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Effect of thermal-annealing on the magnetoresistance of manganite-based junctions*

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Thermal-annealing has been widely used in modulating the oxygen content of manganites. In this work, we have studied the effect of annealing on the transport properties and magnetoresistance of junctions composed of a $La_{0.9}Ca_{0.1}MnO_{3+\delta}$ film and a Nb-doped $SrTiO_3$ substrate. We have demonstrated that the magnetoresistance of junctions is strongly dependent on the annealing conditions: From the junction annealed-in-air to the junction annealed-in-vacuum, the magnetoresistance near 0-V bias can vary from ∼–60% to ∼0. A possible mechanism accounting for this phenomenon is discussed.

Keywords: manganite, magnetoresistance, manganite junction, annealing
PACC: 7530V, 7220M, 7475

1. Introduction

Recently, manganite-based p–n heterojunctions have received much attention because their physical properties can be electrically and magnetically controlled simultaneously and thus have potential applications in spintronics. In previous studies [1−10] a wide range of manganites, from the completely insulating $Pr_{0.7}Ca_{0.3}MnO_3$ to the completely conducting (below room temperature) $La_{0.67}Sr_{0.33}MnO_3$, have been used to form junctions. Good rectifying properties were observed in most of these junctions and striking magnetoresistance (MR) was also observed in a few junctions.[2,3,5−9] However, the exploration is far from exhausting. It has been well established that the oxygen content can affect significantly the physical properties of manganites [11−13] and the properties of the corresponding junctions are expected to be affected accordingly. To date, work in this field is still lacking.

In this paper, we study the effect of oxygen content, which is controlled by annealing the samples under different conditions, on the transport properties and MR of $La_{0.9}Ca_{0.1}MnO_{3+\delta}$(LCMO)/Nb-doped $SrTiO_3$ junctions. We show that the MR is extremely sensitive to the annealing conditions. From the junction annealed-in-air to the junction annealed-in-vacuum, the MR near 0-V bias can vary from $\sim -60\%$ to ∼0. A possible mechanism accounting for this phenomenon is discussed.

2. Experiment

The junctions were prepared by growing LCMO film about 100 nm in thickness on 1 wt.% Nb-doped (001) $SrTiO_3$ (STON) substrate using the pulsed laser ablation technique. LCMO was chosen partly because of its small lattice mismatch with $SrTiO_3$ [14] and partly because its property is sensitive to the oxygen content.[12] To ensure the same film quality, three STON substrates and three (001) $SrTiO_3$ (STO) substrates were used to grow LCMO simultaneously. During the deposition, the substrate temperature was kept at 750°C and the oxygen pressure was kept at 100 Pa. Samples so prepared were called as-prepared. Then one set of as-prepared films (one was deposited on STON and the other was deposited on STO) were annealed at 550°C in air for 10 min, called annealed-in-air. Another set of as-prepared films were annealed at 450°C in vacuum ($< 3\times10^{-4}$ Pa) for 30 min, called

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annealed-in-vacuum.

The details of the fabrication of the junctions have been described elsewhere.[7,8] The area of the junction is 1 × 1 mm^2. Contacts to LCMO and STON were made of Ag films of ∼300 nm. The contact resistance between Ag and LCMO was less than 50 Ω at below 300 K, estimated by comparing the values of two-probe and four-probe resistances of LCMO film with Ag contacts. A Schottky barrier usually exists between Ag and STON. Here we break the barrier by a large electrical pulse. The electrically processed Ag/STON contact is nearly ohmic, and its resistance is less than 2 Ω. These contact resistances are small compared with the resistance of the junctions, as will be seen below, and would not affect the quantitative analysis of the transport. Systematic current–voltage ($I-V$) relations of the junctions were measured by tuning the bias voltage at temperatures from 30 K to 300 K, with or without 5-T magnetic field.

3. Results and discussion

Figure 1 shows the in-plane resistivity of the LCMO films on STO measured using standard four-probe technique. Metal-to-insulator transition (MIT) was observed, and the transition temperatures for the films annealed-in-air, as-prepared, and annealed-in-vacuum are 226, 222, and 189 K, respectively. Since the stoichiometric $La_{0.9}Ca_{0.1}MnO_3$ is completely insulating below room temperature, the appearance of MIT of the LCMO films indicates excessive oxygen content.[12] The excess oxygen can provide the conduction networks with holes by effectively increasing the Mn^{4+}/Mn^{3+} ratio, and thus enhances the metallic conduction. Based on our previous research on the effect of oxygen content,[13] the values of δ for the films annealed-in-air, as-prepared, and annealed-in-vacuum are roughly estimated to be 0.091, 0.087, and 0.055, respectively.

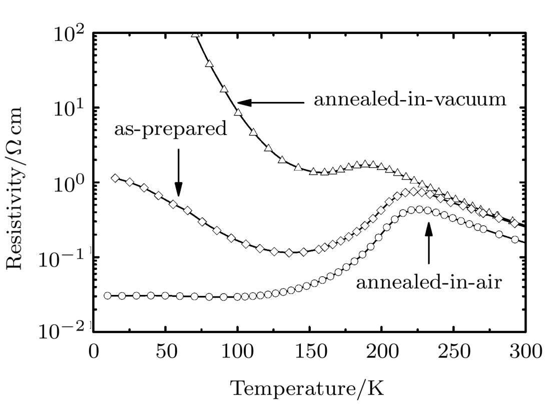

Fig.1. Temperature dependence of the in-plane resistivity of the LCMO films grown on STO substrate.

Figure 2(a)–2(c) shows $I-V$ relations of the three junctions at various temperatures. The scheme of junctions is given in the lower inset of Fig.2(a). All the junctions exhibit good rectifying characteristics, as demonstrated by the significant asymmetry of the $I-V$ curves against the polarity of the electric bias. However, there are obvious differences between them. For example, at the same bias, the reverse current of the junction annealed-in-vacuum is significantly larger than that of the junction annealed-in-air. This observation reveals that the annealing in air or vacuum has

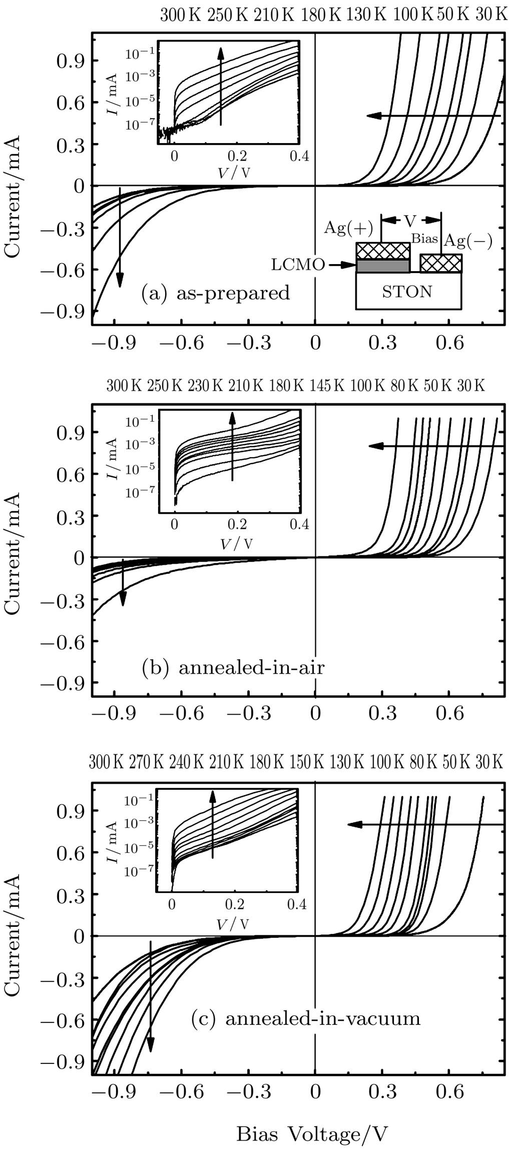

Fig.2. Selected $I-V$ curves for the LCMO/STON junctions. Insets re-plot the respective forward $I-V$ relations in semi-logarithmic coordinates. The lower inset of (a) shows the schematic configuration of junctions.

significantly changed the transport properties of the junctions.

From $I - V$ relations, junction resistance ($R_{\rm junction}$), defined as V/I, can be deduced. Figure 3(a) compares the typical electrical bias dependence of $R_{\rm junction}$ for the three junctions. All the junctions have a maximum resistance around 0 V (generally slightly less than 0 V), and the resistances decrease monotonically with increasing absolute value of bias. In low bias range, the junction as-prepared has the largest resistance, and the junction annealed-in-air has the smallest resistance. The $R_{\rm junction} - V$ curves for the three junctions are very much alike when electrical bias exceeds ~ 0.2V. In negative bias range, the $R_{\rm junction} - V$ curves of the junction as-prepared and the junction annealed-in-vacuum have the similar slope, while the resistance of the junction annealed-in-air decreases much more smoothly with bias. Figure 3(b) shows the maximum $R_{\rm junction}$ as a function of temperature. It is clear that the $R_{\rm junction} - T$ curves are very different for the three cases and are also completely different from the corresponding in-plane $R{-}T$ curves (Fig.1), which is understandable since only the manganite layer near the interface, a layer whose property is much different from that of the bulk film, has the significant influence on the properties of the junctions. There is a small resistance peak at ~145 K for the junction annealed-in-air, where the largest MR occurs, as will be seen below.

Undoubtedly, the most attractive feature of the manganite junctions is the MR. In the following we discuss the MR $[R_{\rm junction}(5{\rm T})/R_{\rm junction}(0\,{\rm T})–1]$ of the junctions. Figure 4 shows the MR–V relations of the junction as-prepared (we only show the results at higher temperatures because below 120 K $R_{\rm junction}$ around 0 V is too large to be measured). The MR is large, negative, and varies with bias. Generally, the minimum MR appears near 0 V at each temperature. Annealing in air significantly enhances the MR. As shown in Fig.5 (right column), the MR of the junction annealed-in-air is much more notable than that of the junction as-prepared. Its largest value can be as high as ~–60%, while that of the junction as-prepared is no more than –40%. For the junction annealed-in-air, the largest MR appears near 0 V, which is completely contrary to that of the junction as-prepared. Another distinct feature of the MR behaviour of the junction annealed-in-air is that the MR only changes slightly with increasing reverse bias. This feature may have to do with the smooth change of the junction resistance in the reverse direction (Fig.3(a)). Contrarily, annealing in vacuum significantly depresses the MR. The left column of Fig.5 shows the MR–V curves of the junction annealed-in-vacuum. Similar to the junction as-prepared, its minimum MR appears near 0 V. However, this time the minimum value is near 0. That is, in this case there is almost no magnetic effect. With increasing absolute value of the bias, the MR increases and a value as large as ~–30% can be achieved at a high negative bias.

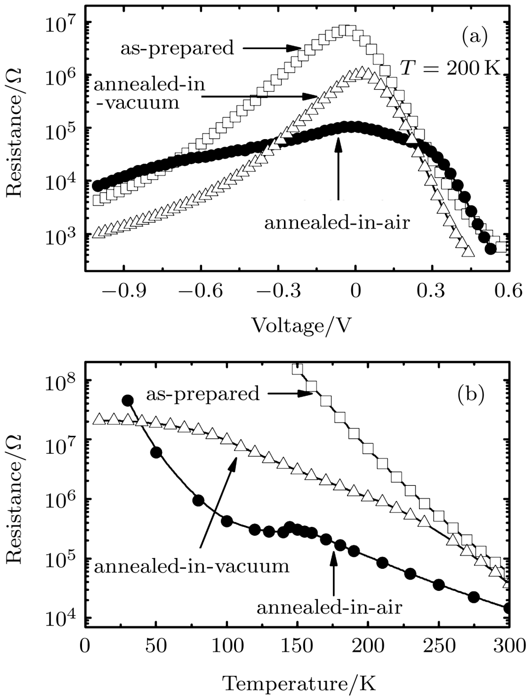

Fig.3. (a) Bias dependence of junction resistance at 200 K. (b) Temperature dependence of the maximum junction resistance.

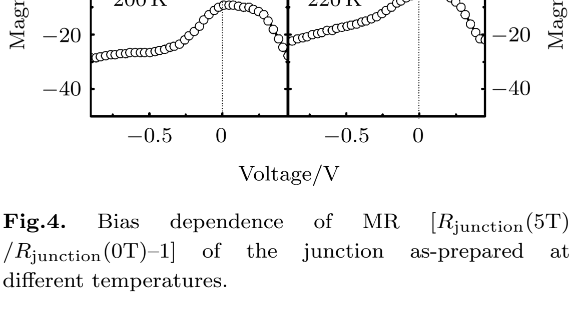

Fig.4. Bias dependence of MR $[R_{\rm junction}(5{\rm T})/R_{\rm junction}(0{\rm T})–1]$ of the junction as-prepared at different temperatures.

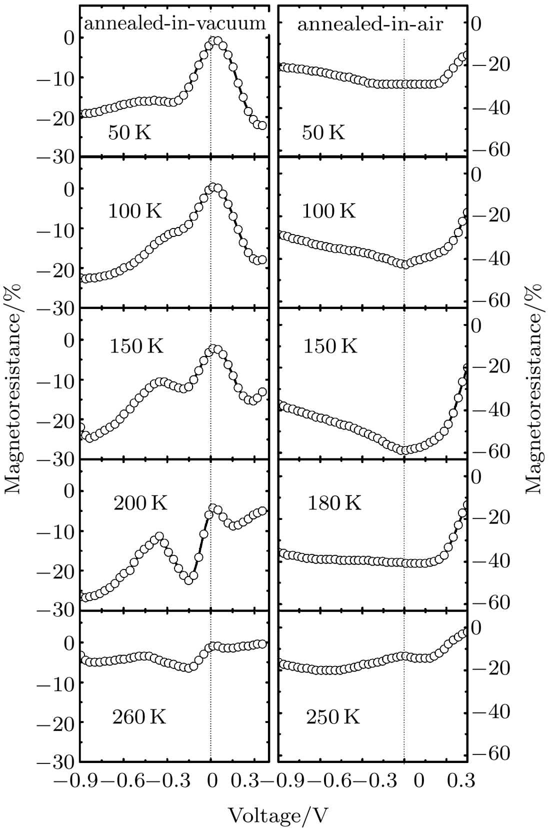

Fig.5. Bias dependence of MR [R_{junction}(5T) /R_{junction}(0T)–1] of the junction annealed-in-vacuum (left column) and the junction annealed-in-air (right column) at different temperatures.

In order to understand the striking effect of annealing on the MR of the junctions, an analysis of the transport is necessary. In our previous work[7] we have demonstrated that tunnelling is the main transport mechanism for the manganite junctions composed of heavily doped STON substrate (1 wt. %, as used in this study), and the magnetic field depresses junction resistance by reducing depletion width of the junction. The depletion width ($d = d_1 + d_2$)) can be estimated based on the formulae $d_1 = \{2N_{\mathrm{D2}}\varepsilon_1\varepsilon_2\varepsilon_0 V_{\mathrm{D}}/[qN_{\mathrm{A1}}(\varepsilon_1 N_{\mathrm{A1}}+\varepsilon_2 N_{\mathrm{D2}})]\}^{1/2}$ and $d_2 = \{2N_{\mathrm{A1}}\varepsilon_1\varepsilon_2\varepsilon_0 V_{\mathrm{D}}/[qN_{\mathrm{D2}}(\varepsilon_1 N_{\mathrm{A1}} + \varepsilon_2 N_{\mathrm{D2}})]\}^{1/2}$,[15,16] where d_1/d_2 is the depletion width in LCMO/STON, $\varepsilon_1/\varepsilon_2$ is the permittivity of LCMO/STON, $N_{\mathrm{A1}}/N_{\mathrm{D2}}$ the hole/electron density of LCMO/STON, ε_0 the permittivity of the vacuum, and V_{D} the diffusion potential. The main effect of annealing is to tune the oxygen content of LCMO, which will in turn tune the effective carrier concentrations of LCMO. As a result, the depletion width and the junction resistance are tuned. A simple estimation[7] showed that at equilibrium the depletion width will be thinnest in the junction annealed-in-air and thickest in the junction annealed-in-vacuum.

However, this estimation is not consistent with the junction resistance (Fig.3), which should be proportional to the depletion width. As shown in Fig.3, the junction annealed-in-vacuum has a smaller resistance (near 0-V bias) than the junction as-prepared. This disagreement may come from the phase-separation nature of LCMO.[11,17,18] The total depletion width includes d_1 (in LCMO) and d_2 (in STON). Because the STON is electrically homogeneous, the boundary of the depletion layer in STON will be sharp and parallel to the interface between STON and LCMO, with a constant distance of d_2. However, because of phase separation, the LCMO is electrically inhomogeneous. In the direction parallel to the interface, the distribution of effective carriers is not homogeneous. Therefore, the boundary of the depletion layer in LCMO should be fluctuant and d_1 is the average distance from the interface. It is evident that the tunnelling effect will be determined by the thinnest part of the depletion layer. The junction annealed-in-vacuum has the largest ratio of d_1/d_2 and thus its depletion layer will be most severely affected by the electronic inhomogeneity in LCMO. Therefore, although its apparent depletion layer should be thickest, its thinnest part could be thinner than that of the junction as-prepared.

Magnetic field can release the localized electrical carriers[11] and the depletion layer will become thinner, which explains the MR of the junctions.[7] For the junction as-prepared and the junction annealed-in-vacuum, a simple estimation[7] shows that a quite large part of their depletion layers is distributed in LCMO. As analysed above, because of electronic inhomogeneity, the depletion width is fluctuant. The thinnest part of the depletion layer should pass through the zone having the largest carrier concentration, for example, large metallic clusters. Because the carrier concentration in such a zone is high, the change of the depletion thickness of such a zone by external magnetic field will be small. It seems as if the thinnest part of the depletion layer (in LCMO) was pinned. Therefore, although the average depletion width layer is decreased, the thinnest part could have relatively small change. This explains the relatively small MR around 0 V in the junctions as-prepared and annealed-in-vacuum. As expected, since the junction annealed-in-vacuum has the largest ratio of d_1/d_2, it has the smallest MR near 0 V.

It should be pointed out that structural inhomogeneity, especially the interfacial defects such as anion or cation vacancies, can also lead to the fluctuation of the effective depletion width. The real mechanism could be a combination of the phase transition and the structural inhomogeneity. Anyway, the above model gives only a much heuristic explanation. In a practical junction thermal current, tunnelling current, and leakage current could coexist, though their contributions may vary with temperature and electric bias. Due to the strong coupling between spin, charge, and lattice degrees of freedom in manganites, the physical process undergoing in the junctions could be much more complex, and a thorough understanding of it requires further work.

4. Conclusion

We have demonstrated that annealing under different conditions has significant influence on the MR of manganite-based junctions. From the junction annealed-in-air to the junction annealed-in-vacuum, the MR near 0-V bias can vary from ∼–60% to ∼0. This phenomenon could be a combined effect of charge tunnelling across the junction and the electronic inhomogeneity in LCMO.

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