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Room temperature ultrahigh magnetoresistance in $La_{0.67}Sr_{0.33}MnO_3$ thin films with ordered nanometer structure

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Abstract

We report the preparation and investigation of ferromagnetic $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) thin films with orthogonally (along (110) and $(1\bar{1}0)$) distributed nanometer-scale cracks. When the density of cracks reaches $\sim 10^4\ cm^{-1}$, the magnetoresistance $MR = (R_H - R_0)/R_0 > -30\%$ was observed in the magnetic fields ≤ 200 Oe and temperature range from 5 to >300 K. The discussion about such unique feature will be done based on the spin-polarized electron tunneling and spin scattering.

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Keywords: A. Magnetic films and multilaylers; A. Nanostructures; B. Epitaxy; D. Electronic transport

1. Introduction

The family of manganites is known to show colossal magnetoresistance (CMR) [1,2], which is believed to have considerable application potentials such as magnetic sensor technology. However, practical use has been hindered by the fact that the CMR in most manganite thin films is restricted to high magnetic fields and a narrow temperature range around the metal–insulator transition temperature (T_{M-I}). Several effective ways, such as tunnel junctions [3–7], superlattices [8,9], and artificial boundaries [10,11] have been created to produce large magnetoresistance (MR) effect in low magnetic field. But, so far, the large MR obtained in low magnetic fields and at room temperature has not been realized.

A fact was found that due to the release of stress accumulated during the film growth, a kind of nanometer-scale cracks can form in the epitaxially grown manganite thin films [12,13]. Such cracks were believed to act as the barrier to induce spin-polarized electron tunneling, and resulting in a larger MR effect [12,14]. Therefore, fabricating nanometer-scale cracks in those thin films with high spin polarization and high Curie temperature (T_C) may be promising to achieve large low filed MR at higher temperature region.

In this letter, we report the preparation of ferromagnetic (FM) $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) thin films with high density of nanometer-scale cracks. The obtained MR value is in excess of 30% in the magnetic fields ≤ 200 Oe and at temperature of up to 300 K.

2. Experiment

LSMO thin films were deposited by pulsed laser deposition (PLD) method on $SrTiO_3$ (STO) single crystal substrate at 900 °C and in oxygen of 50 Pa, followed by in

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situ annealing at the same temperature and in oxygen of 0.8 atm for 30 min, then cooled down to the room temperature for about 1 h. In order to grow highly epitaxial thin film and form crack with certain orientation, the STO substrates with (001) normal and (100), (010) along the two sides were used.

X-ray diffraction (XRD) and atomic force microscope (AFM) analyses were used for characterization of the films. It is found that the films are single phase with the *c*-axis perpendicular to the film plane. It particularly exhibits the character that if the films grow very flat with average roughness better than 0.4 nm and thickness larger than 150 nm, the nanometer-scale cracks can form with orientation along (110) and $(1\bar{1}0)$ axes of the substrate. No cracks can be observed in those films for which the surface is relative rough. This should be attributed to the existence of the defects, which can release the stress prior to the formation of cracks. Fig. 1(a) is the AFM image of the film surface. Fig. 1(b) shows the AFM image of the enlargement of the crack in which a saw-tooth-like shape with the width less than 5 nm was observed. It should be very well to match the barrier width of magnetic tunnel junction [3]. Fig. 1(c) is the scanning transmission electron microscope (STEM) image of the crack's profile, which runs from the film surface into the substrate to a certain depth. At the same time, it was found that, the linear density of cracks (n_c) strongly depends on the thickness of the film. When the thickness of the flat films is as higher as 200 nm, the n_c can approach $\sim 10^4\ \mathrm{cm}^{-1}$, i.e. the width of the areas separated by cracks can be as small as $\sim 1\ \mu\mathrm{m}$.

3. Transportation measurements and results analyses

The transport measurement was performed on microbridge made from the thin film with and without magnetic fields in a superconducting quantum interference device (SQUID) magnetometer by using the standard four point method. The microbridge is 30 μm in width, 100 μm in length and with the long direction perpendicular to (110) of the film. So that, it crosses a certain number of cracks according to the n_c of the film. In the present study, we selected three typical samples with thickness ~200 nm and different n_c: sample M-1 with $n_c \approx 1\times10^4\ \mathrm{cm}^{-1}$, M-2 with $n_c \approx 2\times10^3\ \mathrm{cm}^{-1}$ and M-3 without cracks. The measured current of 10^{-6} A was used parallel to the magnetic field. To avoid the delay effect, all measurements were controlled to start after 5 s when the current was applied.

Fig. 2 shows the resistance vs. temperature (R–T) curves and the corresponding $\mathrm{MR} = ((R_\mathrm{H} - R_0)/R_0)$ vs. temperature (MR–T) curves of the microbridges made from these samples in zero field and in fields of up to 5 T. Fig. 2(a) and (b) show the R–T and MR–T for the microbridge M-1, respectively. It shows clearly that at 200 Oe, the MR obtained at 5, 300 and 350 K are −41, −33 and −26%, respectively. Fig. 2(c) and (d) show the data of microbridge M-2. Comparing with M-1, the low field MR of M-2 is much smaller, especially in the low temperature region. But in the high temperature region (≥300 K), we still observed the MR of −26% at 200 Oe. For the microbridge M-3, we cannot observe the MR effect at low field, in the whole measured temperature region (Fig. 2(e) and (f)). It only shows a detectable MR effect in the high magnetic field (5 T) and at the temperature around $T_{\mathrm{M-I}}$, indicating the real CMR effect. These results obviously show the strong role of nanometer-scale cracks on the low field MR effect in LSMO thin films.

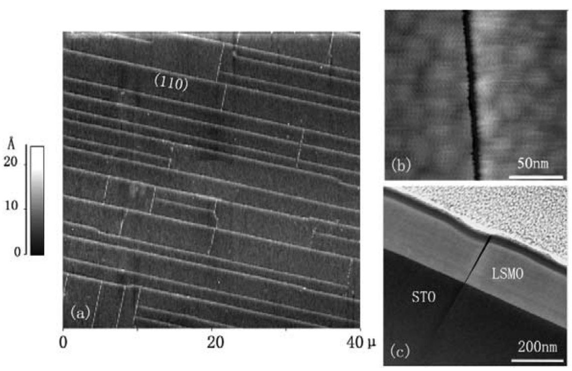

Fig. 1. (a) AFM image of the film surface. The orthogonally distributed nanometer-scale cracks exist along (110) and $(1\bar{1}0)$ axes of the film. (b) Enlargement of the crack with the width less than 5 nm. (c) Annular Dark Field STEM image of the crack's profile.

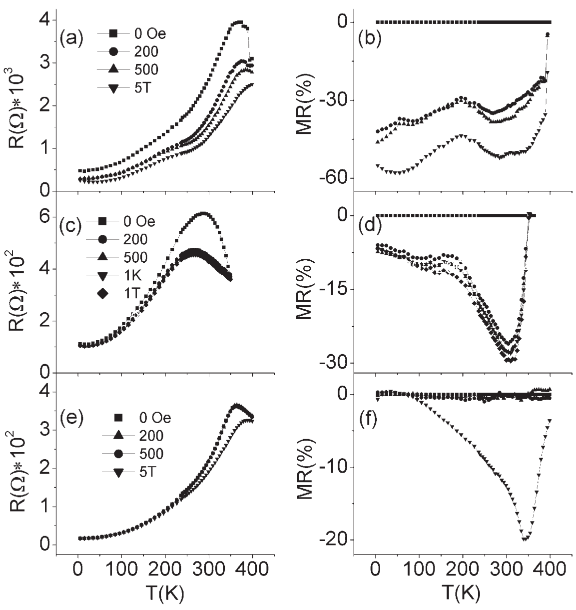

Fig. 2. R–T (a) and MR $[(R_\mathrm{H} - R_0)/R_0] - T$ (b) in zero field and in different fields obtained from microbridge from M-1 with $n_c = 1\times10^4\ \mathrm{cm}^{-1}$; the same results obtained from M-2 with $n_c = 2\times10^3\ \mathrm{cm}^{-1}$ (c) and (d); and obtained from M-3 without crack (e) and (f).

To further reveal the role of the nanometer-scale cracks on MR effect, the current–voltage (I–V) characteristic crossing the cracks was tested. Fig. 3 shows the I–V curves obtained from the M-1 in zero field and at 5, 100, 200 and 300 K, respectively. They show the non-linear characteristic, especially in the low temperature region, quite different from that of the film without cracks in which just linear I–V characteristic was observed, but similar to the case in the bulk manganite material [15], in which the spin polarized electron tunneling occurs across the weak-link boundaries of grains. As has been known that the high spin polarization of the electrons in Fermi surface of LSMO was observed [7,16–18]. So, we suggest based on our experiment results that the spin-polarized electron tunneling may occur in the present thin film with high density of cracks, especially in the low temperature region.

Fig. 4 shows the field dependence of magnetoresistance (MR(H)) of M-1 at different temperatures. The MR(H) obtained by initial magnetic field scan from 0 to +1k Oe and cycled field scan from +1 k to −1k Oe, then back to +1k Oe are defined as $MR(H)_I$ and $MR(H)_C$, respectively. The double-peaks in $MR(H)_C$ is obviously observed, but it has strong temperature dependence as shown in Fig. 4(a)–(d). It is commonly known that, the magnetic field of such double-peaks corresponds to the coercive field. For the present sample, the nanometer-scale cracks divide the film into different areas, which can be seen as the weak-linked FM domains. The cracks (<5 nm in width) and the FM domains in both sides of them can be seen as the tunnel barriers and FM electrodes, respectively. Under magnetization, each domain has its own coercive field. Every two areas separated by a crack may not be identical, so the coercive fields should be different each other. But the whole bridge can be seen as a junction with isotropic FM electrodes, which should show symmetrical double-peaks. The temperature dependence of $MR(H)_C$ is similar as that obtained from the artificial spin-polarized electron tunnel junction [3–7]. Therefore, it is rational to consider that the $MR(H)_C$ of the present bridge obeys the relation [19]

$$MR = (R_A - R_P)/R_A = 2P^2/(1 + P^2), \quad (1)$$

where R_A and R_P are the resistances of the two neighbouring areas in both sides of a crack with magnetization antiparallel and parallel, respectively, and P is the electron spin polarization which should be identical for all separated areas. From Fig. 4(a), we take the resistance of the bridge at ±1k Oe as the minimum (the MR is maximum) corresponding to the magnetization parallel. Then, the spin polarization for LSMO is estimated to be about 0.8 at 5 K. With increasing temperature, the amplitude of double-peaks decreased, clearly reflecting the strong temperature dependence of P of LSMO thin film. The $MR(H)_I$, however, is still large even at temperature region above 250 K (Fig. 4(d)–(f)) showing a quite weak temperature dependence. This implies another reason for the MR effect under the initial magnetic field scan. As mentioned above, the cracks divide the film into the micrometer-scale areas. These areas should be magnetic weak-linked, which will have strong spin scattering to charge carries crossing the cracks and lead the film resistance about one order larger than the film without cracks (seen the Fig. 2(a) and (e)). A low magnetic field may align the random spin and suppress the spin scattering, which will lead the resistance of the film

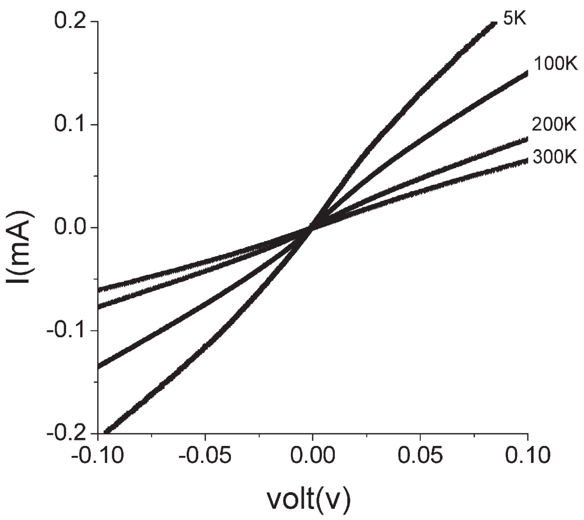

Fig. 3. I–V curves of the microbridge from M-1 at 5, 100, 200 and 300 K, respectively. The tunneling behavior becomes stronger with decreasing temperature.

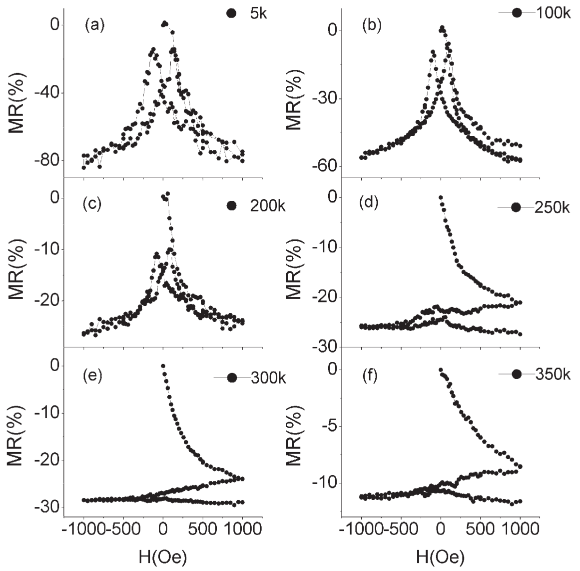

Fig. 4. MR(H) of the microbridge from M-1 obtained at 5 K (a), 100 K (b), 200 K (c), 250 K (d), 300 K (e) and 350 K (f). The ultrahigh MR from the initial magnetic field scan shows a slight temperature dependence, but the field cycled scan is heavily temperature dependent.

dramatically drop. Therefore, comparing with spin polarization tunneling, the ultrahigh MR in such LSMO thin film is mainly attributed to the spin scattering in nanometer cracks. The effect leading the low field MR also has been discussed in the bulk manganite sample and polycrystalline thin films [20,21], which have the magnetic weak-linked grains ($\sim 1\ \mu m$). Here, we may conclude that increasing the density of cracks and minimizing the width of cracks (being beneficial for tunneling) are the key to get large MR in wide temperature region.

4. Conclusions

A MR $\geq 30\%$ at room temperature and low magnetic field (≤ 200 Oe) has been obtained in LSMO thin films with high density of nanometer-scale cracks. It is indicated that dividing the magnetic thin film into weakly coupled magnetic domains by naturally grown nanometer-scale cracks is a unique way to enhance MR effect, which may be explained by two reasons: (1) forming magnetic tunneling junction (nanometer-scale crack serves as the barrier) to induce spin-polarized electron tunneling; (2) magnetic weak-linked nanometer-scale cracks lead to making strong spin scattering for charge carriers transport passing through it. Only low magnetic fields may suppress such scattering to drop the resistance. Therefore, films with high density of nanometer-scale cracks may be promising for highly sensitive magnetic sensors in practical use.

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