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Enhanced magnetoresistance in nanocrystalline $La_{0.6}Pb_{0.4}MnO_3$ thin films

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Abstract

The nanocrystalline $La_{0.6}Pb_{0.4}MnO_3$ thin films have been grown on (1 0 0) $SrTiO_3$ substrates using pulsed-laser ablation technique. The atomic force microscopy and X-ray diffraction measurements show that the films consist of single-crystalline grains of an average size of ~ 17 nm with *c*-axis perpendicular to the substrate plane. These nanocrystalline films exhibit an enhanced magnetoresistance of $>100\%$ at 1 T in the vicinity of the Curie temperature. Magnetization data suggest that grain boundaries act as tunnel barriers leading to an enhancement in the magnetoresistance.

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1. Introduction

Thin films of colossal magnetoresistance (CMR) materials $R_{1-x}A_xMnO_3$ (R = trivalent rare-earth ion, e.g. La, Nd, etc., and A = divalent ion, e.g. Ba, Sr, Ca, Pb, etc.), which exhibit a large change in electrical resistance on application of magnetic field, are potential candidate for several device applications [1] such as magnetic read heads [2], magnetoresistive random access memory (MRAM) [3], spin-polarized quasi-particle devices (SPQUID) [1,4,5], etc. The CMR thin films exhibiting higher magnetoresistance at low magnetic fields is a prerequisite for many of these device applications [6,7]. This has prompted researchers to grow CMR thin films—using different techniques such as laser ablation [8,9], molecular beam epitaxy [10], sputtering [11], chemical vapor deposition (CVD) [12–15] etc.—to investigate the correlation between microstructure and magnetotransport properties. The films

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grown by different techniques were found to be either epitaxial or polycrystalline [8–16]. The magnetoresistance of CMR films has been found to depend on the crystallinity of the films [16]. For epitaxial films, the temperature dependence of magnetoresistance exhibits a peak just below the ferromagnetic transition temperature and has a very small value at low temperatures. This behavior is similar to those observed for single crystals [16] and has been theoretically explained using electron hopping via "double exchange" between Mn^{3+} and Mn^{4+} ions [17]. On the other hand, the polycrystalline films show a large magnetoresistance over a wide temperature range between the ferromagnetic transition and 5 K. The additional low-field magnetoresistance in polycrystalline films has been attributed to spin-dependent tunneling across the grain boundaries [12,18]. This in fact has been experimentally verified by measuring the magnetoresistance across the controlled grain boundaries, such as CMR films on a bi-crystal substrate [6,19] and trilayer tunnel junctions, i.e. a thin insulating layer is sandwiched between two CMR layers [20]. It is therefore evident that preparation of crystalline films having very small crystallite grains (of the order of nanometer scale) is important for achieving high magnetoresistance. This is essentially due to the fact that a large surface-to-volume ratio of nanocrystallites would result in the enlarged grain boundaries and hence in an enhanced magnetoresistance. Growth of nanocrystalline films also assumes significance from the basic studies as the physical properties at nanosize are expected to differ from those of bulk crystalline or amorphous materials. So far growth of such nanocrystalline CMR films has not been reported in the literature.

Recently, we reported the optimization of growth parameters for epitaxial thin films of $La_{1-x}Pb_xMnO_3$ for the in situ fabrication of multilayers comprising of high-temperature superconductors (HTS) and CMR material [8]. We have found that the structural and magnetoresistive properties of the $La_{1-x}Pb_xMnO_3$ films grown on (1 0 0) $SrTiO_3$ substrates strongly depend on the growth temperature. The $La_{1-x}Pb_xMnO_3$ films were found to grow epitaxially at a substrate temperature of 600°C. For growth temperatures >600°C, the microstructure of films turned granular (grain size in hundreds of nanometers) due to Pb evaporation from the film.

In this paper, we report on the morphological, structural, magnetotransport and magnetic properties of laser-deposited $La_{0.6}Pb_{0.4}MnO_3$ thin films grown at substrate temperatures lower than 600°C. It was found that at lower substrate temperatures the grown films have nanocrystalline character and their properties are different than those of epitaxial or polycrystalline films of same chemical composition.

2. Experimental details

The $La_{0.6}Pb_{0.4}MnO_3$ (LPMO) thin films were grown on (1 0 0) $SrTiO_3$ (STO) single-crystal substrates by pulsed-laser ablation technique, as described earlier [8]. Briefly, a laser beam from a KrF excimer laser of wavelength 248 nm, pulse width of 20 ns and repetition rate of 5 Hz was focused onto a rotating target of nominal composition $La_{0.6}Pb_{0.4}MnO_3$. The depositions were carried out at a substrate temperature of 550°C under an oxygen partial pressure of 0.2 Torr. All other growth parameters were same as those reported in earlier paper [8]. The thickness of the grown films was 50 nm.

The film morphology was assessed using atomic force microscopy (AFM). AFM measurements were carried out in contact mode using a scanning probe microscope (model-SPM Solver P47). The crystallographic orientation of the films was analyzed by means of X-ray diffraction (XRD) using Cu K_α radiation. The electric resistance of films was measured using standard four-probe DC method. The magnetic properties were measure using a SQUID magnetometer. In both measurements, the magnetic field was applied parallel to the plane of the substrate.

3. Results and discussion

A typical 1400 nm $\times$ 1400 nm AFM scan of LPMO films is shown in Fig. 1(a). The film consists of very fine grains, which is seen more

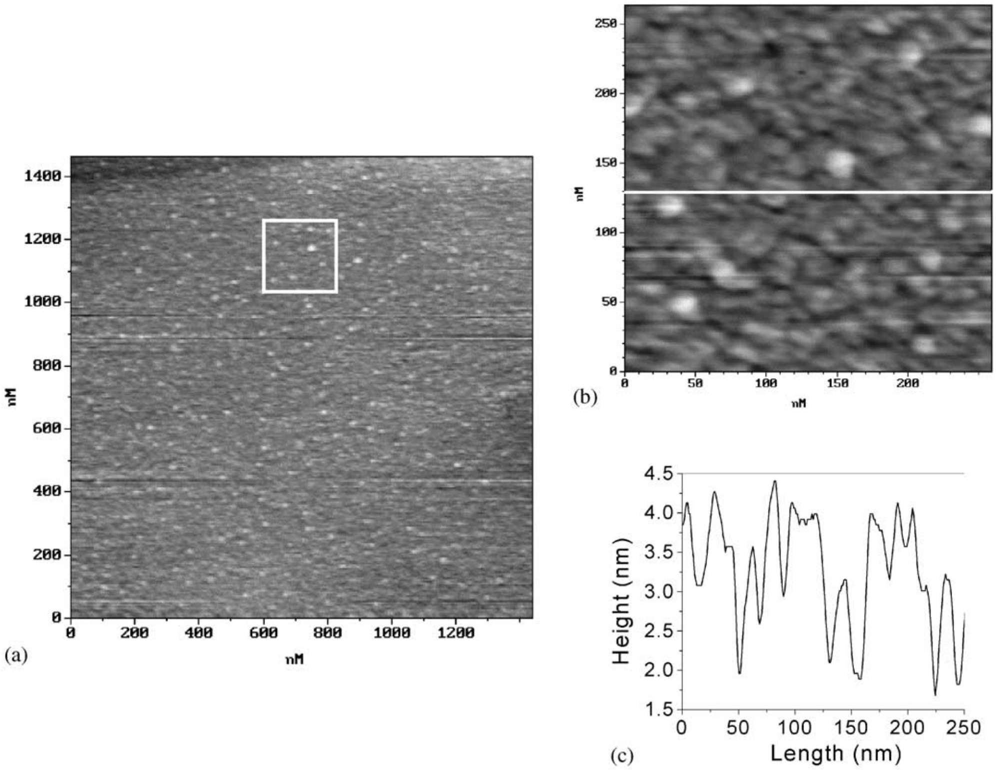

Fig. 1. (a) 1400 nm × 1400 nm AFM scan of a nanocrystalline LPMO film, (b) 250 nm × 250 nm AFM scan corresponding to the white square drawn in (a), and (c) the height profile across the white line drawn in (b).

clearly from a smaller AFM scan of 250 nm × 250 nm (as shown in Fig. 1b). The height profile, recorded across a white line drawn in Fig. 1b, is presented in Fig. 1c. An analysis of the height profile revealed (i) that the average surface roughness of the film is ∼0.7 nm indicating very smooth surface of the films and (ii) an uniform distribution of grains with an average size of ∼17 nm.

A typical XRD pattern for the grown nanocrystalline LPMO film is shown in Fig. 2. The presence of only (0 0 *l*) reflections of the LPMO films, which are superimposed on (*h* 0 0) peaks of STO substrate, indicates that all the crystallites or grains have *c*-axis perpendicular to the substrate plane. The overlapping of (0 0 2) LPMO and (2 0 0) STO peaks is resolved clearly in the expanded plots, as shown in the insets of Fig. 2. The *c*-lattice parameter of the nanocrystalline film (computed from the *d*-value of (0 0 2) reflection) was 0.389 nm, which is the same as that grown for an epitaxial film at 600°C [8]. This suggests that the Pb content in both nanocrystalline and epitaxial films is close to that in the target.

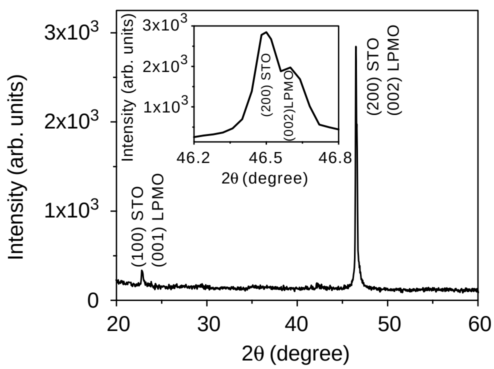

Fig. 2. XRD pattern recorded for a nanocrystalline LPMO film. The inset shows the expanded plot in the vicinity of (2 0 0) peak of STO.

The temperature dependence of the normalized resistance (measured in zero-field and in 1 T) for a typical nanocrystalline film is shown in Fig. 3. It is seen that the $R(T)$ plot exhibits a sharp insulator-to-metal transition (marked by T_{IM} in the figure) at around 156 K and an application of magnetic field sharply reduces the film resistance. The computed vale of MR%, defined as $(R_0 - R_H)/R_H \times 100$ (R_0 and R_H are the film resistance in zero and 1 T magnetic field), is also plotted in Fig. 3. It is seen that the magnetoresistance starts increasing from ~ 230 K (marked by point X in the figure) and exhibits a peak at ~ 132 K. This behavior of magnetoresistance matches with that of epitaxial thin films or single crystals [16]. It is interesting to note that the temperature dependence of magnetoresistance, in spite of the enlarged grain boundaries, does not follow the behavior observed for polycrystalline films [16]. Furthermore, a comparison to epitaxial LPMO films, having identical chemical composition and c-lattice parameter, shows that the nanocrystalline films have a reduced Curie temperature of 226 K (as compared to 295 K of epitaxial films), while the highest MR% has increased from 19% to $\sim 103\%$ [8]. The observed magnetoresistance of 103% at 1 T in the grown nanocrystalline films is the highest reported value so far as compared to any other CMR films [21]. This indicates that in nanocrystalline films the charge is confined to the individual crystallites or grains and the grain boundaries act as tunnel barriers suggesting that the enhanced magnetoresistance is due to tunneling phenomena.

In order to delineate the role of grain boundaries, the magnetization as a function of temperature for nanocrystalline films, in zero-field-cooled (ZFC) and field-cooled (FC) conditions, was measured. The obtained data are shown in Fig. 4. For the measurement of ZFC data, the samples are first cooled to 5 K. Subsequently, a field of 100 G is applied and magnetic moment as a function of slowly increasing temperature is recorded. To obtain FC data, the sample is cooled from room temperature under a fixed field of 100 G and magnetic moment is measured. It is seen that the paramagnetic-to-ferromagnetic transition i.e. Curie temperature (T_c, as marked by arrows in the figure) takes place at ~ 230 K, which is same as the temperature at which the magnetoresistance starts increasing (see Fig. 3). This result is in agreement with double-exchange mechanism. However, both ZFC and FC magnetization data show an upturn at ~ 27 K (marked by T_c(GB) in Fig. 4), which has been attributed to the grain boundaries undergoing a ferromagnetic transition. This suggests that grain boundaries have crystalline structure with suppressed T_c. It may be noted

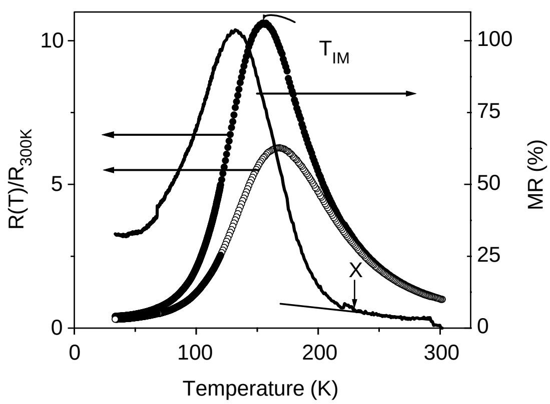

Fig. 3. Temperature dependence of normalized resistance (solid circles in zero and open circles in 1 T magnetic field) and MR (solid line) recorded for a nanocrystalline LPMO film. The T_{IM} is the insulator-to-metal transition temperature and X is the temperature at which the MR appears in the film.

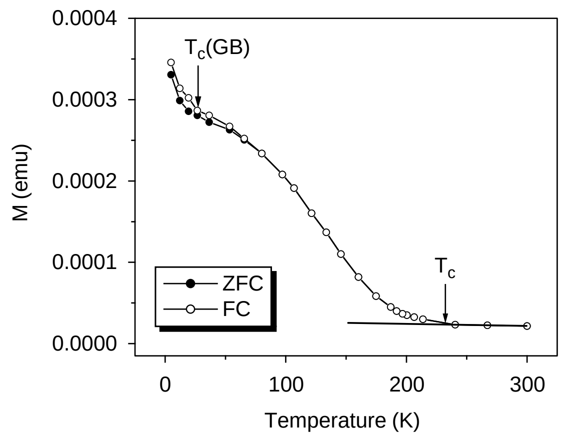

Fig. 4. Temperature dependence of ZFC and FC magnetization recorded for a nanocrystalline LPMO film. T_c and T_c(GB) are the Curie temperature for the grains and grain boundaries, respectively.

the in the case of disordered grain boundaries a cusp in ZFC data is expected [22]. This implies that at temperatures above 27 K the grain boundaries are paramagnetic insulators and therefore form tunnel junctions between the nanocrystallites.

4. Conclusions

The $La_{0.6}Pb_{0.4}MnO_3$ thin films grown using pulsed-laser ablation technique at low substrate temperatures, i.e. at 550°C are found to be nanocrystalline in character. The nanocrystalline films have an average grain size of 17 nm and the grains are oriented perpendicular to the substrate plane. The magnetization data show that grain boundaries act as tunnel barriers, which leads to an enhanced magnetoresistance of $>100\%$ at 1 T.

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