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Significant increasing of onset temperature of FM transition in LSMO thin films

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ABSTRACT

$La_{0.67}Sr_{0.33}MnO_3$ (LSMO) thin films with a significant increased onset temperature of ferromagnetic transition were prepared using an on-axis *dc* magnetron sputtering from a stoichiometric ceramic target onto one-side polished MgO (0 0 1). The highest temperature of insulator-metal transition was observed at $T_P = 416$ K. Magnetization hysteresis curves taken at $T = 398$ K indicate the beginning of the ferromagnetic transition above 400 K. The negative magnetoresistance reaches 15% at a temperature of 400 K. We show that the LSMO thin films with increased temperature values of resistance peak T_P and Curie temperature T_C are characteristic by a proper microstructure with distorted orthorhombic unit cells. This microstructure is developed during the layer growth, it is not caused by the underlying substrate and it is linked with an appropriate pseudocubic out-of-plane lattice parameter $a_c^{\perp}$, splitted Bragg reflections in rocking curves and as well as in reciprocal space maps.

1. Introduction

Perovskite manganites, especially $La_{1-x}Sr_xMnO_3$ group have attracted much attention due to the observation of a colossal magnetoresistance (CMR) effect and high Curie temperature (T_C). Manganite thin films have many potential applications exploiting their magnetic properties, e.g. low-cost magnetic sensors, SFS junctions, etc.

Recently, Boschker et al. [1] have presented an overview of the fabrication and properties of high quality $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) thin films. They compare the properties of LSMO films on $SrTiO_3$ substrates prepared by different groups using mainly pulsed laser deposition technique. They show that the maximum of the Curie temperature for LSMO thin films does not exceed the $T_C = 370$ K which was observed for the LSMO single crystal [2]. However, Sadoc et al. [3] have recently shown the possibility of the Curie temperature increasing by an appropriate strain application in the film. It is expected that the LSMO film deposited on a cubic substrate with $a = b$ parameters slightly larger than the bulk manganite value should ensure an increase of the manganite in plane parameters and a decrease of the *c*-parameter. With $c/a < 1$ the $d_{x^2-y^2}$ orbital occupation and large T_C is expected. They claim that the control of the orbital ordering [4] responsible for the spectacular T_C increase cannot be imposed by the substrate only. The authors stress that the strain applied by the substrate need to be maintained over the growth direction by the alternation of the manganite layers with another appropriate material–$BaTiO_3$ insulating layers. This is in an agreement with some authors who were not able to increase T_C only using of a suitable substrate [5].

The CMR materials exhibit very large negative magnetoresistance at temperatures close to the T_C. At this temperature the materials undergo a ferromagnetic (FM)–paramagnetic (PM) transition. Simultaneously, in most cases, they reach the resistivity peak at a temperature T_P (close to the T_C) indicating a correlation between transport and magnetic properties. At the T_P, the CMR materials undergo a metal-insulator transition with metal properties for the $T < T_P$. In spite of favoring substrates like $SrTiO_3$, $NdGaO_3$, $DyScO_3$ [1] with a perfect lattice matching to the LSMO very interesting results on MgO substrates [6] or MgO buffer layers [7] were obtained. A $T_C = 365$ K [6] and a $T_P = 382$ K [7] were presented.

In this paper we show the possibility of the LSMO film preparation with a reproducible increased T_P value above 400 K (and also FM as well as magnetoresistance properties). The LSMO films are grown directly on single crystal MgO substrates without any additional layer producing strain in the LSMO films. This fact is in contradiction to the results presented in [3]. The enhanced $T_P \geq 400$ K for LSMO films was presented in [8–10] but without any detailed structural study.

2. Experimental

The LSMO films were deposited using an on-axis *dc* magnetron sputtering from a stoichiometric ceramic target onto a one-side polished MgO (0 0 1) substrate [11,12]. Everything, the *dc* magnetron

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sputtering system, the stoichiometric ceramic target and the substrates were obtained from the commercially available sources. The deposition was performed in an Ar(80%) + O_2(20%) atmosphere at a total pressure of 65 Pa. The substrate was heated to 800 °C during the deposition. The thickness and the growth rate of the LSMO films were in the range of about 26–150 nm and 12 nm/min, respectively. The LSMO films were subsequently in situ annealed in O_2 (104 Pa) at 800 °C for an hour.

Auger electron spectroscopy (AES) depth profiling was carried out in a Varian Auger electron spectrometer equipped with a cylindrical mirror analyzer and EX 05 VG ion gun. XRD analyses were carried out using Bruker D8 DISCOVER diffractometer equipped with X-ray tube with rotating Cu anode operating at 12 kW. All measurements were performed in parallel beam geometry with medium resolution set-up with parabolic Goebel mirror in the primary beam but without monochromator.

For the resistance vs. temperature (*R–T*) dependence a standard four-point method was applied in two different equipments: a furnace without the possibility to apply an external magnetic field but with a temperature range up to 480 K, and a commercially available Physical properties measurement system (PPMS) equipment (fy. Quantum Design) with limiting temperature range to 400 K for the magnetoresistance measurements. The electrodes on the samples were formed with silver paint and Cu wires. Such electrodes showed high stability and reliability up to temperatures of 600 K. The magnetic properties of the films were measured in magnetic properties measurement system (MPMS) equipment (fy. Quantum Design) in the temperature range 250–400 K.

3. Results and discussion

The composition of the prepared films determined by AES is the same as the stoichiometric sputtering target (Fig. 1). In spite of the same stoichiometric composition of both- the LSMO target and the thin film- we observed a significant difference in the *R–T* dependences. The optimization of the LSMO film preparation enables to prepare films with some parameters significantly exceeding the parameters of the bulk material. The beginning of the transition from the insulator into metal state was reproducibly reached close to or above 400 K. In the Fig. 2 the *R–T* dependence of the LSMO thin film with a resistance maximum at the temperature of T_P = 416 K is shown. This value is about 40 K higher than the bulk value T_P = 374 K. In the case of some films the resistance peak is broad and it is composited from two parts with two different maxima. One maximum appears in the temperature range 350–360 K and it may characterize the bulk properties of the LSMO.

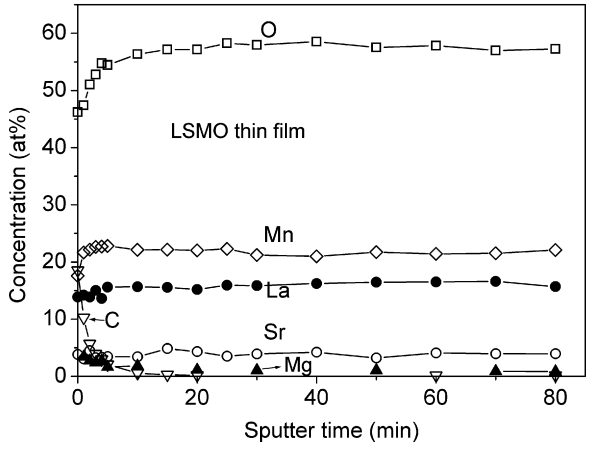

Fig. 1. AES concentration profile of a 100 nm thick LSMO film prepared at a total pressure of 65 Pa.

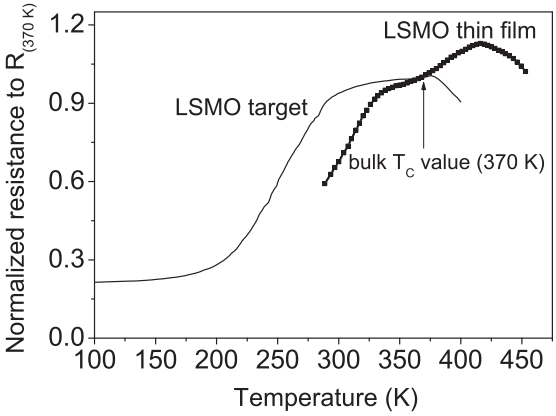

Fig. 2. *R–T* dependences of the LSMO thin film and the LSMO target (bulk) material with the T_P at 416 and 374 K, respectively. The *R–T* dependences were taken in zero applied magnetic field.

This maximum is visible on the *R–T* dependence as a bump at the temperature *T* = 350 K (Fig. 2). The second maximum is registered between 380–416 K, where the T_P = 416 K is the highest temperature of the insulator-metal transition for our LSMO films prepared on single crystal MgO substrate.

To verify the ferromagnetic properties of the LSMO films with the T_P > 400 K (Fig. 3 inset) we measured their electrical magnetoresistance with the PPMS equipment. The *R–T* dependences from 2 to 400 K of the film with T_P = 406 K in applied magnetic field of *B* = 0, 4.5 and 9 T parallel to the film surface are shown in the Fig. 3. The negative magnetoresistance at a temperature of 400 K is apparent (−15%). All three curves exhibit a monotonous decreasing behavior with their maxima above 400 K indicating the FM–PM transition at this temperature. This value is well above the bulk LSMO properties.

On the other side the resistance peak in zero magnetic field is broad with low decrease of the resistance between the T_P = 406 K and the temperature of around 350 K. The change in the resistance represents only 10%. Since the magnetic properties of the manganites are closely linked to electron transport properties (below the T_P the CMR material is in ferromagnetic metal state) the FM properties of the LSMO thin films in this temperature range are weak. The highest magnetoresistance response (−35%) to the applied magnetic field (9 T) was observed at a temperature of 350 K (at the beginning of the strong resistance decrease). The typical low temperature resistivity reaches values of $\rho_{(0)}$ = 100–200 μ Ω cm and at temperature *T* = 400 K ρ_{max} = 3–6 m Ω cm in zero magnetic field.

The magnetic properties (magnetization, *dc* susceptibility) of the LSMO thin films were investigated by the MPMS equipment. The measurement of *dc* susceptibility revealed the main (bulk)

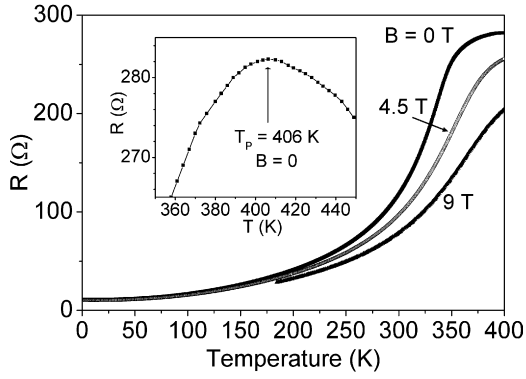

Fig. 3. *R–T* dependences of the 60 nm thick LSMO film with the T_P = 406 K for various magnetic field.