Unusual colossal positive magnetoresistance of the *n*-*n* heterojunction composed of $La_{0.33}Ca_{0.67}MnO_3$ and Nb-doped $SrTiO_3$

C. M. Xiong, Y. G. Zhao,[a] B. T. Xie, and P. L. Lang
Department of Physics, Tsinghua University, Beijing 100084, China

K. J. Jin
Institute of Physics, Chinese Academy of Science, Beijing 100080, China

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An *n*-*n* heterojunction composed of $La_{0.33}Ca_{0.67}MnO_3$ and Nb-doped $SrTiO_3$ was fabricated, and it shows good rectifying property. The temperature variation of junction resistance for high reverse voltage exhibits a metal-insulator-like transition that shifts to high temperatures with further increasing voltage. The heterojunction presents a remarkable positive magnetoresistance under the reverse bias voltage at low temperatures, and the maximum of magnetoresistance can even reach ~400% under a field of 1 T. A qualitative explanation is given based on the analysis of the electron filling near the interface and its tunable feature under the bias voltage and magnetic field. This result can be helpful for both the understanding of the manganites and the future applications of the manganite-based devices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2203204]

Manganite heterojunctons have been a subject of intensive studies because of their rich physics and potential applications.[1–8] Remarkable negative magnetoresistance (MR) has been found in these designed structures.[2,3] Amazingly, a few manganite heterostructures were found to present positive MR absent in their constituents. For example, a large positive MR has been demonstrated in a $Fe_3O_4/SrTiO_3/La_{0.7}Sr_{0.3}MnO_3$ magnetic tunnel junction.[4] Recently, the positive MR was also reported in several heterojunctions consisting of hole-doped manganites and Nb-doped $SrTiO_3$.[5,6] It is believed that the interface of the heterostructure plays an important role in the positive MR, but the detail mechanism remains to be an open question.

It is well known that the band filling (e_g band) of $La_{1-x}D_xMnO_3$ (where D represents divalent alkaline-earth ions), as well as its Fermi level (E_F), decreases with the D ion doping. Simultaneously, the dominant carrier in the manganites experiences a change from hole to electron type around $x=0.5$. Notably, most work has focused on the heterojunction composed of hole-doped manganites and Nb-doped $SrTiO_3$, while the heterojunction based on the electron-doped $La_{1-x}D_xMnO_3$ with x between 0.5 and 1 was rarely studied. More recently, Sun *et al.* studied a junction composed of $CaMnO_3$ and Nb-doped $SrTiO_3$, and found that the behavior of this junction is akin to a conventional *p*-*n* junction, but they did not study the MR of this junction.[7] Moreover, information on the heterojunction based on the other heavier Ca-doped manganites is still limited. Considering the phase separation and charge ordering in $La_{1-x}D_xMnO_3$ with $0.5<x<1$, the behaviors of the heterojunction based on this kind of electron-doped manganites should be an interesting topic. In this letter, we constructed an *n*-*n* heterostructure by combining an electron-doped manganite $La_{0.33}Ca_{0.67}MnO_3$ (LCMO) with a 1 wt % Nb-doped $SrTiO_3$ (SNTO). This *n*-*n* junction shows a good rectifying property and colossal positive MR. The band diagram of this junction is proposed. It was found that the electron filling and conduction behavior in the interface region play a crucial role in the occurrence of the positive MR.

Two LCMO films were grown on (001) SNTO (LCMO/SNTO) and (001) $SrTiO_3$ (LCMO/STO) substrate using laser ablation. The temperature of the substrate was kept at 800 °C and the oxygen pressure at 50 Pa during the preparation process. The thickness of both films was about 150 nm. After the deposition, the films were furnace cooled to room temperature in an oxygen atmosphere of 0.8 atm. X-ray diffraction analysis showed good epitaxy of the films. Resistance of the LCMO/STO was measured by standard four-probe method, which shows an insulating behavior over a wide temperature range (see the left top inset in Fig. 1). Further analysis showed that the conduction of this film proceeds via a variable-range hopping of the charge carriers below a characteristic temperature of 230 K, signifying an onset of the charge-ordering (CO) phase which is similar to the previous reports.[9,10]

The *I*-*V* curves of LCMO/SNTO, measured under the fields of the $H=0$ and 1 T, are presented in Fig. 1. The electrode settings are also illustrated schematically in the right

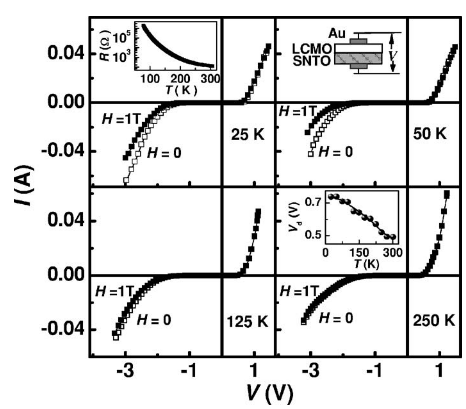

FIG. 1. *I*-*V* curves of the LCMO/SNTO junction at different temperatures, measured under the fields of $H=0$ and 1 T. The top insets show the temperature dependence of the in-plane resistance of LCMO and the schematic illustration of the heterojunction, respectively. Bottom inset displays V_d as a function of temperature.

[a]Electronic mail: ygzhao@tsinghua.edu.cn

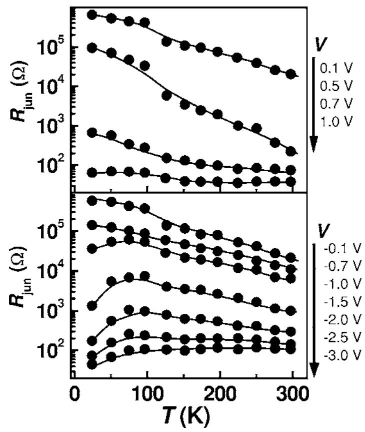

FIG. 2. Temperature dependence of R_{jun} at various positive voltages (top panel) and negative voltages (bottom panel).

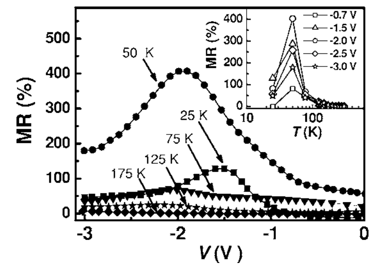

FIG. 3. Bias voltage dependence of MR at different temperatures. Inset: temperature dependence of MR at various voltages.

top inset of Fig. 1. The positive bias (i.e., forward bias) is defined as the current flows from the LCMO film to SNTO. It is interesting to note that the *I-V* curves exhibit a good rectifying property which mimics the conventional *p-n* diode. Below $V<0$, the notable increase of current appears at ~ -1.2 V. In contrast, with a positive voltage, the current starts to increase dramatically at a threshold voltage (diffusion potential, V_d), and the room temperature value of V_d is ~ 0.5 V. As temperature decreases from room temperature to 25 K, V_d increases from 0.5 to 0.7 V (see the right bottom inset in Fig. 1).

To further characterize the transport properties of the LCMO/SNTO junction, the junction resistance (defined by $R_{jun}=V/I$) was calculated, and the temperature dependences of R_{jun} at different voltages under $H=0$ are displayed in Fig. 2. When $|V|$ is smaller than 0.1 V, R_{jun} decreases with increasing temperature, and the magnitude of R_{jun} is above 10^4 Ω, indicating an insulating behavior. Under the same condition, our measurement shows that the contact resistance of the electrode is below 20 Ω, which cannot explain the large values of R_{jun}. Therefore, R_{jun} should mainly come from the junction. The top panel of Fig. 2 shows that R_{jun} decreases rapidly with increasing positive voltage. However, R_{jun} reduces slowly as V decreases from 0 to ~ -0.7 V. An important phenomenon is that when the reverse voltage is larger than 1 V, R_{jun} exhibits an obvious reduction and, simultaneously, a metal-insulator-like transition appears, manifested by a peak in the $R_{jun}-T$ curves at low temperatures. This transition shifts slightly to high temperatures with further decreasing V, as shown in the bottom panel of Fig. 2.

The most important observation of the present work is that, for $V<0$, the LCMO/SNTO junction exhibits a remarkable positive MR under a magnetic field of 1 T, particularly at low temperatures. On the contrary, the MR for $V>0$ is less perceptible, thus we mainly discuss the MR behavior below $V<0$ here. Figure 3 displays the voltage dependence of MR at different temperatures, where MR is defined by $[R_{jun}(H=1\text{ T})-R_{jun}(H=0\text{ T})]/R_{jun}(H=0\text{ T})$. It is noted that MR presents a maximum at a certain voltage (V_p). With increasing temperature, $|V_p|$ varies in the range of 1.5–2.5 V, meanwhile, the signature of the maximum in MR becomes blurred and undistinguishable gradually. At 50 K, MR even reaches a maximum of 400% at −1.9 V. The temperature dependences of MR at various voltages are shown in the inset of Fig. 3. It is found that all the MR-*T* curves exhibit a peak around 50 K. It is, for example, 80% at 25 K, 390% at 50 K, and 20% at 125 K at −2 V. For comparison, the MR of the LCMO/SNTO system under 1 T was also measured in the same temperature range with the current-in-plane mode with the four probes on the film surface. Its value is negative and only notable at low temperatures: at 25 K, the MR reaches −24%. Obviously, the negative MR of LCMO (current in plane) is different from that of the LCMO/SNTO junction (current perpendicular to plane). Thus, it is not LCMO but the electric transport across the interface accounting for the positive MR of LCMO/SNTO. Additionally, it is noted that the large value of MR occurs just at those low temperatures where the metal-like behavior in R_{jun} appears, which implies a correlation between these two observations. This behavior will be explained later. Different from the previous study of the hole-doped manganite *p-n* junction, the resulting MR in this work is produced from a junction containing an electron-doped (heavier Ca-doped) manganite. Therefore, the exploration of the underlying physics behind this phenomenon may be helpful for a comprehensive understanding of the manganite heterojunctions.

The band diagram for the LCMO/SNTO is plotted schematically in Fig. 4. In this sketch, region I denotes the LCMO homogenous region far away from the interface, region II the LCMO depletion layer closer to the interface,

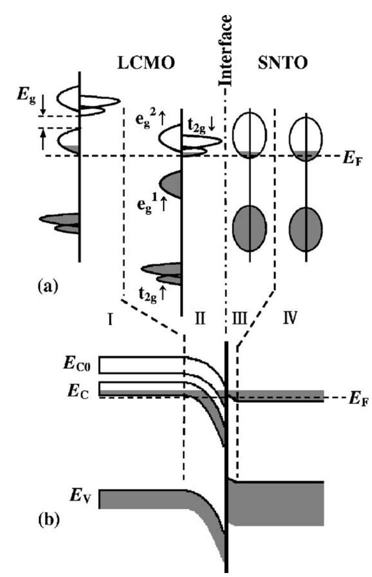

FIG. 4. (a) Schematic DOS of the LCMO/SNTO junction. (b) Band diagram for each region, where E_V and E_C denote the energies of valence band and conduction band, respectively. E_F is the Fermi level. For LCMO, E_V and E_C are associated with $t_{2g}\uparrow$ and $e_g^1\uparrow$, respectively. E_{C0} is the energy of the band that is jointly determined by $t_{2g}\downarrow$ and $e_g^2\uparrow$. The gray areas mark the states being occupied by electrons.

region III the SNTO depletion layer closer to the interface, and region IV the SNTO homogenous region far away from the interface. E_F is near the bottom of the e_g band for the homogenous LCMO due to the heavy doping of Ca in $LaMnO_3$, while slightly above the bottom of the Ti 3*d* conduction band for SNTO, which is consistent with electron conductivity of these two materials concluded from the Hall measurements.[6,11] According to the semiconductor theory, when two materials are brought into contact with each other, V_d appears, which corresponds to the work function difference between them. Noting that the E_F of SNTO is generally larger than that of manganites, when they attach, some electrons in SNTO will flow into LCMO to line up the Fermi level and the same number of holes in SNTO will be left. This carrier flowing causes the space charge (electron) region in LCMO and SNTO (hole) near the interface. Due to this build in field, the diffusion potential (V_d) appears. As a result, the $t_{2g}\downarrow$ band in region II can be partially filled by the diffused electrons from SNTO, because the band gap (E_g) between $t_{2g}\downarrow$ and $e_g^1\uparrow$ is smaller than the band gap between $e_g^1\uparrow$ and $e_g^2\uparrow$ due to the weak Hund's rule coupling near the interface.[12] Based on the distribution of spin in bands, the electrons in the $t_{2g}\downarrow$ band and that in the $e_g^1\uparrow$ band are minority spin and majority spin carriers, respectively.

In this junction, R_{jun} is mainly determined by the depletion layer of LCMO. With a reverse voltage, the energy band in region I is raised with respect to that in region II. When $|V|$ is larger than a certain value, the electron can overcome the barrier of the depletion region and starts to tunnel from $e_g^1\uparrow$ in region I to $t_{2g}\downarrow$ in region II, yielding a rapid decrease of R_{jun} for $|V|>-1$ V. In this case, it has been demonstrated that, by applying a magnetic field to the system, the scattering between the majority carriers and the minority spin may cause a reduction of the current due to their antiparallel spins between $e_g^1\uparrow$ in region I and $t_{2g}\downarrow$ in region II. It is the origin of large positive MR in this voltage range. However, if voltage keeps increasing over a certain value, the electron can be activated to reach the channel of $e_g^2\uparrow$ in region II. The latter, then, starts to contribute to the total current. As a result, the dominant role of $t_{2g}\downarrow$ in transport weakens, and the positive MR decreases. However, the detail feature of the MR-*V* dependence of this LCMO/SNTO junction is different from that of $La_{0.9}Sr_{0.1}MnO_3$.[6] In the latter, the reversed bias voltage corresponding to the maximum of the MR is about 0.7 V, whereas $|V_p|$ in the former is around 1.5–2.5 V. This larger $|V_p|$ in LCMO/SNTO can be attributed to the higher interface barrier, which arises from the significant shift of the energy band of its constituents because of the lower E_F of LCMO compared with the hole-doped manganites. On the other hand, with a forward voltage, the excess electrons in region II are drawn out and the width of the depletion layer decreases. Then, fewer electron exists in the $t_{2g}\downarrow$ band, leading to the smaller positive MR effect for $V>0$. It should be pointed out that the influence of interface effect on the strongly correlated electron system is usually complicated. To quantitatively understand the present observation, further work in this regard is required.

With increasing temperature, the thermionic emission of carriers may thin the depletion layer, which accounts for the smaller value of R_{jun} at high temperatures. It is known that with a reverse voltage, the Mn^{3+}/Mn^{4+} ratio near the interface is enhanced due to the injection of electrons into the depletion layer, which disfavors the coherence of the CO ordering. More importantly, Asamitsu *et al.* has shown that when the electric field is large enough, the CO phase could be disrupted, even accompanied with the emergence of the metal-like behavior.[13] Noting that the magnitude of the width of depletion layer is less than 10 nm, the electric field in the case of $|V|=1$ V can be as large as 10^6 V/cm, which is comparable to that in the literature. Based on the two reasons mentioned above, the melting of the CO phase in the depletion layer and the emergence of the metal-like behavior, as depicted by the R_{jun}-T curves for $V<-1$ V (see Fig. 3), can be explained. Because of the magnetic-electronic correlation in the manganite, the large change of spin polarization usually occurs around a metal-insulator transition, which favors the occurrence of the significant MR effect. Therefore, it is not hard to understand the presence of peaks in the MR-*T* curves at low temperatures, as shown in Fig. 3. Obviously, the present work reveals a possibility in controlling the electron filling in the interface and its transport behavior by a reverse electric field, which is important for the practical application of the manganite heterojunctions.

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