AGEING EFFECTS ON ELECTRICAL RESISTIVITY AND MAGNETORESISTANCE OF NANOSTRUCTURED MANGANITE FILMS

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The long-term stability of electrical resistance and magnetoresistance in nanostructured La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.17$) manganite thin films grown on lucalox (Al$_2$O$_3$ + MgO) substrate by the MOCVD method was investigated. It was found that the storage of up to 3 months of the free surfaces of these films in normal atmosphere (air) conditions increases their resistivity by almost two times, while the annealing of the films in an Ar atmosphere at 450 °C decreases their resistivity only by 15%. It was concluded that the final increase of resistivity is determined by a long-term relaxation of the grain boundaries in the nanostructured films. The magnetoresistance of the films does not change significantly, which produces an advantage for magnetic field sensor applications. The passive protective coating of the free surfaces of the films stabilizes their electrical and magnetic properties. The results were analysed using various electron scattering mechanisms when the films were in a ferromagnetic state, and the Mott's variable range hopping model when they were in a paramagnetic insulating state.

Keywords: manganites, electrical resistivity, colossal magnetoresistance, polycrystalline thin films, magnetic field sensors, ageing effects

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1. Introduction

Doped perovskite manganites exhibiting colossal magnetoresistance (CMR) effects have attracted considerable attention not only for fundamental research, but also for potential device applications [1]. The investigations of such polycrystalline films and bulk materials have revealed several advantages in comparison with epitaxial films or single crystal manganites [2]. The polycrystalline films have low-field magnetoresistance (MR), significant values of MR over a wide temperature range, and their MR values increase almost linearly up to very high fields (50 T) with a low tendency for saturation. It was demonstrated that such thin polycrystalline manganite films can be successfully used for the development of B-scalor sensors, which are able to measure the magnitude of high-pulsed magnetic fields up to 40 T in very small volumes ($=10^{-2}$ mm$^3$) [3, 4]. The operation of such magnetic field sensors is based on the changes of the electrical resistance of these thin polycrystalline manganite films when exposed to external magnetic fields. Polycrystalline or nanostructured films are very complicated systems which can be viewed as networks of nanocrystallites, whose crystalline structure and grain boundaries exhibit a great number of point defects. During the growth of these films, it is energetically advantageous to spontaneously distort their lattices, thus creating various defects. Such a system can be characterised by a strong structural and magnetic disorder which can arise from a large amount of defects, dislocations, non-stoichiometry, oxygen vacancies, etc. [3, 5] contained in them. Thin films grown on polycrystalline substrates have relatively large free surfaces, which can interact with the ambient atmosphere. The most important factor in this interaction is
the possible migration of oxygen atoms in the film volume and in the boundaries with the surface because oxygen has the strongest influence on the electrical conductivity of manganites \[\text{LSMO} \text{ - slow}\]. The partial substitution of the trivalent rare earth ion (La\(^{3+}\)) by the divalent ion (Sr\(^{2+}\), Ca\(^{2+}\)) defines the ratio of the Mn valence states Mn\(^{3+}\) and Mn\(^{4+}\) which determine the main electric and magnetic properties of such doped manganites \[\text{LSMO} \text{ - fast}\]. However, a change in this ratio can also be produced by the creation of vacancies at the oxygen sites and the divergent ion. The properties of such manganite films can also change over a long term due to the migration of such vacancies or ions to energetically more favourable sites. Usually the devices based on manganite films have two terminals. Therefore, the formation of electrodes having low contact resistance is also of great importance. This technological process and annealing in a different gas atmosphere can change the electrical parameters of the active element (manganese film) of the device.

Therefore, the ageing effects which influence the stability of the electrical resistivity of thin polycrystalline manganite films over time play an important role in the development of these devices \[\text{LSMO} \text{ - slow}\].

Two time scales need be considered during the investigation of the changes of the electrical and magnetic properties of managnite thin films over time \[\text{LSMO} \text{ - fast}\]: the short-time scale (up to seconds or hours), which is generally referred to as “relaxation” and is performed in a non-zero applied magnetic field \[\text{LSMO} \text{ - slow}\], and a much longer time scale (up to several months), which is called the “ageing” of the sample in a zero applied field \[\text{LSMO} \text{ - fast}\].

In this paper, we focus on the study of the ageing effects of nanostructured La\(_{4-x}\)Sr\(_x\)MnO\(_3\) (x = 0.17) films. In particular, the kinetics of electrical resistivity and magnetoresistance were measured when the free surfaces of the films were stored for several months in a normal atmosphere (air), after this annealed in an argon atmosphere and covered with special protective glue.

2. The preparation of samples and the experimental technique

These thin La\(_{0.88}\)Sr\(_{0.12}\)MnO\(_3\) (LSMO) films were grown onto lucalox (99.9% Al\(_2\)O\(_3\) + 0.01% MgO) substrates at a 750 °C temperature by means of the Pulse Injection MOCVD technique \[\text{LSMO} \text{ - slow}\]. Due to the polycrystalline structure of the lucalox and the large mismatch between the lattice parameters of the manganite and the substrate, nanostructured films were produced. The average dimensions of nanocrystallite formations (clusters) in these films obtained by Atomic Force Microscopy were about 150–200 nm. Two types of films were prepared: films grown at a deposition rate of 15 nm/min (LSMO-slow) and 36 nm/min (LSMO-fast). The thickness of the films was about 400 nm.

The silver (Ag) electrodes were fabricated by the thermal deposition of Ag placed in a tungsten melting pot in a vacuum (about 10\(^{-5}\) Pa). During the deposition of the contact areas, the temperature of the substrate was kept at 150 °C. The thicknesses of the Ag electrodes were about 1 μm. After Ag deposition, the samples were annealed at 420 °C for 50 minutes in an argon atmosphere. The cooling to room temperature process lasted approximately 10 minutes. The Ag electrode areas had rectangular shapes and were separated by distances of 50 μm.

The electrical resistance and the magnetoresistance of such LSMO films was investigated over a 5–300 K temperature range and 0–0.8 T magnetic flux density (B) range using a closed cycle helium gas cryocooler and an electromagnet. MR was measured in two different configurations: when the magnetic field was oriented along the current direction in the film plane (MR\(_c\)) and when it was perpendicular to the film plane (perpendicular MR\(_p\)). The resistance and magnetoresistance measurements were performed by using the two-terminal method. Our preliminary investigations showed that the contact resistances were approximately 1 000 times smaller than the resistances of the prepared samples.

3. Results and discussion

3.1. The ageing influence on the electrical resistivity of LSMO films

The resistivity (ρ) as a function of temperature (T) measured just after sample preparation, i.e. after deposition of the Ag electrodes and annealing them at 420 °C for 50 minutes, for the LSMO-slow films is presented by the square symbols (1) in Fig. 1. This dependence is typical of manganite films and has a maximal resistivity value of
\( \rho_m = 1.1 \, \Omega \text{cm} \) at \( T_m = 240 \, \text{K} \) corresponding to the insulator-metal transition. The dependence of \( \rho \) vs. temperature for the films prepared at the higher deposition rate (LSMO-fast) was similar \((T_m = 250 \, \text{K} \) and \( \rho_m = 1.75 \, \Omega \text{cm} \)). The higher \( \rho_m \) values in the latter case can be explained by a more disordered grain boundary structure of the film due to non-equilibrium conditions during faster growth. In order to investigate the ageing effects, the samples were maintained for 3 months under normal atmospheric conditions (in air), and then the \( \rho \) dependences on temperature were measured again (triangular symbols (2) in Fig. 1). As can be seen, resistivity significantly increased. This phenomenon can be explained by the hydration process of the free surface of the films and the interaction of the air water molecules with the Mn ions \([12]\). As a result, the \( \text{Mn}^{4+} / \text{Mn}^{3+} \) ion ratio can be reduced and thus the resistance of the film increases. The value of \( T_m \) did not change in this case. After this, the annealing of the samples in an Ar atmosphere at a 450 °C temperature for 50 min. was performed. The same tendency was observed for the LSMO-fast sample. It was found that the resistivity of both samples decreased by 15%, i.e. \( \rho_m(3)/\rho_m(2) = 1.15 \) (circular symbols (3) in Fig. 1). However, it did not again reach the primary values of resistivity, indicating that several processes had taken place during the ageing of the films. The ratios of the resistivity maximum after annealing (2) compared with that of the as-prepared film (1), i.e. \( \rho_m(2)/\rho_m(1) \), were found to be 1.8 for the samples grown at the high deposition rate (LSMO-fast) and 1.5 for those grown at the slower (LSMO-slow) deposition rate. Therefore, the resistivity of a more structurally disordered film changed more under the same conditions. Such a result can be explained by a long-term lattice relaxation of the polycrystalline films, which produces more defects. An additional indication of the validity of this explanation can be the ageing result obtained from the samples prepared from a similar LSMO film \((x = 0.17)\) which were stored for 2 years at normal atmosphere conditions. After fabricating the sample electrodes and covering the samples’ free surfaces with special thermoglu, these samples were stored for 6 months in a normal atmosphere. The measurement of their resistance showed that it changed only by 2.5–3%.

The obtained results were analysed by considering their low-temperature metallic ferromagnetic \((T < T_m)\) and their high-temperature insulating paramagnetic \((T > T_m)\) resistivity regimes.

It was shown that the electrical resistivity of such manganites in a low-temperature regime can be analysed by evaluating the various conduction mechanisms which occur: electron–electron, electron–magnon, electron–phonon scattering and others \([13-15]\). Assuming all the temperature dependent scattering processes are described by a single power law, one can use the following empirical equation for this purpose:

\[
\rho(T) = \rho_o + \rho_n T^n,
\]

where \( \rho_o \) is the residual resistivity due to the domain/grain boundary and point defects scattering independent on temperature, \( n \) is the exponent indicating which scattering process is predominant.

The experimental dependences of metallic resistivity on temperature below \( T_m \) can be well fitted by Eq. (1). The fitting parameters are presented in Table. The exponent value close to \( n = 2 \) indicates that inelastic electron–electron scattering is the predominant mechanism. The change of the fitting parameters over time shows the change of the scattering mechanisms during the ageing process. The higher value of \( \rho_o \) of the LSMO-fast sample indicates the higher ratio of disorder in this film.

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Fig. 1. The resistivity change vs. temperature during the ageing and treatment of the LSMO-slow film. Symbols represent experimental data, lines are fitting by Eq. (1) results.
In the high-temperature region and in the insulating paramagnetic state \((T > T_m)\) which is important for sensor operation (room temperature), the experimental data can be analysed using models based on Mott’s variable range hopping (VRH), small polaron hopping (SPH) or the activation mechanism [16].

The activation model was incompatible with our experimental data, while the limited measured high-temperature range did not allow for a distinction between the VRH and SPH models. Our previous experiments on similar LSMO films having lower \(T_m\) revealed better agreement with the VRH model. Therefore, we used it additionally to analyse the influence of the ageing process on the electrical properties of the films. It was assumed that the \(e_g\) electrons are localised by the random spin-dependent potential above the Curie temperature and there is a competition between the potential energy difference and the hopping distance that the electrons can hop. In this case, conductivity is expressed by variable range hopping [16]:

\[
\sigma = \sigma_0 \exp(-2\alpha R - \Delta E / kT),
\]

where \(\sigma_0\) is residual conductivity, and \(1/\alpha\) is localisation length. The hopping occurs to a site at a distance \(R\) where the energy of the carrier is \(\Delta E\) higher than at the origin. According to Viret et al. [16], resistivity \((\rho = 1/\sigma)\) can be expressed as follows:

\[
\rho = \rho_\infty \exp[2.06(\alpha^2/N(E)kT)^{1/4}],
\]

which is the Mott expression with the characteristic temperature \(T_0\):

\[
kT_0 = 18\alpha^3 / N(E).
\]

Here \(N(E)\) is the density of available states, \(\rho_\infty\) is residual resistivity, \(k\) is the Boltzmann constant. The average hopping distance can be expressed as:

\[
R = [9 / (8\pi\alpha N(E)kT)]^{1/4}.
\]

The values of the characteristic temperature \(T_0\) were evaluated by fitting the experimental data to Eq. (3). It was obtained that \(T_0\) increases during the ageing of the films (during 3 months) and decreases after annealing. Following the ageing procedure, the \(T_0\) values were found to be 1.17 · 10⁶ K¹⁴, 8.7 · 10⁶ K¹⁴ and 5.0 · 10⁶ K¹⁴ for the LSMO-fast sample and 3.0 · 10⁶ K¹⁴, 3.4 · 10⁶ K¹⁴ and 1.7 · 10⁶ K¹⁴, respectively, for the LSMO-slow sample. The value of the parameter \(T_0\) can be a measure of the strength of the lattice distortion and is inversely proportional to the extent of the localised states (see Eq. (4)). Therefore, the increase of \(T_0\) can be an indication of the decreased localisation length \((1/\alpha)\) and thus the reduced average hopping distance \(R\). Such behaviour can be explained by the increased lattice relaxation of the polycrystalline material during long-term storage, thus producing additional defects or vacancies. Following Viret et al. [16], we evaluated the variation of localisation length during the ageing of the films. \(1/\alpha\) was calculated from Eq. (4) using the value of the density of states from [16] adopted for the composition \(x = 0.17\): \(N(E) = 6 \cdot 10^{26} \text{ m}^{-3} \text{eV}^{-1}\). Following the ageing procedure and using Eqs. (4) and (5), the localisation length and the average hopping distance at room temperature (in brackets) were found to be: 0.67 nm (2 nm), 0.34 nm (1.67 nm), 0.41 nm (1.77 nm) for the LSMO-fast samples and 1.05 nm (2.2 nm), 0.46 nm (1.82 nm), 0.59 nm (1.94 nm) for the LSMO-slow samples. These values are similar to those obtained by [3] and physically plausible because \(1/\alpha\) exceeds the ionic radius of manganese and \(R\) is several Mn–Mn separation distances.

Table 1. The main parameters obtained by fitting the resistivity data to Eqs. (1) and (2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ageing conditions</th>
<th>(\rho_0), Ωcm</th>
<th>(\rho_\infty) 10⁻⁵ Ωcm/K¹⁴</th>
<th>(n)</th>
<th>(T_0), 10⁶ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSMO-slow</td>
<td>as-prepared</td>
<td>0.45</td>
<td>0.000009</td>
<td>1.66</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>3 months in air</td>
<td>0.74</td>
<td>0.000002</td>
<td>2.05</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>annealed in Ar</td>
<td>0.68</td>
<td>0.000026</td>
<td>1.54</td>
<td>1.7</td>
</tr>
<tr>
<td>LSMO-fast</td>
<td>as-prepared</td>
<td>0.73</td>
<td>0.000005</td>
<td>1.84</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>3 months in air</td>
<td>1.42</td>
<td>0.000004</td>
<td>2.0</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>annealed in Ar</td>
<td>1.43</td>
<td>0.000028</td>
<td>1.62</td>
<td>5.0</td>
</tr>
</tbody>
</table>
3.2. The ageing influence on the magnetoresistance of LSMO films

The measurements of magnetoresistance $MR = \frac{R(B) - R(0)}{R(0)} \times 100\%$, where $R(B)$ and $R(0)$ were the resistances in non-zero and zero magnetic fields, respectively, were performed in the ferromagnetic metallic and paramagnetic insulating regions for both samples before and after the ageing process. The magnetic field was oriented in the film plane ($MR_\parallel$) and perpendicular to it ($MR_\perp$). The $MR_\parallel$ measured at $T < T_m$ (230 K) is presented in Fig. 2a for the LSMO-fast sample. It should be noted that all tendencies of MR behaviour were similar to that of the LSMO-slow sample; however, the obtained values in the same magnetic field were slightly lower. For example, for the LSMO-fast sample $MR_\parallel = -7.3\%$ at 0.8 T (see Fig. 2a), while for the LSMO-slow sample, $MR_\parallel = -6.2\%$ at 0.8 T. The higher MR values are usually obtained in the polycrystalline films having higher resistivity, which is consistent with the LSMO-fast sample. One can see (Fig. 2a) that the MR values are almost the same after the storage of the samples for 3 months in air and annealing them in an Ar atmosphere. The low-field magnetoresistance (abrupt drop of MR up to 0.1 T) which is related to spin-polarised tunnelling through grain boundaries [17] does not change either. Similar results were obtained at high temperature (see Fig. 2b). Such results are promising for the application of manganite films for the development of magnetic field sensors, whose response to the action of a magnetic field is proportional to its magnetoresistance value.

Figure 3 presents measurements of perpendicular magnetoresistance ($MR_\perp$) at low and room temperatures. At 230 K the demagnetisation field ($B_d$) due to the effect of its geometric shape (high aspect ratio, when film thickness is much smaller than width or length) is significant. Therefore, the tendency of the changes of the MR value is different. One can notice that $B_d$ decreases after storing the sample in air and again increases after annealing (Fig. 3a). It is known that the demagnetisation field is high due to the high aspect ratio of the sample [13]. However, the long-range ferromagnetic order at low temperatures is found only in single crystals or epitaxial films. For nanostructured films, we need to take into account the decreased long-range connectivity of the local magnetic moments of crystallites having a perfect structure and structurally and magnetically disordered grain boundaries. Due to the hydration of the sample after storage in air for 3 months, the connectivity between the crystallites is decreased due to the reduction of the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ion ratio in the grain boundary regions. After the annealing of the sample, the long-range interaction of magnetic moments is restored and can be even improved. As a result, the demagnetisation field is again increased. At paramagnetic state of 290 K (see Fig. 3b), the demagnetisation field is zero and the MR values remain similar: it slightly decreases

Fig. 2. The parallel magnetoresistance dependences vs. magnetic induction at (a) 230 and (b) 290 K temperatures after a series of treatment of the sample LSMO-fast.
during ageing from 2.5 to 2.2% at 0.8 T and again increases up to 2.35% after annealing.

The observed results cannot be explained simply by the above-mentioned processes of oxygen migration and the interaction of the surface of thin film with water molecules. Therefore, this requires further detailed study of the relaxation at the grain boundaries [5]. The treatment of the films at various temperatures which accelerate the ageing processes can be used in future experiments.

One of the possible methods of minimising the influence of ambient atmosphere conditions is to coat the surface of the samples with a special protective dielectric film. After the above-mentioned treatments, the samples were coated with a protective film (thermoglue TG-600, QingDao HengZhiJuan Chemicals Co, Ltd, China) and stored under normal conditions for 1 month. It was found that the measured resistance and magnetoresistance dependencies on temperature almost did not change.

In conclusion, it was determined that the resistivity of nanostructured La$_{0.83}$Sr$_{0.17}$MnO$_3$ manganite thin films changes significantly after long-term storage under normal conditions (in air). Treatment by heating in an Ar atmosphere does not restore the original values. Such long-term changes can be related to the long-term relaxation of the grain boundaries in the nanostructured films. The magnetoresistance of the films does not change significantly and this is an advantage for the development of magnetic field sensors. The passive protective coating of the surface of the films stabilises their electrical and magnetic properties.

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References


SENĖJIMO ĮTAKA NANOSTRUKTŪRIZUOTŲ MANGANITŲ SLUOKSNIŲ SAVITAJAI VARŽAI IR MAGNETOV ARŽAI

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Santrauka

Siekiant panaudoti manganitų sluoksnių įvairių prietaisų kūrimui, labai svarbu, kad jų parametrai ilgą laiką išliktų stabilūs. Ištirta senėjimo įtaka nanostruktūrizuotų La_{1-x}Sr_xMnO_3 (x = 0.17) sluoksniių, užaugintų MOCVD metodu ant polikoro (Al_2O_3 + MgO) padėklo, savitajai varžai ir magnetovaržai. Nustatyta, kad sluoksniui esant (keletą mėn.) atmosferoje, beveik du kartus padidėja jo varža (kaitiant 420 °C temperatūroje), o atmosferoje ji sumažėja 15 %. Padaryta išvada, kad sluoksnio savitosios varžos ilgalaikiaus pokyčių lemia tarpkrystalinių sričių relaksacija, todėl atsiranda papildomai defektai ir vakansijos. Sluoksnų magnetovarža mažai pakinta. Pasysvai žiauriai nuostabūs išmatavimai, esant sluoksniui feromagnetinėje būsenoje bei Motto šiuolinio laidumo modelui paramagnetinėje būsenoje.