

Metal–Insulator Transition in Epitaxial Films of LaMnO_3 Manganites Grown by Magnetron Sputtering

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Abstract—We have studied thin films of LaMnO_3 manganite grown by RF magnetron sputtering at high pressure on crystalline substrates with cubic symmetry. It is established that these films exhibit a metal–insulator transition, whereas LaMnO_3 grown on orthorhombic substrates remains in a dielectric state. The parameters of the metal–insulator transition have been studied as dependent on the level and symmetry of mechanical stresses that arise during the epitaxial growth of LaMnO_3 films on various substrates. The resistance of LaMnO_3 films grown on SrTiO_3 substrates has been studied as a function of the film thickness. It is found that the presence of excess oxygen due to substitution in the cation system can significantly influence the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ion ratio in the film and thus lead to the appearance of the metal–insulator transition.

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Manganites have been extensively studied in view of their possible use for creating functional elements of electronic and spintronic devices with unusual properties, including colossal magnetoresistance, a close relationship between ferromagnetism and conductivity [1], and high spin polarization of conduction electrons [2]. A distinctive feature of manganites of the $\text{La}_{0.66}\text{Sr}_{0.33}\text{MnO}_3$ type is the metal–insulator transition at a temperature that coincides (to within several kelvins) with the temperature of a transition to the ferromagnetic state. The formation of a magnetic phase in manganites significantly depends on the magnitude and symmetry of mechanical distortions that can either be created by an external action or arise during the growth of epitaxial films [3]. Single crystals of manganites of the LaMnO_3 (LMO) system are Mott insulators and antiferromagnets with a Néel temperature of about 140 K. However, thin epitaxial LMO films frequently exhibit a ferromagnetic transition at 100–150 K, while still remaining in a dielectric state [4]. However, weak deviations of the LMO composition from stoichiometry, e.g., due to La deficiency, can lead to the appearance of both ferromagnetism and the metal–insulator transition [5]. The present work was aimed at studying the effect of mechanical stresses arising during epitaxial growth of LMO films on their electrical and magnetic properties.

We have prepared and studied epitaxial LMO films with thicknesses from 4 to 40 nm on crystalline substrates with two types of symmetry: (i) cubic (001) LaAlO_3 (LAO), (001) SrTiO_3 (STO), and (001) $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$

(LSAT) and (ii) orthorhombic (110) NdGaO_3 (NGO). All samples were prepared using RF magnetron sputtering technique in oxygen at high pressure with substrate temperature of 760°C in $\text{O}_2 + \text{Ar}$ mixture at 0.15 mbar, followed by cooling in oxygen. Platinum contacts were then formed on the films and the resistance of samples was measured by the four-point-probe method at various temperatures in the 4.2–300 K range. The magnetic properties of LMO films were studied by the magnetic resonance method on a Bruker ER-200 spectrometer operating at 10 GHz in a field of up to 4 kOe. The crystalline structures of samples were determined by X-ray diffraction (XRD) techniques.

The obtained temperature dependences of the resistance of LMO films grown on cubic LAO and LSAT substrates revealed a transition from the metallic ($d\rho/dT > 0$) to insulator ($d\rho/dT < 0$) state at temperatures within 150–300°C (Fig. 1). A peak of resistance has been also observed for the films grown on STO substrates. The passage of this peak is accompanied by the transition to a ferromagnetic state, which is manifested by a shift of the magnetic-resonance field from 3 kOe (for a paramagnetic phase) to lower fields at decreasing temperatures (see the inset to Fig. 1). In the case of a constant magnetic field applied parallel to the substrate, this shift is related to the appearance of shape anisotropy in the magnetic film, which can be used to calculate its magnetization (see the inset to Fig. 1). For LMO films on orthorhombic NGO substrates, the temperature dependences of resistance exhibited dielectric-type behavior in the

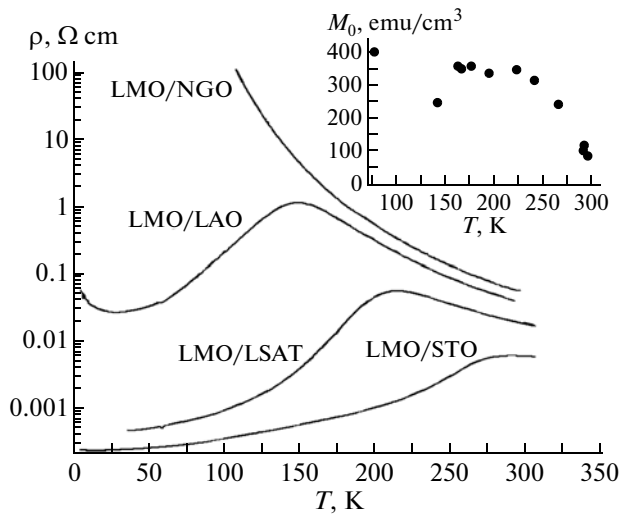


Fig. 1. Plots of electric resistance ρ vs. temperature T of 11-nm-thick LMO films grown on substrates with different types of crystalline symmetry: cubic (001)LAO, (001)STO, and (001)LSAT and orthorhombic (110)NGO. The inset shows the temperature dependence of magnetization M_0 of the LMO/STO film.

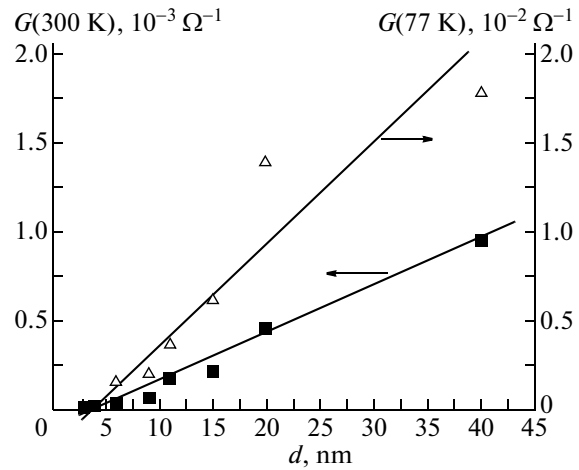


Fig. 2. Plots of electric conductivity G vs. thickness of LMO films on STO substrates measured at different temperatures: (squares) 300 K; (triangles) 77 K; solid lines show linear approximation of the experimental data.

entire range of temperature (100–300 K) and film thicknesses (5–100 nm) studied.

In order to determine the distribution of conductivity over the film thickness, we have prepared a series of LMO/STO samples with film thicknesses varying from 4 to 40 nm. The obtained dependence of conductivity G (calculated as the inverse resistance) on the film thickness is close to linear and intersects with the thickness axis at about 4 nm (Fig. 2). The presence of a “dead” layer at the film–substrate interface is characteristic of manganites with various compositions, and its thickness varies within 2–5 nm according to published data [6]. Thus, the distribution of conductivity over the film thickness outside the “dead layer” is nearly uniform and, hence, the appearance of metallic conductivity is not related to doping of the LMO film due to diffusion (in the given case, of Sr atoms) from the substrate material, since the depth of diffusion during epitaxial growth of manganites on STO substrates does not exceed several nanometers [7].

The crystalline structure of LMO films was studied by the XRD method. Measurements in the 2θ – ω scan regime were used to determine the LMO lattice parameter in the [001] direction. Figure 3 shows the typical XRD patterns for LMO films on STO and NGO substrates. Results of structural investigations are summarized in the table. A difference in the (002) peak widths of LMO films on STO and NGO substrates is explained by different thicknesses of the LMO films in samples used for these measurements. Assuming that, for epitaxial films with thicknesses below 40 nm, lattice constants in the ab plane correspond to those of the substrate, we have calculated the volume of elementary cells in the pseudocubic representation. For comparison, the table also presents the lattice parameters of single-crystalline LMO. As can be seen, the LMO unit cell volume in all samples is significantly smaller than that in stoichiometric volume LMO crystal (for which $V \approx 61 \text{ \AA}^3$).

Parameters of crystalline structure of LMO films on various substrates

Sample	Substrate symmetry	$c, \text{ \AA}$	$V, \text{ \AA}^3$	δ	$T_p, \text{ K}$
LMO/NGO(110)	Orthorhombic	3.909	58.19	0.17	–
LMO/LAO(001)	Cubic	3.862	55.42	–	141
LMO/LSAT(001)	Cubic	3.905	58.64	0.15	215
LMO/STO(001)	Cubic	3.864	58.92	0.13	290
LMO	–	3.952	61.16	–	–

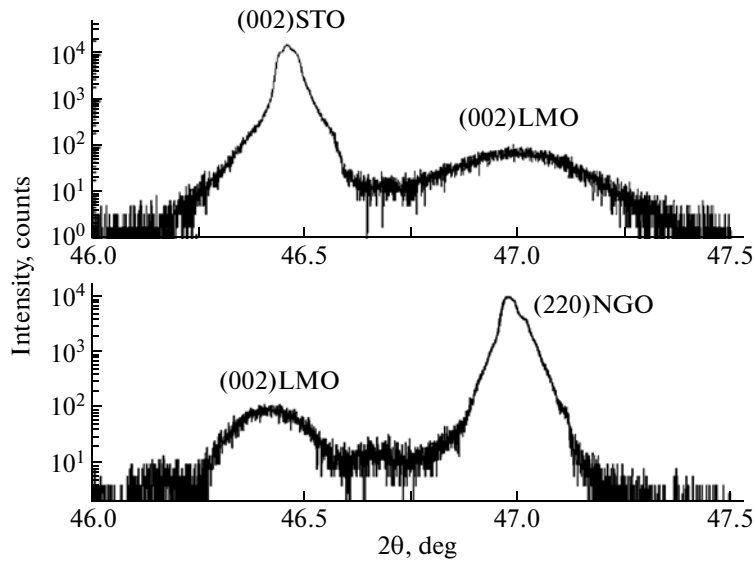


Fig. 3. Typical XRD patterns measured in the 2θ – ω scan regime for LMO films on STO and NGO substrates.

A decrease in the unit cell volume compared to that in stoichiometric volume LMO crystal amounted to 3–5% for films of NGO, LSAT, and STO substrates and was above 8% for the films on LAO substrates. This change can be related to the presence of excess oxygen in $\text{LaMnO}_{3+\delta}$ films [8]. Indeed, it was shown [8] that the oxygen excess in LMO is manifested by the formation of cationic La and Mn vacancies and accompanied by a significant decrease in the unit cell volume. The relationship between cell volume V and oxygen excess δ was described by a linear dependence as $V = 61.2 - 17.2\delta \text{ \AA}^3$ [8]. Using this dependence, it is possible to quantitatively estimate the oxygen excess in LMO films on STO, LSAT, and NGO substrates as $\delta = 0.13, 0.15,$ and $0.17,$ respectively. The obtained unit cell volume of LMO on LAO falls outside the range of applicability of the above phenomenological relationship and is probably explained by the formation of a crystalline structure that significantly deviates from the cubic symmetry and, hence, cannot be described in the pseudocubic approximation. Assuming that the excess oxygen is most probably uniformly distributed over La and Mn vacancies [8], one can approximately evaluate the average degree of oxidation for manganese ions and the ratio of concentrations of Mn^{3+} and Mn^{4+} ions, which determines the temperatures of the transition to a ferromagnetic state and the metal–insulator transition in the double-exchange model. For LMO films on STO, LSAT, and NGO substrates, the corresponding average degrees of Mn oxidation are +3.26, +3.3, and +3.34, respectively. These values correspond to an optimum doped region of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ -type manganites [9], which explains the appearance of the metal–insulator transition in LMO films on STO and LSAT substrates. The

absence of this transition in LMO/NGO films is probably explained by the lift of degeneracy of e_g levels in manganese ions under the action of substrate-induced orthorhombic distortions.

Thus, we have studied epitaxial LMO films grown on various substrates with different crystalline symmetries and lattice misfits. The appearance of excess oxygen during film growth and the related substitution in the cation system can significantly influence the ratio of concentrations of Mn^{3+} and Mn^{4+} ions and, hence, the temperatures of phase transitions. The metal–insulator transition is also significantly influenced by the symmetry of the crystalline structure of a substrate. The possibility of controlling crystal-lattice distortions in the films under consideration—e.g., by using piezoelectric substrates—will make possible new functional applications of manganite films.

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REFERENCES

1. G. H. Jonker and J. H. Van Santen, *Physica A* **16** (3), 337 (1950).
2. K. Chahara, T. Ohno, M. Kasai, and Y. Kozono, *Appl. Phys. Lett.* **63**, 1990 (1993).

3. G. A. Ovsyannikov, A. M. Petrzhik, I. V. Borisenko, A. A. Klimov, V. V. Demidov, and S. A. Nikitov, *J. Exp. Theor. Phys.* **108**, 48 (2009).
4. A. M. Petrzhik, G. A. Ovsyannikov, V. V. Demidov, A. V. Shadrin, and I. V. Borisenko, *Phys. Solid State* **55**, 759 (2013).
5. P. Orgiani, C. Aruta, R. Ciancio, A. Galdi, and L. Maritato, *Appl. Phys. Lett.* **95**, 013510 (2009).
6. A. A. Sidorenko, G. Allodi, R. De Renzi, G. Balistrino, and M. Angeloni, *Phys. Rev. B* **73**, 054406 (2006).
7. A. Kalabukhov, T. Claeson, P. P. Aurino, R. Gunnarsson, D. Winkler, E. Olsson, N. Tuzla, J. Borjesson, Yu. A. Boikov, I. T. Serenkov, V. I. Sakharov, and M. P. Volkov, *MRS Proc.* **1454**, 167 (2012).
8. J. A. M. Van Roosmalen and E. H. P. Cordfunke, *J. Solid State Chem.* **110** (1), 106 (1994).
9. S. M. Dunaevskii, *Phys. Solid State* **46**, 193 (2004).

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