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Giant magnetoresistance in $La_{0.7}Pb_{0.3}MnO_3$ thin film

S. I. Khartsev

A. Galkin Physicotechnical Institute, National Academy of Sciences of the Ukraine, Ukraine, 340114, Donetsk, R. Luxemburg st., 72
E-mail: khartsev@host.dipt.donetsk.ua

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Epitaxial thin films of $La_{0.7}Pb_{0.3}MnO_3$ have been grown on (100) $LaAlO_3$ and (110) $SrTiO_3$ substrates by dc magnetron sputtering. The magnetic-field and temperature-dependent resistivity of as-deposited and post-annealed films was examined. At $H = 10$ kOe the maximum observed magnetoresistance ratio $(R_0 - R_H)/R_0$ was 62%. The bolometric response to 0.94-μm low-frequency modulated radiation in the film with the temperature coefficient of resistance $d \ln R/dT = 14\%$ was studied. The transport properties are described using Zhang's spin-polaron theory. An unusual approach to stabilizing the film temperature at the point corresponding to the maximum of the magnetoresistance ratio and responsivity is discussed.

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Perovskite metal-oxide manganites with the formula $La_{1-x}A_xMnO_3$, where A = Ca, Sr, Ba, Pb, have attracted interest [1–4] in recent years due to presence of the semiconductor–metal (SM) transition coupled with the paramagnetic–ferromagnetic one and the demonstration of a giant magnetoresistance (MR) in the vicinity of the transitions. Epitaxial thin films of the above-mentioned compositions are more attractive for an application due to greater MR ratio in comparison with the bulk and due to the possibility of controling the transition temperature (T_c) by changing the oxygen contents [3–4]. Abrupt character of the temperature dependence of the resistivity allows us to use such films as a bolometric detector, as has been shown recently [5].

The transport and bolometric optical response measurements were performed on series of $La_{0.7}Pb_{0.3}MnO_3$ epitaxial films of thickness 300 nÅ *in situ* grown by dc magnetron sputtering. The target of nominal composition was fabricated by reaction of the high-purity component oxides at 900 °C (36 h), followed by grinding, pressing into disk form (40×1 mm^2), and conglomerating at 1150 °C (10 h). X-ray diffraction measurements indicate orthorhombically distorted, single-phase, perovskite structure.

All films were made in 15-mTorr argon-oxygen mixture (1:1). Deposition rate was ~ 0.1 nm/s at a plasma current of 100 mA and substrate-target distance of 5 cm. Film 1 was grown on a (100)-oriented $LaAlO_3$ (LAO) substrate at temperature $T_{sub} = 575$ °C. Film 2 was grown on a (110)-oriented $SrTiO_3$ (STO) substrate at $T_{sub} = 625$ °C. After the deposition films were cooled to room temperature in 250-Torr oxygen at the rate of 5 K/min. Their crystal orientation was determined by X-ray diffraction measurements. Film 1 was found to be ⟨100⟩-oriented, while film 2 had ⟨110⟩-orientation. All films had epitaxial in-plane alignment.

Magnetoresistance and electrical resistance of the films were measured by standard four-probe dc technique in an electromagnet with a field of up to 10 kOe. The sensing current varied from 1 μA to 100 μA. The MR ratios were defined as

$$\Delta R/R \equiv (R_0 - R_{10\,\mathrm{kOe}})/R_0 \ .$$

All as-deposited films demonstrate a sharp drop of $\rho(T)$ below T_c and activated behavior above T_c (Fig. 1). The MR effect reaches its maximum at a point close to the temperature at which the maximum value of dR_0/dT occurs (inflection point). The film grown on STO substrate shows the highest $T_c = 256$ K, while the films deposited on LAO substrates have $T_c = 225$ K. These transition temperatures are too far from $T_c = 326$ K obtained by Searle and Wang [6] for a single crystal of $La_{0.7}Pb_{0.3}MnO_3$. The decrease in the oxygen content, as we know, could also decrease the SM

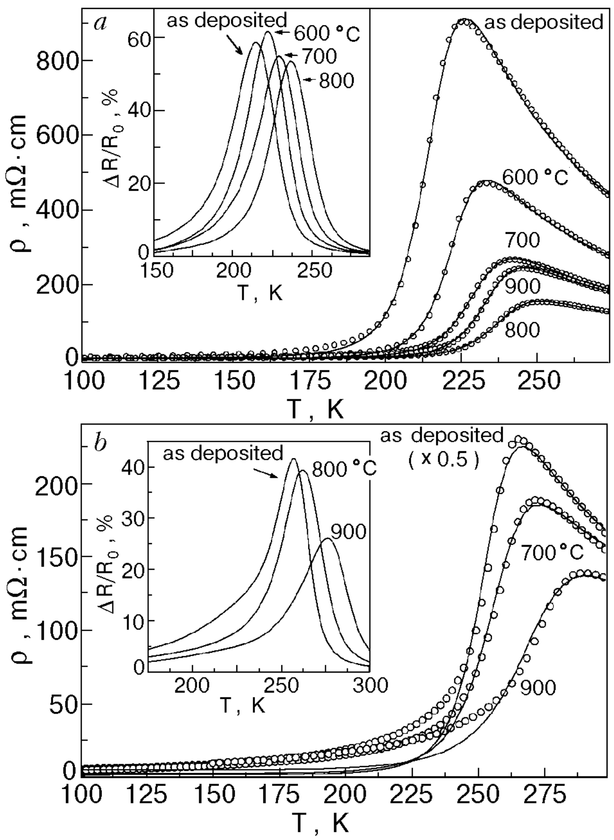

Fig. 1. Resistivity vs. temperature for $La_{0.7}Pb_{0.3}MnO_3$ films deposited on a $LaAlO_3$ substrate (*a*) and $SrTiO_3$ substrate (*b*) annealed at different temperatures. The open circles are representative data points and the lines are a least-squares fit of Eq. (1) to the data. The inset shows 10-kOe magnetoresistance.

transition temperature in the La-Pb-Mn-O system [3], because oxygen deficiency leads to a decrease in Mn^{4+} concentration. That was the reason for carrying out the series of post-deposition annealings in oxygen flow. Each film was subsequently annealed at different temperatures for 0.5 h. The results of treatments are shown in Fig. 1. The increase in the annealing temperature (T_a) leads to a monotonic increase of T_c only for on STO deposited film 2, while film 1 demonstrates the increase of T_c only to $T_a = 800$ °C. Note that the sharpness of the $\rho(T)$ peak, which can be correlated with the film quality, increases only for film 1 after annealing at 600 °C, in contrast with the other cases which lead to a degradation of this characteristic. Such development of film 1 results in improving the MR ratio from 58.8% for as-deposited film to 62%. Finally, an attempt to attain bulk single-crystal T_c has not been successful. It can be suggested that a possible reason could be elastic stress that arises in film clamped to substrate from substrate-film lattice mismatch. In general, epitaxial film must be considered as complex with the substrate, particularly when we face sharp phase transition with a discontinuity in the lattice parameters [7]. The different behavior of transport properties of the films under study grown on LAO and STO substrates is argument in favor of such conclusions.

For interpretation of the obtained $\rho(T)$ behavior it is convenient to use Zhang's spin-polaron theory [8] based on a Hamiltonian which consists of a single-electron kinetic energy term, a term represents a magnetic interaction between localized spins, and a term of the interaction between mobile carriers and localized spins. By this model the current carriers are magnetic polarons in the entire temperature range under consideration. There are two independent processes of the carrier scattering: elastic and inelastic. The first process dominates at low temperatures the transport by coherent elastic electron hopping leads to decreasing of conductivity as the temperature increases. The second process (high temperatures) corresponds to incoherent, inelastic, thermally activated hopping, where the resistivity decreases with increasing temperature. Using an approximation of a single optical magnon frequency ω_0 , we can describe these processes by a simple formula [8]:

$$\frac{\rho(0)}{\rho(T)} = \exp\left[-\alpha N(\omega_0)\right] + \frac{b^2}{E_a k_B T} \exp\left(-\frac{E_a}{k_B T}\right), \quad (1)$$

where $N(\omega_0) = [\exp(\omega_0/k_B T) - 1]^{-1}$ is the number of thermal magnons, E_a is the activation energy of the spin polaron, α is the structure factor, and b is the function of the basic Hamiltonian. Using E_a , ω_0 , b, and α as the fitting parameters, we can fit Eq. (1) to the experimental $\rho(T)$ data. The solid lines in Fig. 1 represent the results of least-squares fitting. Table contains our parameters.

Reasonable agreement between theory and resistivity data for the temperature region close to the peak of resistivity (especially in case of film 1) is evident. It is appropriate to mention here that Zhang's model omits well-knowns binding [9,10] between the low-temperature conductivity of ferromagnetic perovskite structures and magnetization. Apart from the basic Hamiltonian of the theory ignores the term that describes the film—substrate stress. Neglect of these factors may introduce the observed disparity between predicted and experimental low-temperature resistivity. Nevertheless, good prediction of resistivity transformations and acceptable values of the phenomenological parameters (particularly, polaron hopping energy E_a is close similar to reported in [11]) allows the observed $\rho(T)$ dependences to be described as a cross-

Table

Parameters of the least-squares fit of Eq. (1) to the resistivity data

Film	ω_0, K	E_a, meV	b, K	α
Film 1 as deposited	1399 ± 20	114 ± 1	636 ± 15	3976 ± 361
Film 1 (T_a = 600 °C)	1664 ± 22	105 ± 0.9	451 ± 13	10247 ± 720
Film 1 (T_a = 700 °C)	1600 ± 25	100 ± 0.9	427 ± 12	5862 ± 440
Film 1 (T_a = 800 °C)	1846 ± 30	91 ± 0.8	396 ± 11	11733 ± 804
Film 1 (T_a = 900 °C)	1764 ± 41	104 ± 0.8	431 ± 17	10619 ± 973
Film 2 as deposited	1943 ± 180	98 ± 10	369 ± 57	13240 ± 345
Film 2 (T_a = 700 °C)	2009 ± 120	80 ± 7.9	316 ± 67	11555 ± 172
Film 2 (T_a = 900 °C)	2098 ± 137	77 ± 11.7	435 ± 56	6360 ± 215

over from metallic conduction at low temperatures to the hopping-type conduction at high temperature in accordance with the model under discussion.

The resistivity as a function of applied magnetic field as well as $T_H(H)$ and $T_\Delta(H)$ dependences (where T_H and T_Δ are temperatures of the resistivity and MR peaks) were measured. The results are shown in Fig. 2. The behavior of $R(H)$ curves is too far from saturation up to a field of 10 kOe and completely isotropic in regard to the field orientation in the film plane. The MR ratio for the field perpendicular to the film plane is close to the ratio for the field parallel to the film plane for $H = 10$ kOe, but there is sufficient difference for a weak field due to the shape factor. The question of full MR isotropy in the films under study is unanswerable without magnetization versus field measurements. Unfortunately, no such measurements can be carried out by us. The fact that the temperature of the MR ratio maximum for a perpendicular field orientation is always higher than T_Δ for parallel orientation has been established. For example, this difference is above 3 K for film 1 at $H = 3$ kOe. The $T_H(H)$ dependences are almost linear, in contrast with $T_\Delta(H)$, which demonstrates threshold character. In our opinion, such difference can be accounted for by possible indirect magnetization dependence: magnetic state is ferromagnetic when we measure $T_\Delta(T < T_c)$ and paramagnetic with $M \to 0$ at $T > T_c$ $(T_H > T_c)$.

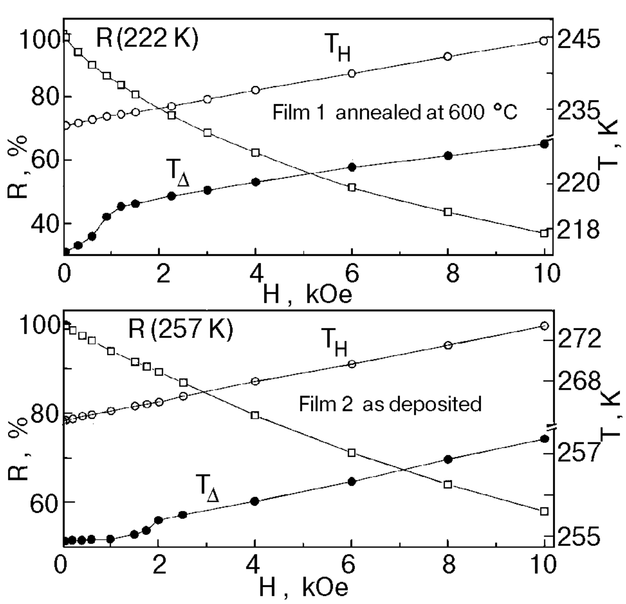

Fig. 2. Resistivity (❐), temperatures of the magnetoresistance (T_Δ) and resistivity (T_H) peaks as a function of the magnetic field for film 1 (*a*) and for film 2 (*b*).

Annealing of film 1 at 600 °C improves the sharpness of semiconductor-metal transition, as was indicated above. The value of the temperature coefficient of resistivity (TCR = $d \ln R/dT$) is about 12–14% K^{-1} in the vicinity of the phase transition. As is well known, the voltage of the optical response caused by the resistance modulation due to radiation-induced temperature modulation in the presence of a bias current is proportional to the temperature derivative of the electrical resistance [12]

$$\Delta V = I \frac{dR}{dT} \Delta T , \qquad (2)$$

where I is the bias current, R is the electrical resistance of the sensor (MR film), and ΔT is the temperature difference between the film-substrate composite and the heat sink. Hence, the value of TCR is a key factor of the detector performance. The responsivity S of the radiation detector (the ratio output voltage to the incident power) can be calculated from the equation

$$S = \frac{\alpha I(dR/dT)}{G_{\mathrm{eff}}(1 + \omega^2\tau^2)^{1/2}} , \qquad (3)$$

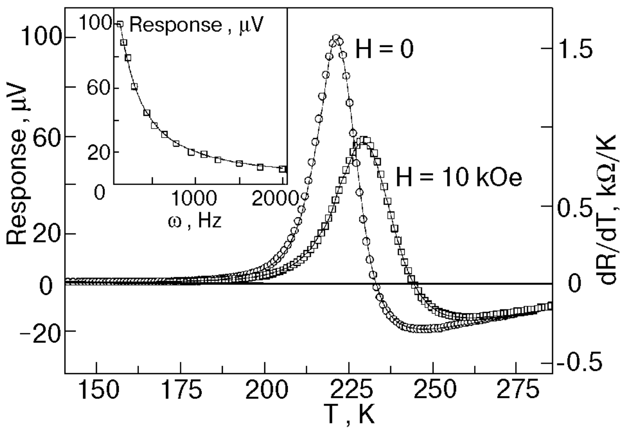

Fig. 3. Infrared response of film 1 with modulation frequency 20 Hz and bias current 100 μA for $H = 0$ (❍) and $H = 10$ kOe (❒). Solid lines are corresponding temperature derivatives dR/dT. The inset shows modulation angular frequency dependence of the response at 222 K. Here the solid line is the best fit of Eq. (3) to the data.

where α is the absorptance of the detector, G_{eff} is the effective thermal conductance, ω is the modulation angular frequency, and τ is the thermal time constant of the detector.

Infrared response measurements were performed in a thermostat cooled by liquid nitrogen flow. The film was clamped to sapphire plate mounted on the cooper holder. Four-probe technique was used with a direct 100-μA bias current. A 500-μW infrared diode with $\lambda = 0.94$ μm served as a radiation source. The distance from the output diode window to the film surface was 5 mm. The response was metered by a lock-in amplifier. The modulation voltage and reference signal were taken from a low-frequency oscillator. The temperature dependence of the response voltage is shown in Fig. 3 for zero applied magnetic field at $H = 10$ kOe. The solid curves correspond to data obtained by differentiating $R_0(T)$ and $R_{10\text{kOe}}(T)$ (see Fig. 1). The strong correlation between the response voltage and corresponding derivative of $R(T)$ is apparent. This correlation signifies the bolometric character of infrared response. Using Eq. (2), we found the amplitude of the temperature modulation to be ~ 0.6 mK.

The inset in Fig. 3 represents the best fit of Eq. (3) to the modulation angular frequency dependence of the response. The fitting parameter τ was found to be ~ 6 ms. Preliminary studying shows that the detector is suitable even at room temperature (but with the responsivity only 10% of the maximum) and with long-wave infrared radiation such as hand heat. We hope to obtain a set of data concerning the thermal properties of films and substrates in our future research.

The practical application of MR films for magnetic field as well as radiation detection demands a reliable temperature stabilization of the operating point (T_{op}). Under this condition the maximum possible detectivity can be reached. The exponential character of a $R(T)$ dependence promises to facilitate the solution of this problem. The solution is possible when a film has $T_{\text{op}} > T_s$, where T_s is the surrounding temperature. In such a situation T_{op} can be reached at the expense of Joule power U^2/R, where U is the voltage applied to a film. In so doing, a film temperature would be relatively independent of T_s and stabilized due to the positive value of dR/dT. On the one hand, increasing T_s leads to an increase of the film temperature and resistance and, on the other hand, a higher R causes the Joule power to decrease. Such a feed back is valid for the opposite case in which T_s starts to decrease. In order to check this speculation the following experiment was carried out. Film 1 was situated in a thermostat and clamped to the holder with low thermal conductance. The holder temperature was controlled by a thermocouple, while for the film temperature control its resistance was used as a resistive thermometer. The operating point of the $R(T)$ dependence (at which MR ratio and optical response reach the maximum value) was estimated to be 222 K. A thermostat was cooled to 200 K, while film was heated to 222 K by increasing the bias current. The corresponding voltage was fixed. Then the thermostat temperature was changed to 215 K ($\Delta T_s = 15$ K). Under this condition the film temperature variation did not exceed 4.5 K, which is ~ 3 times less than ΔT_s. The $I-V$ characteristic corresponding to the Joule heating of the film 1 at the rate of 0.2 V/s is shown in Fig. 4. The ending of the linear part of the $I-V$ characteristic indicates the beginning of heating the film. Of

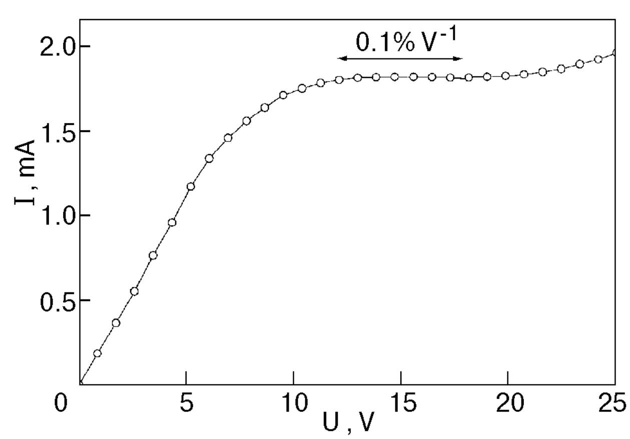

Fig. 4. The current-voltage characteristic demostrates the heating of film 1 at the start temperature of 200 K.

special interest is the plateau in the vicinity of the operating point with $d \ln I/dU < 0.1\%\ V^{-1}$ within the interval $\Delta U \sim 5$ V. In this case the film works as a low-frequency stable current device.

In conclusion, $La_{0.7}Pb_{0.3}MnO_3$ epitaxial thin films were grown on LAO and STO substrates at different substrate temperatures. The film properties, including transition temperature, resistivity and MR ratio, depend on the type of substrate, deposition regime and oxygen content. Using Zhang's magnetic polaron theory, we established the phenomenological relation describing the temperature dependence of the film resistivity. An essential value of temperature coefficient of resistivity allows to use these films as an infrared bolometric detector as well as a low-frequency stable current device.

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1. K. Chahara, T. Ohno, M. Kasai, and Y. Kozono, *Appl. Phys. Lett.* **63**, 1990 (1993).
2. G. Srinivasan, V. Suresh Babu, and M. S. Seehara, *Appl. Phys. Lett.* **67**, 2090 (1995).
3. K. M. Satyalakshmi, S. S. Manoharan, M. S. Hedge, V. Prasad, and S. V. Subramanyam, *J. Appl. Phys.* **78**, 6861 (1995).
4. H. L. Ju, C. Kwon, Qi Li, R. L. Greene, and T. Vekatesan, *Appl. Phys. Lett.* **65**, 2108 (1994).
5. M. Rajeswari, C. H. Chen, A. Goyal, C. Kwon, M. C. Robson, R. Ramesh, T. Venkatesan, and S. Lakeou, *Appl. Phys. Lett.* **68**, 3555 (1996).
6. C. W. Searle and S. T. Wang, *Can. J. Phys.* **47**, 2706 (1969).
7. A. M. Grishin, S. I. Khartsev, and K. V. Rao, *Appl. Phys. Lett.* **68**, 2008 (1996).
8. S. Zhang, *J. Appl. Phys.* **79**, 4542 (1996).
9. F. M. Hundley, J. J. Neumeier, R. H. Heffner, Q. X. Jia, X. D. Wu, and J. D. Thompson, *J. Appl. Phys.* **79**, 4535 (1996).
10. J. Fontcuberta, B. Martinez, A. Seffer, S. Pinol, J. L. Garcia-Munoz, and X. Obrador, *Phys. Rev. Lett.* **76**, 1122 (1996).
11. M. Rubinstein, D. J. Gillespie, and J. E. Snyder, *Phys. Rev.* **B56**, 5412 (1997).
12. Z. M. Zhang and A. Frenkel, *J. Superconduct.* **7**, 871 (1994).