Voltage induced ultrasharp current jump and magnetic tunability of $CaMnO_{3-\delta}/La_{0.69}Ca_{0.31}MnO_3$ heterojunction

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The authors report the current-voltage characteristics of $CaMnO_{3-\delta}/La_{0.69}Ca_{0.31}MnO_3$ heterojunctions prepared under different oxygen pressures. The most interesting observation is that the heterojunctions made under low oxygen pressure shows an ultrasharp current jump in the current-voltage curves and the nonlinear coefficient can reach $\sim 2\times 10^4$. They also show remarkable magnetoresistance. The results can be understood in terms of the oxygen vacancy related defects at the junction interface. This work shows that all-manganite-based heterojunctions can show giant nonlinear coefficient, which may have potential applications.
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Recently, manganites heterojunctions have been the focus of intensive study due to their rich physics and potential applications.[1,2] These heterojunctions show interesting properties absent in the constituents, such as the rectifying property with magnetic tunability[1] and reversible resistance switching effect.[2,3] Although the mechanism detail is not very clear, the intrinsic-band-structure coupling and the interfacial state between the different constituents are believed to be important.

Up to now, most works have focused on the heterojunctions integrating manganites with other kinds of materials, such as doped $SrTiO_3$, cuprate, or metal electrode,[1–3] while work on the coupling between manganites with different properties is relatively limited. Particularly, the combination of the hole-doped (p) $La_{1-x}A_xMnO_3$ ($x<0.5$, where A represents the divalent alkaline-earth ions) with the electron-doped (n) $La_{1-x}A_xMnO_3$ ($0.5<x\leqslant 1$) and their coupling are not well studied. It is known that the band filling, as well as the Fermi level (E_F), decreases with A ion doping.[4] As a result, the Fermi level (E_F) of the n-type $La_{1-x}A_xMnO_3$ is lower than that of the p-type $La_{1-x}A_xMnO_3$. This is interesting since E_F of the n-type material is generally higher than that of the p-type material in ordinary p-n junctions. Based on the standard semiconductor theory,[5] the p-n junction made of n-type and p-type $La_{1-x}A_xMnO_3$ may not show rectifying characteristics. So it is interesting to check it. Moreover, it has been shown very recently that oxygen vacancies at the interface of the manganite heterojunctions play an essential role in determining the junction property,[3] thus the effect of oxygen vacancy on the property of manganite heterojunctions is also an interesting and important topic.

We have prepared all-manganite-based heterojunctions by growing $CaMnO_{3-\delta}$ (CMO) on hole-doped $La_{0.69}Ca_{0.31}MnO_3$ (LCMO) single crystals. Details about the LCMO single crystal substrates can be found in our previous paper.[6] Two CMO films with thickness of ~ 220 nm were grown on LCMO (001) (CMO/LCMO) and $SrTiO_3$ (001) (CMO/STO), respectively, using pulsed laser deposition. During deposition, the temperature of the substrate was kept at 730 °C, and the oxygen pressure at 5 Pa. In order to study the effect of oxygen content, two other junctions denoted as CMO/LCMO-H1 and CMO/LCMO-H2 were also deposited under the same condition as that of CMO/LCMO except that the oxygen pressure during deposition was kept at 50 and 85 Pa, respectively. X-ray diffraction analyses illustrate that the films are in single phase with c-axis orientation. The temperature dependence of resistivity for CMO/STO, measured by the standard four-probe method, reveals an insulating behavior, while the resistivity for LCMO substrate presents a sharp metal-semiconductor transition at 230 K (T_P).[6] Current to voltage (I-V) data were collected by using a pulsed-modulated voltage source (model 2400, Keithley) with a width of 0.5 s and interval of 2 s. The positive bias is defined as the current flowing from LCMO to CMO, and the layout of this device is illustrated in the left top inset of Fig. 1(a). Our measurements show that the electrode contact resistance of Au/CMO or Au/LCMO is below 10 Ω, and the contact is Ohmic.

I-V curves for CMO/LCMO, CMO/LCMO-H1, and CMO/LCMO-H2 at 78 and 150 K are shown in Fig. 1(a). All the I-V curves are symmetric indicating the absence of p-n junction rectifying behaviors in this junction, which is consistent with the prediction of the standard semiconductor theory,[5] because the E_F of the n-type CMO is lower than that of the p-type LCMO and there is no depletion layer at the interface. The most important observation is that the I-V curves for CMO/LCMO at temperatures below 150 K exhibit an ultrasharp current jump at certain voltage (V_T), as shown in Fig. 1(a). With increasing oxygen content, the current at the same voltage increases; simultaneously, the I-V curves become smooth and the ultrasharp current jump is suppressed. This result suggests the importance of the oxygen content for the electric transports of the junctions. Figure 1(b) is the I-V curves for CMO/LCMO at different temperatures. To avoid the breakdown of this junction, the current limit at low temperatures was fixed at 65 mA. A detailed

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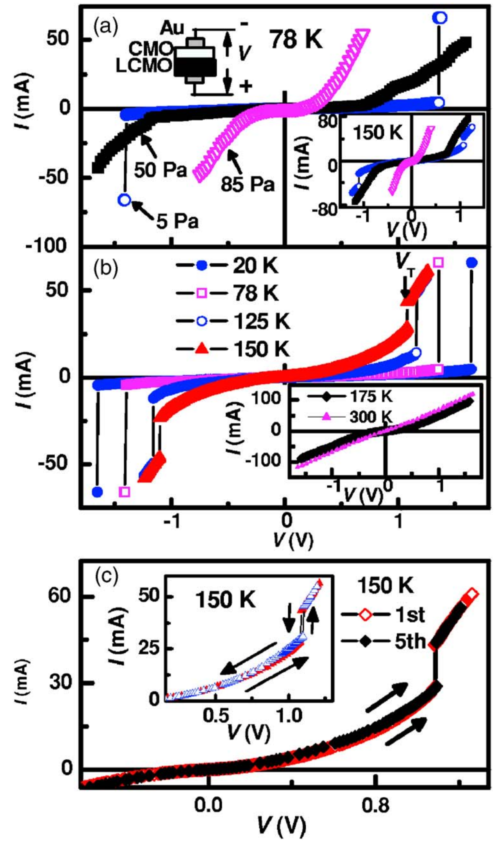

FIG. 1. (Color online) (a) *I-V* curves for CMO/LCMO (5 Pa), CMO/LCMO–H1 (50 Pa), and CMO/LCMO-H2 (85 Pa) at 78 K. The top left inset indicates the layout of the device. The bottom right inset is the curves at 150 K. (b) *I-V* curves for CMO/LCMO at different temperatures. The bottom right inset shows the *I-V* curves at 175 and 300 K. (c) *I-V* curves of the first measurement and the fifth measurement at 150 K. The inset shows the *I-V* curves measured in the voltage increasing and decreasing processes. The sweep directions of voltage are indicated by arrows.

measurement with 0.2 mV voltage increment shows that the nonlinear coefficient α, defined as $\alpha = d(\log I)/d(\log V)$, can reach $\sim 2\times 10^4$ for the current jump at 20 K. As shown in Fig. 1(c), the *I-V* curves of the first measurement and the fifth measurement at 150 K indicate a good reproducibility. Inset of Fig. 1(c) also shows that the currents measured in the voltage increasing and decreasing processes are consistent. Similar result was also obtained at other temperatures. These facts indicate that the nonlinear feature of the *I-V* curve is intrinsic for CMO/LCMO.

The nonlinear coefficient per grain boundary is often cited as the figure of merit for the varistors. The commercially available ZnO-based materials[7] generally have a value in the range of 30–80 for α. Recently, Chung *et al.* found a value of 900 for α in bulk $CaCu_3Ti_4O_{12}$ and they believed that this value is the highest yet seen among varistors.[8] The value of α for our CMO/LCMO is much larger than this record.

The CMO/LCMO junction also shows a negative magnetoresistance (MR)over wide temperature range. As shown in the inset of Fig. 2(a), the current increases when a 5 T magnetic field is applied, indicating a reduction of the junction resistance (defined as $R_j = V/I$). It is noteworthy that both V_T and α remain almost unchanged with the applied magnetic field. The voltage dependences of MR at different temperatures are displayed in Fig. 2(a), where MR is defined by $[R_j(5\ \mathrm{T}) - R_j(0\ \mathrm{T})]/R_j(0\ \mathrm{T})$. At temperatures lower than

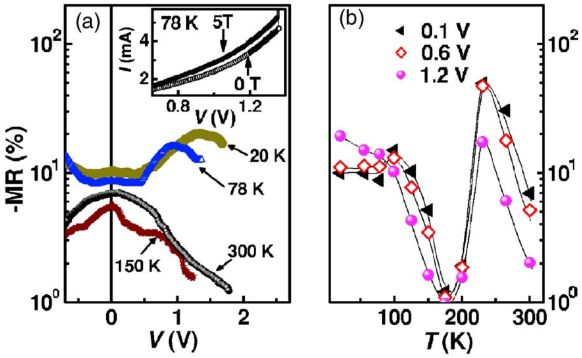

FIG. 2. (Color online) (a) Voltage dependence of MR for CMO/LCMO at different temperatures. The inset shows the *I-V* curves measured at 78 K under 0 and 5 T. (b) Temperature dependence of MR at different voltages.

150 K, MR peaks at a certain voltage, while it decreases with increasing voltage for temperature around and above 150 K. Figure 2(b) shows the temperature dependences of MR at different voltages. MR gains considerable values at temperatures below 125 K and around T_P, respectively. The appearance of maximum MR appears around T_P implies that the MR at high temperatures is related to LCMO.

Since the junction resistance R_j is much larger than the electrode contact resistance of Au/CMO and Au/LCMO, the observed large nonlinearity of *I-V* at V_T should come from the CMO/LCMO junction. Based on the *I-V* measurements of CMO/LCMO, CMO/LCMO-H1, and CMO/LCMO-H2, no obvious rectifying properties are observed in them. Therefore, the role of the interfacial states could not be ignored in this case. Considering the large lattice mismatch between CMO ($a/\sqrt{2} \sim 3.724$ Å) and LCMO ($a/\sqrt{2} \sim 3.875$ Å), the lattice strain at the interface between CMO and LCMO could accommodate oxygen defects. It is known that the insulating layer usually exists on the surface and interface of manganite films or manganite granular sample due to the presence of oxygen deficiencies or strain in these regions.[9] Analogously, an insulating layer could also exist in the interface region between CMO and LCMO. Then, carriers could be trapped in this insulating layer to form the localized states due to the presence of oxygen defects. This will cause the band bending near the interface, resulting in the large back-to-back potential barrier and large junction resistance as well.[10] In fact, in the intermediate voltage region below V_T, the log I-$V^{1/2}$ plots essentially show linear behaviors, as illustrated in Fig. 3(a), which is a typical feature of the thermionic emission process associated with the back-to-back potential barrier.[7,10] In Fig. 3(b), we proposed a schematic band diagram of CMO/LCMO for temperatures below 150 K. In this band diagram, E_F is below the bottom of $e_g{}^1\uparrow$ band in CMO due to the oxygen deficiencies, while locates in the $e_g{}^1\uparrow$ band in LCMO ($e_g{}^1\uparrow$ is the subband of $e_g\uparrow$ due to the Jahn-Teller splitting). The electric properties of the junction are mainly determined by the movement of e_g electrons.

As V approaches V_T, there is a slight deviation from the log I-$V^{1/2}$ dependence [see Fig. 3(a)], indicating the involvement of other mechanisms around V_T. For the electric transport around V_T, the tunneling process should play an important role considering the negative temperature coefficient of V_T, which is similar to that of the doped ZnO or $CaCu_3Ti_4O_{12}$. Though the detailed tunneling process in these varistors is still under debate,[8] we believed that in mangan-

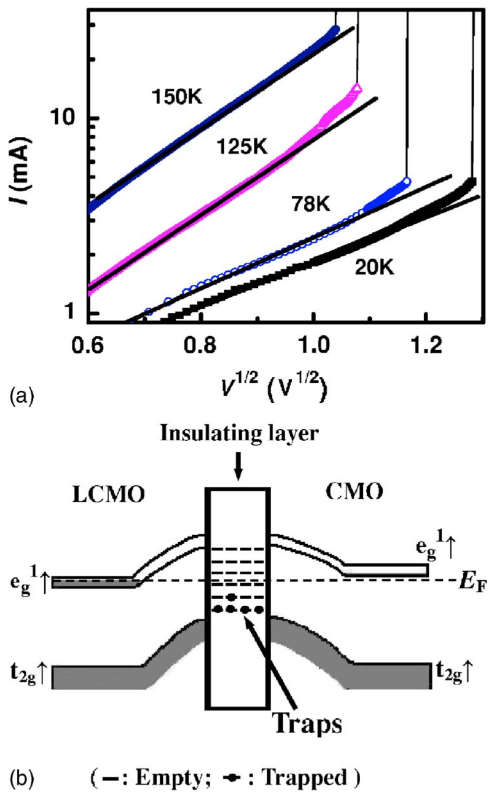

FIG. 3. (Color online) (a) Plots of $\log I$ as a function of $V^{1/2}$. The straight solid lines are fits to the thermionic emission limited current with $\log I \propto V^{1/2}$. (b) Schematic band diagram of the CMO/LCMO junction for $T \leqslant 150$ K. E_F, the Fermi level, is indicated by the dashed line. The region of the insulating layer with traps near the interface is also marked by arrow. The gray areas mark the states being occupied by electrons.

ites the distinctive feature of the interplay between the charge and the lattice should be an indispensable factor. It has been demonstrated that the charge ordering state in manganites can be melted when the electric field is large enough (10^6 V/cm), leading to a dramatic resistivity decrease.[11] Since the thickness of the insulating layer at the interface of the manganites is usually in the order of several nanometers,[9] the electric field with $V=1$ V can be as large as 10^6 V/cm for CMO/LCMO junction. This electric field is expected to lead to the collapse of the charge localized states at the interface of CMO/LCMO and dramatically weakens the insulating property of the tunnel barrier. As a result, an ultrasharp current jump occurs. This could account for the giant α in CMO/LCMO compared with that of ZnO or $CaCu_3Ti_4O_{12}$. With increasing temperature, the thermal fluctuation suppresses the stiffness of the charge localized states and thins down the insulating layer, resulting in smaller V_T or α. The ultrasharp current jump in CMO/LCMO junction provides a way to get giant nonlinear coefficient by controlling the tunnel barrier with electric field since the tunnel barrier shows dramatic change at a certain electric field.

Considering the presence of insulating layer between CMO and LCMO and the electric tuneability, the MR behaviors of CMO/LCMO can also be understood. It has been demonstrated that the oxygen-deficient $CaMnO_{3-\delta}$ shows large MR at low temperatures.[12] Therefore, the MR at low temperatures can be mainly attributed to the spin dependent scattering in the CMO part near the interface. Accompanied with the increase of voltage, the enhancement of current will suppress the spin disorder near the interface, which may account for the relatively low MR at high voltages. In addition, the main part of the insulating layer is generally insensitive to the magnetic field and acts as a "magnetic dead layer."[9] This should be responsible for the minor effects of magnetic field on both V_T and α. With increasing temperature, the weight of the insulating layer in the junction resistance will be reduced due to the thermal diffusion and MR of CMO at high temperatures is small. So LCMO at the interface dominates the variation of MR of the junction as manifested by the maximum MR occurring around T_P. Additionally, to get some information on the thickness effect on the junction, we fabricated a CMO film with a thickness of 20 nm on LCMO. This junction also presents ultrasharp current jump in the I-V curves, but this behavior is suppressed above 125 K, while it still remains at 150 K for CMO/LCMO. Because the thickness of CMO in such junction is much thinner than that in CMO/LCMO, the electric leakage is notable, manifested by the relatively large current at the small bias, which may account for the suppression of current jump behavior in the former. Therefore, to improve the performance of the junction, an appropriate film thickness of CMO is also necessary. The giant α and magnetic tuneability of CMO/LCMO reveal a promising potential of all-manganite-based devices as a type of electric switching device with high sensitivity and multifunction.

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