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Inelastic Relaxation of Oxygen and Low-Field Magnetoresistance in $La_{0.65}Ca_{0.35}MnO_3$ Films on Ferroelectric Ceramics Substrates

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Galvanomagnetic properties of polycrystalline $La_{0.65}Ca_{0.35}MnO_3$ films with a thickness of 0.2 μm deposited onto $Pb_{2.9}Ba_{0.05}Sr_{0.05}(Zr_{0.4}Ti_{0.6})O_3$ ferroelectric ceramics substrates were investigated. We discovered an irreversible increase in film resistance after numerous inversions of substrate polarization. This phenomenon was investigated several times for three film structures. The typical duration of the process of a monotonic 3–5 times increase in film resistance was 3–6 hours. The long-time relaxation of macroscopic film resistance is explained by dielectrization of film intercrystallite boundaries. The typical size of crystallites of both the film and the substrate is $3-10$ μm. Such small size explains the fact of macroscopic homogeneity of film conductivity, when the specific resistance increases from 1.8×10^{-2} to 1.8 Ω cm. A growth in resistance of narrow (10 nm) regions of film is explained by the redistribution of oxygen anions under the action of inhomogeneous mechanical stress. The stress between crystallites appears due to inverse piezoelectric effect of ferroelectric substrate. The magnitude of diffusion coefficient of oxygen is estimated to be $D \geq 10^{-20}$ m^2 s^{-1}.

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1. Introduction

Double exchange interaction between Mn^{3+} and Mn^{4+} ions through an oxygen anion is the base for understanding the galvanomagnetic properties of manganites [1, 2]. It naturally explains the phase transition of cooled samples from para- to ferromagnetic state at temperature T_c, as well as high (metallic) conductivity of material in the ferromagnetic state. Temperature dependence of electrical resistance $R(T)$ of solid solution $La_{1-x}Ca_xMnO_3$, $La_{1-x}Sr_xMnO_3$ films ($x = 0.2, \ldots, 0.4$) has a peak-like shape with the maximum above the liquid nitrogen temperature. This property is very useful for the bolometric applications. By the selection of solid solution composition and optimal regime of annealing, it is possible to obtain high value of the relative temperature coefficient of resistance $\mathrm{d}(\ln R)/\mathrm{d}T$ up to 10^{-1} K^{-1} at room temperature [3, 4]. In contrast with high-temperature superconductors (HTSC) and semiconductors, the bolometric response of such film to microwave irradiation contains no signals of other nature. This property of the films was used to investigate the bolometric response structure and to develop a computer based method for measurements of a full set of thermal kinetic coefficients of film structures [4, 5].

Another unique property of manganites is the colossal magnetoresistance (MR). Under the action of magnetic field (H) of any orientation the maximum of $R(T)$ curve is decreased and shifted slightly to higher temperatures. The value of the negative MR is defined as $\mathrm{MR} = [R(0) - R(H)]/R(0)$. Usually, MR is measured at $H = 10$ kOe. For single crystals and high-quality films the $\mathrm{MR}(T)$ dependence is similar to $R(T)$ one. The $\mathrm{MR}(T)$ dependence has a peak-like shape. In the region below T_c the $\mathrm{M}R(T)$ decreases monotonically with temperature decrease. The authors of Ref. [6] have found that under certain conditions two kinds of MR-effects can be observed. The additional so-called low-field MR (LFMR) manifests itself in the field of about 100 Oe and has abnormal temperature dependence. The value of LFMR grows with temperature decrease below T_c. It was unambiguously proved that the nature of LFMR in $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ single crystalline film is related to the bicrystal boundary of $SrTiO_3$ substrate with the disorientation angle of 36.8° [6].

It is surprising that the LFMR was not more frequently observed in ceramic samples, except of Ref. [7], where the LFMR was revealed only in the case when the size of grains was about 100 nm and less. It is well known that macroscopic properties of granular manganite follow from the differences between grain size and the size of magnetic domains. The other important factor is the type of grain links. In particular, spin-dependent tunneling through a boundary can also be the cause of the LFMR [8, 9].

In this work, we have investigated the effect of variation of ferroelectric substrate polarization on structure and galvanomagnetic properties of $La_{0.65}Ca_{0.35}MnO_3$ films. The original goal of our experiments involved mechanical stress on the film–substrate interface. Inhomogeneous mechanical stress appears after numerous inversions of substrate polarization and results in dielectrization of film intercrystalline boundaries. This apparently explains the phenomenon of long-time relaxation of macroscopic film resistance and negative LFMR.

2. Experiment

We fabricated and studied three $La_{0.65}Ca_{0.35}MnO_3$ film structures with the thickness of about $d = 0.2$ μm. The films were prepared by pulsed laser deposition (PLD) method. Two films (N1049 and N1050) were produced in the same regime. For the third film (N1055) the power of a laser pulse was increased and the time of deposition was decreased. Films were annealed in air.

Substrate material $Pb_{2.9}Ba_{0.05}Sr_{0.05}(Zr_{0.4}Ti_{0.6})O_3$ [10] was produced by sintering carbonates and oxides of components at 900°C during 2 hours. The obtained grain material was milled to obtain the particle size of about 1 μm and the resultant powder was compacted into pellets with the diameter of 9 mm and thickness of 1.15 mm. The pellets were annealed at 1200−1350°C during 8 hours. Phase composition of the solid solution and quality of solid state reaction were tested with the help of diffractometer DRON-2 and D-500. Single phase samples were selected for the experiment. The structure of films and substrates was investigated by optical microscopy (Neophot-32) and scanning electron microscopy (SEM) methods (JSM-820) with X-ray microanalysis system (LINC AN 10000).

Four-point technique was used for electrical measurements of the film resistance. For polarization of the substrate an additional (common) wire was con-

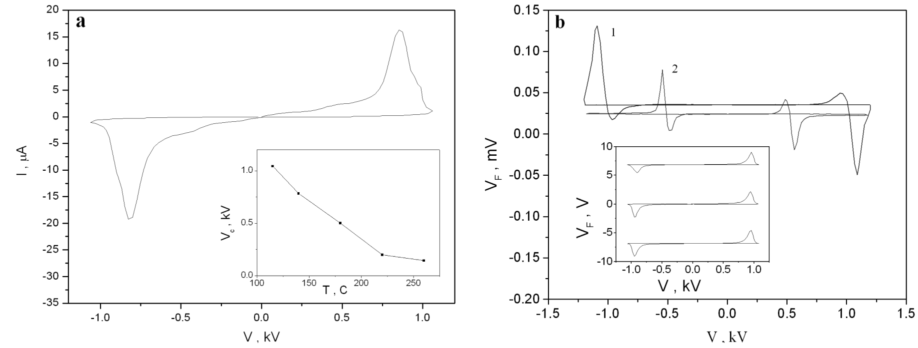

Fig. 1. (a) $I-V$ characteristics of the substrate at 188°C. Inset: temperature dependence of the voltage corresponding to the current maximum in Fig. 1a. (b) Dependence of the voltage at the film on the voltage across the substrate for $I_b = 1$ μA and temperatures of 140°C and 220°C (curves 1 and 2). Inset: the same curves in the case of inhomogeneous macroscopic conductance of the film ($R = 800$ kΩ) for two inverse directions of bias current $I_b = 1$ μA (upper and lower curves, respectively) and $I_b = 0$ (middle curve).

nected to the film. The common wire was placed symmetrically to the "potential" contacts and provided additional experimental possibility for control of macroscopic homogeneity of film conductivity.

Because the maximal output voltage of our small power source (1200 V) was insufficient for full polarization of the substrate at room temperature, we used sample heating. The process of the substrate polarization was controlled by the measurement of current in the circuit of high-voltage source. $I-V$ characteristics of the substrate in the regime of relatively slow scanning of voltage are represented in Fig. 1a. As one can see, the peak of current appears during the repolarization. In the inset of Fig. 1a, the temperature dependence of the voltage of substrate repolarization is shown. The magnitude of voltage decreases with the temperature increase.

3. Results and discussion

It is well known that process of the ferroelectric polarization is realized by means of origination and growth of domains with the appropriate orientation [10]. Therefore, during the inversion of substrate polarization the macroscopic electrical moment does not appear at the film plane. We have investigated the influence of inversion of substrate polarization on the film voltage response. In the absence of film bias current, the voltage response cannot be observed in the film with a macroscopic homogeneity of conductivity. In the presence of bias current, the voltage response is relatively small (10^{-4} V, see Fig. 1b). When the film has a macroscopic inhomogeneity of electrical conductivity, the magnitude of voltage response becomes very large.

All studied films demonstrated the effect of macroscopic resistance increase as a result of numerous inversion of substrate polarization. In Fig. 2a two groups of temperature dependencies of resistance are represented. Four curves of every group correspond to different magnetic fields and each group corresponds to a separate experiment with the N1050 film. One can see the large differences between the values of resistance for presented groups of curves. They are the result of long--time relaxation of resistance after multiple inversions of substrate polarization at the temperature of 160°C. It should be noted that without a change of substrate polarization the film resistance was stable during two months. As a rule, after multiple inversion of substrate polarization there was a 3–5 times increase in film resistance. The relaxation of film resistance occurs during 3–6 hours. The total range of the relative increase in resistance is more than two orders of magnitude. When the film resistance is increased up to $\approx 10^6\ \Omega$ the macroscopic inhomogeneity of film conductivity appears.

Figure 2b shows the anomalous temperature dependencies of MR effect for experiments I and II. The magnitude of MR effect tends to grow with an increase in film resistance. Such type of temperature dependence corresponds to LFMR.

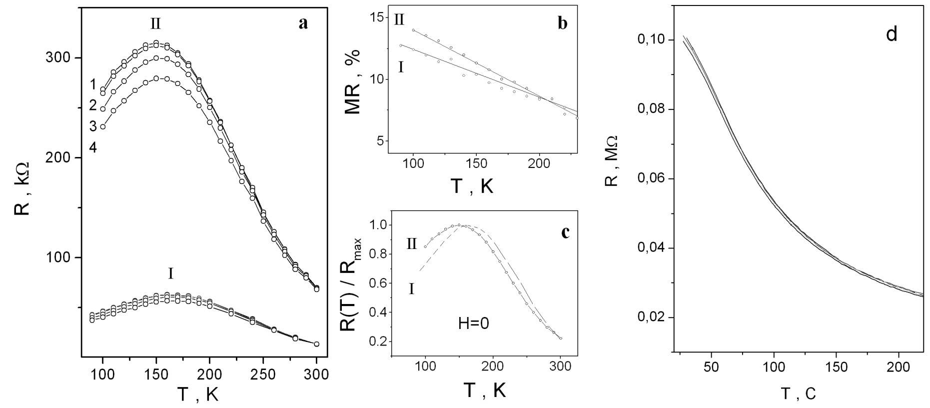

Fig. 2. Temperature dependencies of (a) resistance (curves I, II correspond to two separate experiments, curves 1–4 correspond to different magnetic fields $H = 0$; 1; 5, and 10 kOe, respectively); (b) MR at $H = 10$ kOe; (c) the film resistance $R/R_{\max}$; (d) resistance of film (the curves were recorded by means of scanning of film temperature and inversion of voltage (1000 V) sign on the thickness of substrate at minimal and maximal temperatures).

Indeed, the magnetic field dependence of the absolute value of $\mathrm{d}R/\mathrm{d}H$ in the temperature range $T = 77-150$ K exhibits rapid increase in small fields and saturation in the field of about 1.5 kOe. Figure 2c demonstrates a variation of the shape of $R(T)$ curves for the I and II experiments at $H = 0$. In Fig. 2d, the high-speed and reversible response of film resistance to the inversion of substrate polarization was shown. In contrast with the result of Ref. [11] it is very small in our case.

As the same film on the $\mathrm{SrTiO_3}$ substrate has the usual type of temperature dependence of $\mathrm{MR}(T)$, the nature of LFMR effect as well as the irreversible increase in resistance could be connected with a modification of film structure.

The studied films, as well as the substrates have a polycrystalline structure with a typical size of crystallites $3-10$ μm (see Fig. 3). The influence of the average size of grains on the specific resistance of ceramics samples was investigated by authors of Ref. [12] by using the simple model of constant resistance of grain boundary. According to this model, the specific resistance increases nonlinearly with a decrease in the grain size. In the case of relatively large size of crystallites ($3-10$ μm) the additional increase in resistance must be small. This conclusion agrees with our results because the initial specific resistance of the film is close to that of single crystal ($\rho = 18$ mΩ cm). However, we found no correlation between variation of resistance and the size of film crystallites. Moreover, the additional SEM investigation of the film surface did not reveal either any decrease in the average size of crystallites or the appearance of intercrystalline voids.

Therefore, the increase in macroscopic resistance is stipulated to be caused by the increase in resistance of film intercrystallite boundaries. Relatively small size

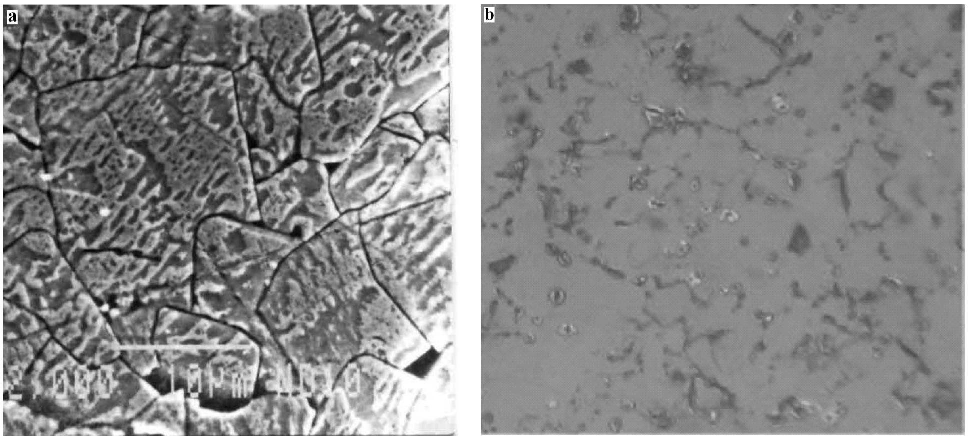

Fig. 3. Microstructures of: (a) substrate surface, SEM (×2500) after chemical etching; (b) film surface, optical microscopy (×500).

of crystallites explains the fact of macroscopic homogeneity of film conductivity when the specific resistance is increased in a wide range.

In Fig. 3a, the crystallite boundaries of the substrate are seen as a geometrical relief which appeared after chemical etching of the surface. The film microscopic structure is represented in Fig. 3b. The typical size of crystallites of both the film and the substrate is $3-10$ μm.

The main mechanism of the increase in intercrystallite boundary resistance could be the inelastic relaxation of atoms under the action of inhomogeneous mechanical stress (relaxation of Gorsky [13]). The scheme of proposed process is as follows. The mechanical stress between crystallites of ferroelectric substrate is accumulated during multiple inversions of polarization. It is the result of the inverse piezoelectric effect. The mechanical stress produces the deformation fields in the film. Appearance of regions with tension and compression of the film material is the immediate cause of a redistribution of oxygen anions by means of diffusion.

High sensitivity of manganites to oxygen non-stoichiometry is well known. Oxygen deficiency results in a decrease in conductivity. Next important question concerns inhomogeneous distribution. In our experiment, a variation of distribution of oxygen anions in narrow regions of the film near the crystallite boundary results in the increase in macroscopic resistance only. Such effect is explained by a nonlinearity of the dependence of film resistance on the oxygen concentration. A decrease in macroscopic resistance of the film is provided by additional annealing.

The possibility of strong dielectrization of narrow regions of the film is explained by a locality of double exchange interaction and a very small radius of impurity centers [14]. If we assume that the width of film region with oxygen deficiency is equal to 10 nm and the time constant of the relaxation process $\tau = 10^3$ s, the diffusion coefficient of oxygen anion is estimated as $D = 10^{-20}$ m^2 s^{-1}. It is a lower estimate. Such magnitude of D is sufficient to observe the increase in macroscopic film resistance, but it is very small in comparison with diffusion coefficient of hydrogen atoms in niobium $D = 5.4 \times 10^{-8}$ m^2 s^{-1}.

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