.Ya. Vovk, and Zh. Wang, J. Appl. Phys. **98**, 043902 (2005).
5. A.G. Belous, O.I. V'yunov, and L.L. Kovalenko, Ferroelectrics **254**, 91 (2001).
6. P. Dutronc, B. Carbonne, F. M'enil, and C. Lucat, Sensors and Actuators B **6**, 279 (1992).
7. A.G. Belous, A.I. Tovstolytkin, O.I. V'yunov, Yu.D. Stupin, and L.L. Kovalenko, Ukr. Khim. Zh. **72**, 21 (2006).
8. Ch.-C. Chen and A. de Lozanne, Appl. Phys. Lett. **73**, 3950 (1998)
9. R. Gross, L. Alff, B. Böchner *et al.*, J. Magn. Magn. Mater. **211**, 150 (2000).
10. X.W. Li, A. Gupta, G. Xiao, and G.Q. Gong, Appl. Phys. Lett. **71**, 1124 (1997).
11. K. Ghosh, S.B. Ogale, R. Ramesh *et al.*, Phys. Rev. B **59**, 533 (2000).
12. A.I. Tovstolytkin, Mater. Sci. Forum **373–376**, 613 (2001).
13. T.K. Nath, R.A. Rao, D. Lavric, and C.B. Eom, Appl. Phys. Lett. **74**, 1615 (1999).

Received 20.06.08

ЕЛЕКТРОПОЛЬОВИЙ ЕФЕКТ В МАНГАНІТОВИХ ПЛІВКАХ НА СЕГНЕТОЕЛЕКТРИЧНИХ ПІДКЛАДКАХ

О.І. Товстолиткін, А.М. Погорілий, С.А. Солопан,
О.І. В'юнов, Л.Л. Коваленко, А.Г. Білоус

Резюме

Робота концентрується на вивченні електричних та магніторезистивних властивостей перовскітових гетероструктур "заміщений манганіт лантану – легований титанат барію". Показано, що характер температурних залежностей електроопору та магнітоопору суттєво залежить від структури та хімічного складу підкладок. Експериментально продемонстровано можливість керування електричним опором та магнітоопором плівки шляхом зміни електричної напруги, прикладеної до підкладки.