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Large Low-Field Magnetoresistance Observed in Polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ Films *

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Large low-field magnetoresistance (LFMR) of $\Delta\rho/\rho_H = 40\%$ is obtained at 163 K within ±3000 Oe in a polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) films prepared by pulsed laser deposition. The ratio $\Delta\rho/\rho_H$ increases almost linearly with H in the measuring magnetic field range and the peak of LFMR ratios is observed near the resistivity peak temperature, which is different from the observation of spin-polarized intergrain tunnels. This experiment suggests that grain boundaries have large influences on the LFMR. The results indicate that a suitable film process can be used to increase the LFMR of LCMO films.

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Recently, the doped manganese oxides of $R_{1-x}A_xMnO_3$, where R and A are rare-earth and alkaline-earth elements, respectively, have attracted much attention due to the discovery of giant magnetoresistance (MR) with the implicit hope that this feature could be technologically useful.[1-7] In $R_{1-x}A_xMnO_3$ systems the end composition, for example, $LaMnO_3$ is an insulator. The divalent substitution results in a ferromagnetic and metallic transitions. The transport properties of $La_{1-x}M_xMnO_3$ thin films are dependent on the substitution elements and the doping levels.[8] The largest MR ratios[1-3] (up to 10^6%) were observed near Curie temperature T_c of the ferromagnetic transition.

In the doped manganese oxides the MR behavior is broadly explained by the double-exchange interaction between Mn^{3+} and Mn^{4+} ions.[8,9] The conductivity of the materials caused by the e_g carriers is spin dependent. Either applying an external magnetic field near T_c or decreasing the temperature below T_c can increase the parallel alignment of the Mn spins and decrease the resistivity of the samples. However, magnetic fields of several teslas are typically required to obtain a large MR effect, which limits the potential of applications.

Comparing single-crystals with polycrystalline samples, it was found that the property of grain boundaries is important in some samples.[4] The properties of polycrystalline $La_{0.67}Ca_{0.33}MnO_3$ films indicated that domain boundaries are strong spin-dependent scattering centers.[5] In polycrystalline films an MR ratio of 20% in relatively low field (< 2000 Oe) at 25 K was obtained. To provide insight into the role of grain boundaries and to isolate their contribution to the MR, Mathur *et al.* studied devices patterned from $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) films grown on bicrystal substrates.[6] In these devices a large bridge MR (27%) was observed when magnetic field sweeps within ±2000 Oe at 77 K. These results indicate that large low-field MR (LFMR) can be obtained across grain boundaries, however, at relatively lower temperatures. Although, some improvements of LFMR were emerged in the spin-polarized intergrain tunneling samples, the relatively lower working temperature restricted their applications. In this paper we compare the LFMR effects in epitaxial and polycrystalline LCMO films prepared by pulsed laser deposition (PLD) with different film processes. Relatively large MR ratio of 40% in low fields (±3000 Oe) has been obtained near the resistivity peak temperature. The result indicates that a suitable film process can be used to increase the LFMR of LCMO films.

The PLD system used for preparing LCMO films has been described previously.[3] Briefly, an eximer laser with wavelength of 248 nm is used in the system. During deposition, the pulsed laser beam bombards the rotating target that has nominal compositions of $La_{0.7}Ca_{0.3}MnO_3$. The epitaxial LCMO films (with thickness of 300 nm) were grown on (100)-oriented $LaAlO_3$ single-crystal substrates at a substrate temperature of $T_s = 750°C$. During deposition the oxygen partial pressure was kept at 15 Pa. The deposition time for 300 nm films was 10 min. After deposition the as-grown films were directly cooled down to room temperature in O_2. Under these deposition conditions, x-ray diffraction θ-2θ patterns of as-grown LCMO films show (002) and (004) peaks in the region of $20°-50°$, which confirms the (001)-oriented epitaxial growth in as-grown LCMO films.

A standard four-probe method was used to measure the dc resistivity of the films. In resistivity versus temperature ($\rho - T$) measurements the epitaxial films

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show resistivity maximum feature at T_M with MR behavior. Figure 1 shows the $\rho - T$ curve in zero field for an epitaxial LCMO film (film A). It is noteworthy that below the T_M of 241 K the electric resistivity drop in this epitaxial film is quite sharp, which indicates a good crystalline structure. The resistivity maximum of the epitaxial film occurs at about the same temperature of bulk materials. Applying a magnetic field, MR behavior can be observed. In film A, MR ratios have a peak at a temperature slightly below T_M.

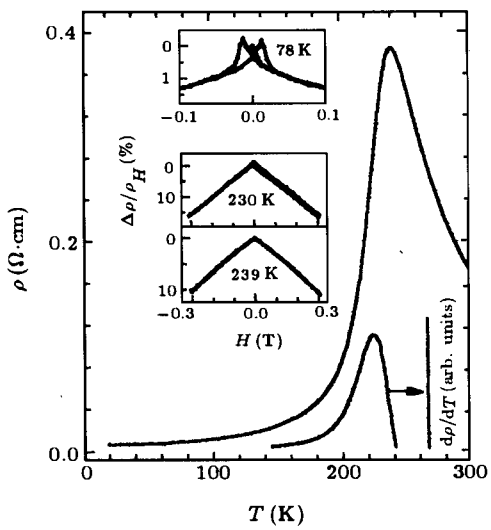

Fig. 1. Resistivity ρ and dρ/dT versus temperature T curves in zero field for the epitaxial LCMO film. The insets show LFMR ratios as a function of applied fields swept within ±3000 Oe at 78, 230, and 239 K.

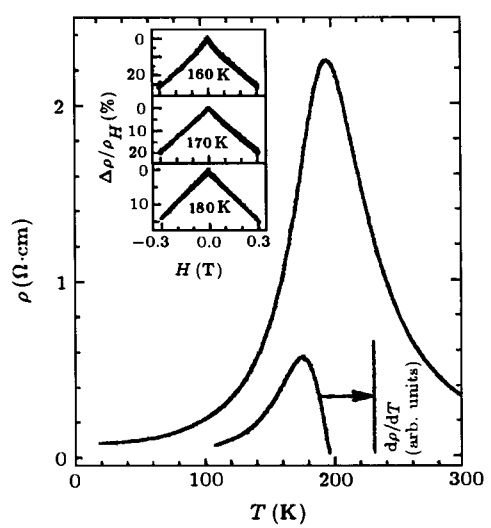

Fig. 2. Resistivity vs temperature ρ–T and dρ/dT–T curves for the polycrystalline LCMO film with low-T_s deposited buffer layer. Ratios $\Delta\rho/\rho_H$ as a function of applied fields swept within ±3000 Oe at 160, 170, and 180 K are shown as the insets.

LFMR ratios of film A as a function of applied fields swept within ±3000 Oe at a series of temperatures are plotted as insets in Fig. 1. The LFMR ratios in different fields are defined according to $\Delta\rho/\rho_H = (\rho_0 - \rho_H)/\rho_H$, where ρ_0 is the zero-field resistivity and ρ_H is the resistivity in an applied field of H. In the measurements, the applied magnetic field $\boldsymbol{H}$ was parallel to the film surface and electrical currents. At low temperature, the measurements revealed hysteresis behaviors in the data of ρ_H vs $\boldsymbol{H}$ for film A, as seen in Fig. 1. In the vicinity of the T_M, the LFMR ratio increases almost linearly with H. Slightly below T_M an LFMR ratio of $\Delta\rho/\rho_H = 10\%$ in 3000 Oe is observed at 239 K. At 230 K (about 0.95 T_M), the ratio $\Delta\rho/\rho_{H=3000\,\mathrm{Oe}}$ increases to 16%. We can use a resistivity ratio of $\rho(T)/\rho(T_M)$ in zero field to evaluate the related value of $\rho(T)$. The resistivity ratio of $\rho(230\,\mathrm{K})/\rho(T_M)$ is 0.83 for the film A.

In order to increase LFMR ratios in LCMO films, special processes were used to prepare polycrystalline films. In the preparation of film B, an LCMO buffer layer with thickness of 10 nm was first deposited on (100) $LaAlO_3$ substrate at 400°C. After the buffer layer deposition, the substrate temperature was directly increased to 750°C. The second LCMO layer with thickness of 300 nm was deposited at 750°C as that in the deposition of film A.

In transmission electron microscopy studies of this kind of films the selected-area electron diffraction patterns indicate that the films are polycrystalline. Bright field images show that quite uniform grains with size about 60 nm are formed in the films. The ρ–T curve of film B with the low-T_s buffer layers is shown in Fig. 2. In the ρ–T curve of film B, a resistivity maximum is observed at $T_M = 196$ K. The electric resistivity drop in the film B is not as sharp as that observed in the epitaxial film A, although the difference between the dρ/dT curves is small.

LFMR ratios of film B as a function of applied fields at a series of temperatures were measured. The insets in Fig. 2 show data of $\Delta\rho/\rho_H$ versus H in the range of ±3000 Oe at 160, 170, and 180 K, respectively. At 160 K (about 0.82 T_M) an LFMR ratio of $\Delta\rho/\rho_H = 27\%$ in 3000 Oe is observed with almost linear behavior. It is interesting that the MR ratios determined at 180, 170, and 150 K are lower than that observed at 160 K, and the resistivity ratio of $\rho(160\,\mathrm{K})/\rho(T_M)$ is 0.46. In film B, the maximum of LFMR ratios is observed at the temperature with $\rho/\rho(T_M) < 0.5$, which is different from that observed in the epitaxial LCMO films. At 78 K a hysteresis behavior in ρ_H vs H is observed in film B, however the LFMR ratio is much lower than that at 160 K.

In the preparing process of the polycrystalline film C, all of LCMO layers (300 nm) were deposited at 400°C and followed with annealing at 900°C for 15 min in 15 Pa of O_2. Figure 3 shows the ρ–T curve of the LCMO film C. Using this film process the polycrystalline film C shows T_M at 210 K. In film C the electric resistivity drop is broader than that observed in the films A and B, which can be easily distinguished from

the $d\rho/dT$ curves.

LFMR ratios of $\Delta\rho/\rho_H$ versus H for film C at 150, 163, and 169 K are shown as the insets in Fig. 3. In applied magnetic fields swept within ±3000 Oe, a relatively large LFMR ratio of 40% is obtained at 163 K (about $0.78\,T_M$). In a temperature range from 150 to 169 K, the ratios $\Delta\rho/\rho_H$ are larger than 30%. The resistivity ratio of ρ (163 K)/$\rho(T_M)$ is 0.44 in film C.

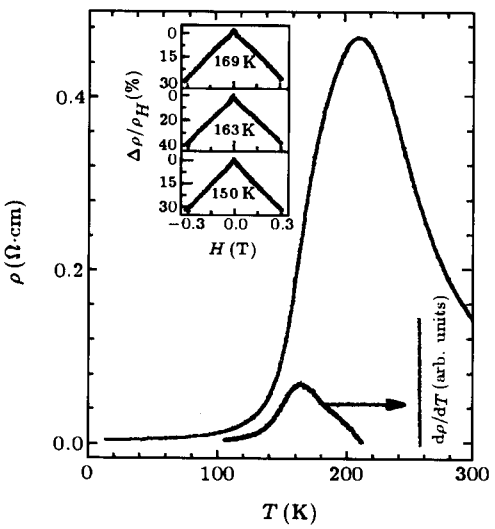

Fig. 3. Resistivity vs temperature $\rho-T$ and $d\rho/dT-T$ curves for the post-annealed polycrystalline LCMO film. The insets show $\Delta\rho/\rho_H - H$ within ±3000 Oe at 150, 163, and 169 K.

In the double-exchange model, the resistivity drop and the magnetotransport behavior near T_c have been attributed to the strong coupling between the conductive electrons and the local magnetic moments.[8,9] With the decreasing temperature of applying a magnetic field the neighboring spins become aligned, which causes the rapid resistivity drops and MR behaviors in epitaxial films. In magnetic tunnel junctions MR is dependent on the density of states of the majority and minority bands, therefore, large LFMR is only observed in low temperature region as that in $La_{0.67}Sr_{0.33}MnO_3$ tunnel junctions.[7] In bulk samples prepared by solid state reaction, the compositions in grains and grain boundaries are different and could lead to an insulated grain-boundary-region. In that case, the spin-polarized intergrain tunneling has contributions on the LFMR behavior at low temperature.[4] In LCMO films deposited on polycrystalline and bicrystal substrates, a large LFMR was obtained at about $0.1\,T_M$,[5,6,10,11] which was attributed to the spin-polarized intergrain tunneling behaviors. The contribution of the spin-polarized intergrain tunneling is important only in low temperature ($T \ll T_M$) region with saturated magnetization. In that situation nonlinear $\Delta\rho/\rho_H$ versus H behaviors were observed. Different from the polycrystalline bulks, in our films the LFMR does not increase at low temperature as expected by the spin-polarized intergrain tunneling model.

In our polycrystalline films, $\Delta\rho/\rho_H$ increased almost linearly with H in the measuring magnetic field range. In the films or the buffer layers deposited at 400°C, the compositions were well distributed. In the polycrystalline films, the difference between the grains and grain boundaries should be considerd as that between well oriented regions and more defective areas. The $\rho-T$ and $d\rho/dT$ curves of film C suggest that there would be two contributions in the resistivity. The first contribution near T_c may come from the well oriented magnetic domains as observed in epitaxial films. The second one at about $0.8\,T_M$ would come from the conductive boundary region with lower T_c. In a desirable sample, the magnetic domains are separated by an abundance of grain boundaries, as the case of film C, a relatively large LFMR effect could be obtained. It should be mentioned that in the post-annealed film C, there is structure disorder scattering contributed to the resistivity. Considering that the resistivity of film C at 50 K is two orders of magnitude less than the value at 210 K, in the vicinity of T_c the magnetic scattering is the majority contribution in the resistivity of the film C.

In summary, relatively large LFMR (27–40%) are observed in the polycrystalline films B and C. It is different from spin-polarized intergrain tunnels that the ratio $\Delta\rho/\rho_H$ of the films B and C increases almost linearly with H in the measuring magnetic field range and the peaks of LFMR ratios are obtained at about $0.8\,T_M$. This experiment indicates that a suitable film process can be used to increase LFMR of the LCMO films.

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