Strong magnetic-field effects in weak manganite-based heterojunction

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Oxide heterojunctions were fabricated by growing a $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ (LCMO) film on a 0.5 wt % Nb-doped $SrTiO_3$ single crystal (STON). By removing the oxygen of LCMO, a junction with a rather small diffusion/breakdown voltage and junction resistance has been obtained. The most striking observation of the present work is the extremely strong magnetic-field effects in this weak junction. A field of $H \approx 1.7$ T can cause an increase of ~1130% of the diffusion/breakdown voltage and a magnetoresistance as high as $R(H)/R(0)-1 \approx 1100\%$. It is interesting to note that the magnetoresistance is positive, which indicates a basically different mechanism from the manganite, for which a negative magnetoresistance is observed, and could be a result of the change of magnetic and electronic structures of LCMO with respect to STON under magnetic field. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1762703]

Perovskite manganese oxides have two promising features. The first one is the strong magnetic field dependence of their magnetic and transport properties. It has been revealed that the resistivity of the manganite underwent a great reduction under magnetic field (H), and sometimes a magnetoresistance $(\mathrm{MR}) = R(H)/R(0)-1 \approx -100\%$ could be achieved,[1] where $R(H)$ and $R(0)$ represent the resistance with and without magnetic field. The other feature is the high spin polarization below Curie temperature (T_C), i.e., electrons at the Fermi level possess essentially the same spin orientation.[2–5] In addition to the attractive underlying physics, these special properties can be used to configure artificial devices of technological interest. In fact, the half-metal character of the manganite has been used in fabricating spin tunnel junctions soon after the discovery of the huge MR, and a tunnel MR as high as −99% has been obtained recently.[5] This is a value much larger than that of the conventional spin tunnel junction.

In a spin tunnel junction, the magnetic field produces MR by altering the relative magnetic orientation of ferromagnetic (FM) layers, which affects the probability for an electron to cross the junction. The magnetically tunable feature of the manganite is actually not involved. In this letter, we report on an artificial material with a magnetoresistive behavior associated with the variation of the magnetic and electronic structures of the manganite under a magnetic field. We selected $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ (LCMO) and Nb-doped $SrTiO_3$ (STON) to compose a heterojunction. The former is a p-type degenerated semiconductor while the latter is n type. By removing the oxygen of LCMO, we obtained a junction that exhibits a rather small diffusion/breakdown voltage and junction resistance. The most striking observation of the present study is the extremely strong magnetic-field effects in this weak $p-n$ junction: Both the rectifying behavior and the resistance of the junction experience a great change under the magnetic field. The MR can be as high as ~1100% under a field of 1.7 T, and its positive sign indicates a basically different mechanism from the manganite.

A 0.5 wt % STON (001) single crystal of the size of 3×5 mm^2 was used as a substrate. To obtain a better interface structure, the substrate was carefully polished and the surface roughness was depressed below 4 Å. A LCMO layer was grown on the substrate by pulsed laser ablation. The temperature of the substrate was kept at 750 °C and the oxygen pressure at ~100 Pa during the deposition. The film thickness is 500 Å, controlled by the deposition time (deposition rate ~0.5 Å/s). To improve the crystal quality and oxygen stoichiometry, the film was maintained at 750 °C for 15 min in flowing O_2 gas after preparation.

Figure 1 shows the x-ray diffraction (XRD) spectrum and the resistivity of LCMO/STON, the latter was measured in the current-in-plane mode. As expected, only the peaks with the same orientation as the substrate were detected, which indicates an epitaxial film growth (top panel). Noting the fact that STON is a semiconductor and there is no resistive abnormal for it down to 5 K, the metal-to-insulator transition at ~253 K (bottom panel) and its shift to high temperatures under a magnetic field can be attributed to LCMO film, they are typical features of stoichiometric LCMO.[6]

To remove oxygen, the LCMO film was further treated at 480 °C for 15 min in a vacuum of $\sim 5\times 10^{-6}$ Torr. Subsequent XRD measurement reveals a low-angle shift of the (004) peak. This is a sign of oxygen release that produces lattice expansion.[7] The content of oxygen vacancies, characterized by δ, is estimated to be $\delta \approx 0.11$ based on the XRD data following the method of Ref. 8. As a consequence of losing oxygen, the metallic conduction in the low-temperature region disappears, and, fascinatingly, the negative MR becomes positive. In fact, the positive MR cannot be ascribed to LCMO alone. Because of the small junction

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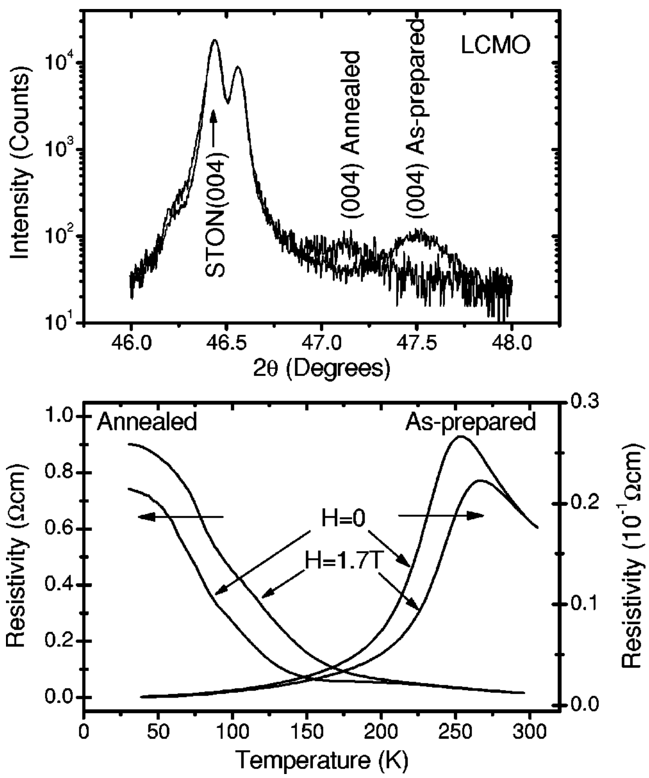

FIG. 1. XRD spectra (λ=1.5405 Å) (top panel) and resistivity (current-in-plane) (bottom panel) of the LCMO film before and after vacuum annealing. The peaks are indexed based on an orthorhombic structure.

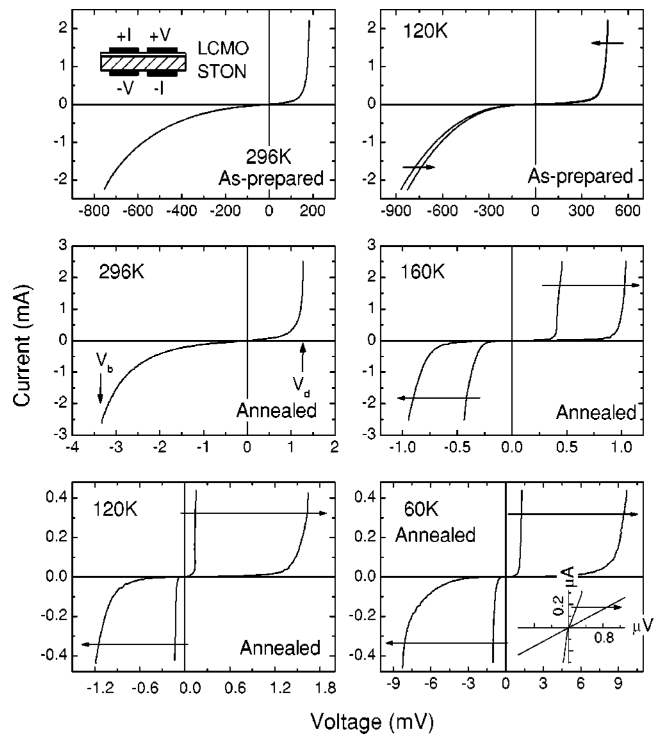

FIG. 2. $I-V$ characteristics of the $p-n$ junction. Note the different scales of the top two and the bottom four figures. The lower inset is a close view of the $I-V$ curve near the origin. Arrows indicate the variation of the $I-V$ curve under a field of 1.7 T.

resistance, STON was also measured in parallel to the film, especially for the vacuum-annealed junction. The positive MR suggests an increase of junction resistance under the magnetic field, which prevents the current from passing through STON, then causes a growth of the total resistance of the LCMO–STON system. This is proven by the following experiment results.

Figure 2 presents typical current versus voltage ($I-V$) curves of the heterojunction before and after vacuum annealing measured by tuning bias voltage under $H=0$ and 1.7 T. As previously reported,[9,10] the $I-V$ curve exhibits an asymmetry for the forward and reverse biases, and there are two critical voltages, respectively called diffusion voltage (V_d) and breakdown voltage (V_b), at which the current shows a snowslidelike increase. It is interesting that losing oxygen can cause a reduction of V_d and V_b by two to three orders of magnitude, resulting in critical voltages of only a few millivolts. As shown in Fig. 3, V_d is ~1.2 mV at the ambient temperature without magnetic field. The minimum and maximum V_d are ~0.12 mV and 1.8 mV, respectively. The extraordinarily small V_d means a weak built-in electric field in the junction region or a low-energy barrier at the LCMO–STON interface. This analysis is consistent with the small junction resistance as will be shown below. Therefore, oxygen-deficient LCMO and STON actually form a weak heterojunction. Fascinatingly, though the critical voltages are small, the rectifying feature of our $p-n$ junction remains clear: The current rush at V_d and V_b is definite and steep despite the significant leakage current.

The most remarkable observation is the strong effect of magnetic field on the weak $p-n$ junction. The applied field yields a decrease of the $I-V$ slope near the origin (inset in Fig. 2) and an upward shift of V_d and V_b. Figure 3 shows that the magnetic-field effect emerges below 220 K, and develops with the decrease of temperature. The maximum effect takes place at ~120 K, where V_d increases from 0.12 mV to 1.5 mV under a field of ~1.7 T ($V_d(H)-V_d(0)/V_d(0)\approx 1130\%$, inset of Fig. 3). V_b exhibits a synchronous variation with V_d, either an increase or decrease. Accompanying the variation of the $I-V$ curves, the resistance of the junction experiences a great change. Figure 4 presents the resistance ($R_j=V/I$) and the corresponding MR of the junction for selected currents and temperatures. R_j varies with temperature in essentially the same way as V_d, suggesting a close relation between these two quantities. As mentioned before, a larger diffusion voltage implies a higher

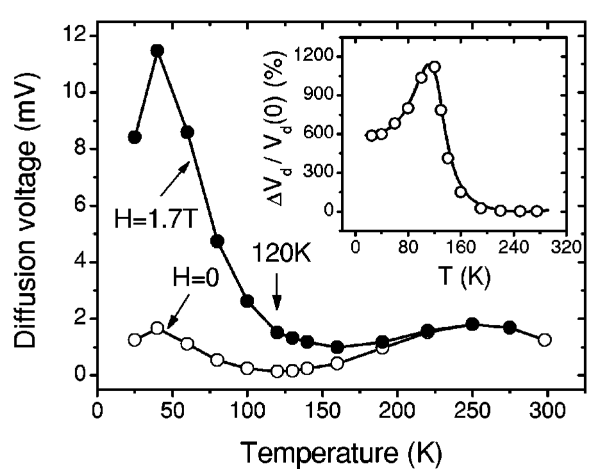

FIG. 3. Diffusion voltage (V_d) as a function of temperature measured under $H=0$ and 1.7 T. The inset displays the relative change of V_d under magnetic field.

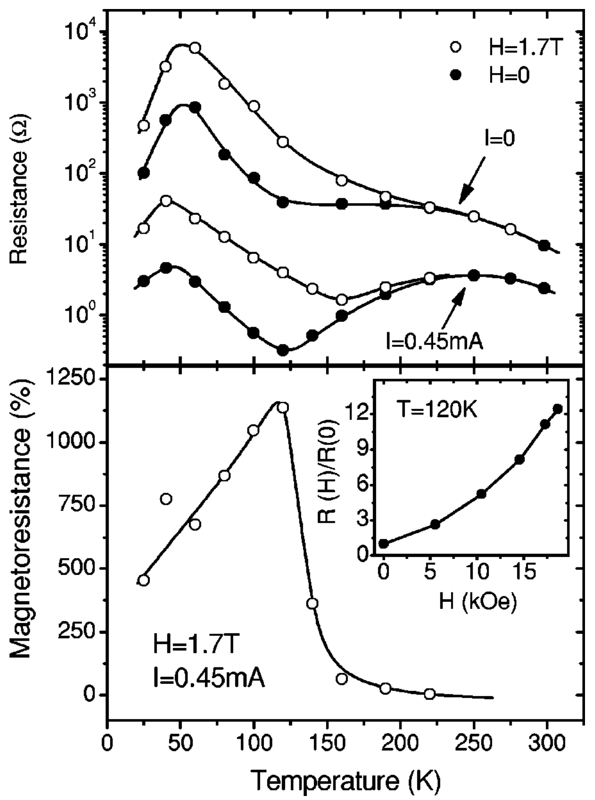

FIG. 4. Resistance (top panel) and magnetoresistance (bottom panel) of the $p-n$ junction as functions of temperature measured under the fields of $H=0$ and 1.7 T for $I=0$ and $I=0.45$ mA. The bottom inset shows the variation of junction resistance with applied field ($I=0.45$ mA).

built-in field, therefore a larger junction resistance. The enhancement of the junction resistance by magnetic field is especially obvious in the temperature region below 150 K. It is apparently a consequence of the diminishment of the $I-V$ slope and the upward shift of V_d and V_b. A direct calculation indicates that the maximum MR is ~1000% for $I=0$ and ~1100% for $I=0.45$ mA under a field of 1.7 T, slightly dependent on applied current. An even larger MR is expected under a higher field noting that the MR of our junction is far from saturation under a field of 2 T, the highest field of our system (inset in Fig. 4).

We have studied heterojunctions composed of different manganites, and found that strong magnetic field effects only occur in weak junctions (compare the data before and after annealing in Fig. 2). In sharp contrast to LCMO, the MR of the junction is positive, though the huge value and the presence of a maximum are also typical features of the MR of a manganite, which implies a different mechanism for the MR of $p-n$ junction: It is a combined effect of LCMO and STON. It is interesting to note that the MR of the as-prepared LCMO/STON is negative, similar to that observed by Tanaka *et al.*[10] in their $p-n$ junction. A further study indicates that negative MR usually appears when the manganites are at a well FM state. The reason for negative MR is not very clear at present, though one may argue that it originates from the negative MR of the manganites. In contrast, a positive MR occurs when the FM order of the manganite is poor. Here, we merely give a primary analysis on the possible reasons for the positive MR, and a thorough explanation requires further work. It is obvious that the only possible change induced by an external field may be the magnetic state of the LCMO film. We failed to get a satisfactory magnetization curve for LCMO because of its weak magnetic signal. A simple calculation shows that the content of Mn^{4+} in LCMO is ~0.11 (corresponding to $\delta \approx 0.11$). If the main features of LCMO mimic those of $La_{1-x}Ca_xMnO_3$ ($x=0.11$), the T_C of LCMO should be ~120 K.[11] It is exactly the temperature where the maximum MR of our junction occurs. This suggests that we consider the relation between MR and the magnetic state of LCMO. A distinctive feature of the manganite is the strong influence of magnetic order on electronic structure: The spin-up and spin-down states will undergo a band splitting when the manganite is cooled through T_C. Based on the semiconductor theory, the appearance of band gap can lead to an increase of the energy barrier at the LCMO–STON interface noting the fact that the Fermi energy locates at the lower e_g subband in LCMO and near the bottom of the conduction band in STON, and LCMO and STON have a common Fermi level. This may be the reason for the increase of V_d and R_j below ~120 K (Figs. 3 and 4). The small V_d and V_b could be a sign that the band gap is not fully opened up, which is understandable considering the poor FM order of LCMO due to the lower Mn^{4+} content or the presence of oxygen vacancies. It is interesting to note that it is for these manganites that the magnetic field demonstrates a strong power in enhancing the magnetic order (Actually, the first huge MR was also observed in such a system),[12] or equivalently, in developing the spin-up and spin-down band gap. Because of the small value of V_d and V_b, any field-induced variations of them can result in sizeable relative changes. This implies that a small V_d/V_b or R_j may always accompany a huge MR.

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