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Electronic transport of the manganite-based heterojunction with high carrier concentrations

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The transport property of the manganite heterojunction $La_{0.9}Ca_{0.1}MnO_{3+\delta}/SrTiO_3$ (doped by 1 wt %Nb) has been experimentally studied. The most important results of the present work are the discovery of the charge tunneling-dominated transport process, characterized by the appearance of the rectifying behaviors fairly described by the Newman equation $I \propto \exp(\alpha T)\exp(\beta V)$ in a considerable temperature range (α and β are constants, and I and V are current and voltage, respectively). Significant modification of magnetic field to charge tunneling is also observed. It is believed that magnetic field depresses junction resistance by reducing depletion width of the junction. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2728750]

Different from the ordinary semiconductors, manganites generally exhibit much higher carrier concentrations. However, experimental results show, from every aspect, that the manganite-based junction still exhibits an excellent rectifying property even when the doping level is extraordinarily high.[1–4] To get a reasonable explanation, charge localization due to inhomogeneous magnetoelectronic structure and enhanced Jahn-Teller effects in the manganite films has been proposed.[1] Evidence of charge trapping has already been observed,[5,6] and the presence of an insulating dead layer of ~60 Å in thickness has been proven for the $La_{0.67}Ca_{0.33}MnO_3$ film.[6]

It is a natural expectation that the distinctive electronic structures due to the strong electron correlation in the manganite junctions should have a strong impact on their transport behaviors. Although there is a lot of work on manganite junctions, researches on the transport mechanisms are still very limited. As a primary attempt, Postma *et al.*[3] undertook a quantitative analysis on the current-voltage characteristics of the manganite junctions and found that the transport behavior of $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3$:Nb (0.1 and 0.01 wt % Nb) can be well described by the thermionic emission model. For a similar junction $Pr_{0.7}Ca_{0.3}MnO_3/SrTi_{0.9998}Nb_{0.0002}O_3$, Sawa *et al.* declared that the thermal diffusion of the charge carriers was dominative.[4] However, it seems that not all of the transport behaviors of the manganite junctions can be explained based on these models. As a matter of fact, if interfacial defects exist, leakage current may be significant. Electron tunneling is also possible when the thickness of the depletion layer is small. These analyses indicate a possibility for the presence of unordinary electronic transport processes in heavily doped manganite junctions. Unfortunately, work in this aspect is still very limited. In this letter, we will perform a systematic study on the transport behavior of a *p-n* junction composed of a $La_{0.9}Ca_{0.1}MnO_{3+\delta}$ (LCMO) film and a 1 wt % Nb-doped $SrTiO_3$ (STON). LCMO was chosen because of its small lattice mismatch with STON. To directly access the property of the interfacial layer and to get a perfect interfacial structure, an ultrathin LCMO film is used for the junction. Special attention has been paid to the transport mechanism of the junction. The most important results of the present work are the discovery of electron tunneling-dominated current-voltage characteristics and the significant modification of magnetic field to charge tunneling.

The LCMO/STON junction was fabricated by epitaxially growing the LCMO film on a (001) STON substrate by the pulsed laser ablation technique. The substrate was kept at ~720 °C and the O_2 pressure at ~100 Pa during the deposition. The film thickness is ~100 Å, controlled by deposition time. To absorb oxygen, the film was further annealed at 550 °C for 10 min in air after deposition.

Resistive measurements were performed on a superconducting quantum interference device magnetometer. Figure 1 shows the resistivity of the LCMO film (grown on $SrTiO_3$ for a comparison study) measured under the fields of $H=0$ and 5 T. Results for a thicker film (1000 Å) are also presented for comparison. An insulating behavior is observed in the whole temperature range studied for the ultrathin film, and the resistivity is much larger than that of the thicker film. The maximum magnetoresistance is ~56, occurring at ~150 K. The degeneration of the conductive property of the thin film has been ascribed to thickness effects.[5,6]

The size of the junction area is 1×1 mm^2, fabricated by the conventional photolithography and chemical etching technique. The two-probe technique was used for the measurements of the current-voltage characteristics to avoid the effects of current distribution in the junction.[7] The contact

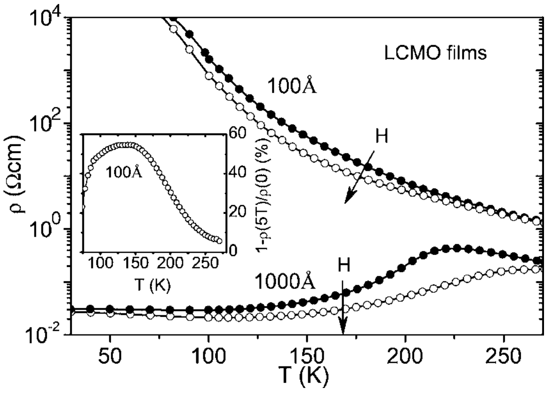

FIG. 1. Resistivity of the LCMO films measured under the fields of $H=0$ and 5 T. Inset plot shows the corresponding magnetoresistance.

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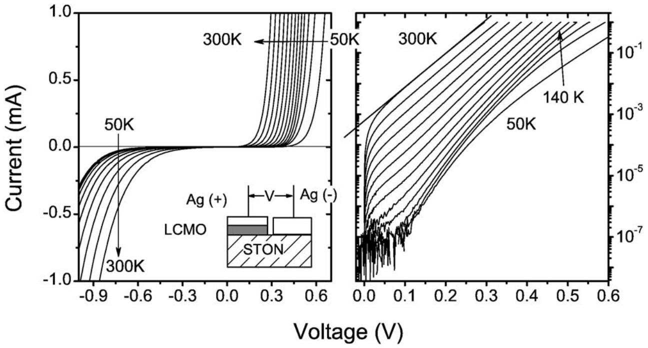

FIG. 2. Left panel: Current-voltage characteristics of LCMO/STON measured under different temperatures. Inset plot is the schematic diagram showing the electrode setting. Right panel: Semilogarithmic plot of the current-voltage characteristics of LCMO/STON (forward direction). Thin line is a guide for the eyes.

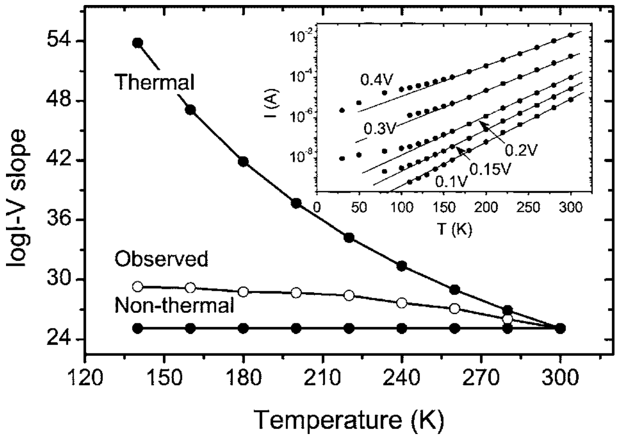

FIG. 3. log *I-V* slopes of the thermal and nonthermal processes as functions of temperature. Experimental results are shown for comparison. Inset: Current as a function of temperature under a fixed voltage. Solid lines are guides for the eyes.

resistance is smaller than 1 and 50 Ω between Ag and STON and between Ag and manganite films, respectively, evaluated by comparing the results of four- and two-probe measurements.[8] It is small compared with junction resistance as will be seen below and, therefore, would not affect the quantitative analysis of the rectifying behavior.

Figure 2 presents the current-voltage (*I-V*) relations of the junction measured by tuning bias voltage. Fairly good rectifying behaviors characterized by strongly asymmetric *I-V* curves are observed. The current remains small up to the reverse bias of 0.6 V but grows rapidly with voltage in the forward direction. Decrease in temperature has no obvious effects except for an expansion of the *I-V* curve along the *V* axis. These are typical behaviors of the manganite junctions though the LCMO film here is only 100 Å in thickness.

To get the information on the transport mechanism of the junction, the *I-V* curves were further analyzed. The right panel of Fig. 2 depicts the semilogarithmic plot of the *I-V* curves under forward bias. An excellent linear relation between log *I* and *V* is observed in the temperature range from 140 to 300 K, which is a phenomenon hardly observed in the p^+-n^+ diode that usually suffers from significant creepage. Decrease in temperature causes a nearly rigid downward shift of the log *I-V* curves. These results imply that the current varies against bias voltage following a similar rule under different temperatures.

According to the semiconductor theory,[9] the forward current can be either thermal or nonthermal. To produce thermal current, charge carriers have to surmount the potential barrier to cross the junction. In this case, the log *I-V* slope is expected to vary with $1/T$, the temperature plays an important role in activating charge carriers. Charge carriers can also tunnel through the potential barrier. If the tunneling occurs predominantly at the base of the potential barrier, the current is nonthermal in nature and can be described by Newman equation

$$I = I_s \exp(\alpha T)\exp(\beta V), \qquad (1)$$

where I_s, α, and β are parameters weakly depending on V. This equation predicts a log *I-V* slope essentially independent of temperature and a linear increase of log *I* with temperature if the electric bias is fixed.

Figure 3 is a comparison of the log *I-V* slopes of the thermal and nonthermal processes. It shows that the temperature dependence of the measured log *I-V* slope is quite weak, much closer to that of the nonthermal one. An exponential growth of the current with temperature is also observed under a constant voltage (inset in Fig. 3). These features are consistent with those predicted by Eq. (1) and strongly suggest the tunneling character of the transport behavior of LCMO/STON.[9]

To justify the assumption of charge tunneling, a further analysis on depletion width is required. The thickness of the depletion layer can be estimated based on the formulas $t_1=\{2N_{D2}\varepsilon_1\varepsilon_2\varepsilon_0V_D/[qN_{A1}(\varepsilon_1N_{A1}+\varepsilon_2N_{D2})]\}^{1/2}$ and $t_2=\{2N_{A1}\varepsilon_1\varepsilon_2\varepsilon_0V_D/[qN_{D2}(\varepsilon_1N_{A1}+\varepsilon_2N_{D2})]\}^{1/2}$,[9,10] where t_1/t_2 is the depletion width in LCMO/STON, $\varepsilon_1/\varepsilon_2$ is the permittivity of LCMO/STON, N_{A1}/N_{D2} the hole/electron density of LCMO/STON, ε_0 the permittivity of the vacuum, and V_D the diffusion potential. Figure 4 presents the depletion width as a function of the hole concentration of LCMO, obtained adopting the parameters $\varepsilon_1=30$, $N_{D2}=1.98\times10^{26}/\text{m}^3$, and $V_D=0.4$ eV.[11,12] The permittivity of STON has been proven to be spatial dependent because of the presence of built-in electric field.[13] It gets the minimum value near interface and grows rapidly apart from the interface. Considering this fact, results for different ε_2 are given. As shown in Fig. 4, with the increase of hole concentration, the depletion width exhibits a monotonic decrease when ε_2 is small and a more complex variation when ε_2 is large. The maximum depletion width is ~110 Å (film thickness=100 Å), occurring when nearly all of the holes of LCMO are trapped. The minimum width is quite small. It is ~49 Å when $\varepsilon_2=300$ (the permittivity of

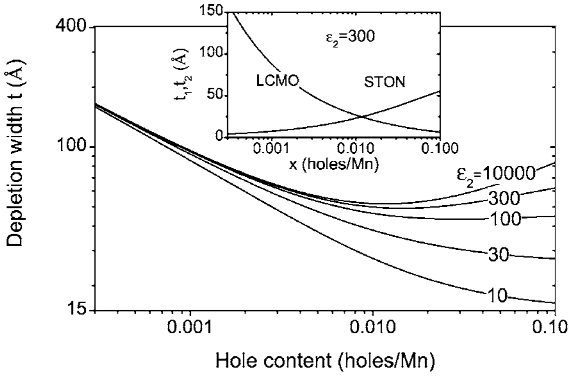

FIG. 4. Depletion width of the LCMO/STON junction as a function of the mobile hole content in LCMO. Inset plot shows the depletion widths of LCMO and $SrTiO_3$.

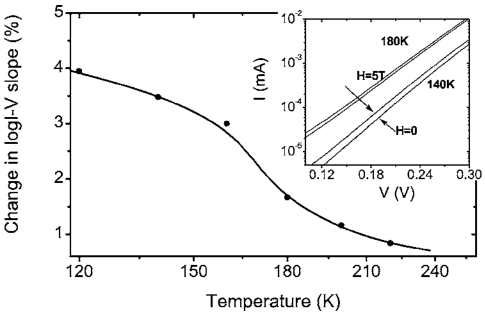

FIG. 5. Variation of the log *I-V* slope under a field of 5 T. Solid line is a guide for the eyes. Inset plot is a close view of the magnetic field effects for two selected temperatures.

$SrTiO_3$ near the ambient temperature) and ~52 Å even when ε_2 is as high as 10 000. According to Suzuki *et al.*,[13] the minimum permittivity of STON decreases from ~190 to ~40 as the Nb content increases from 0.05 to 0.5 wt % in their junction. A direct extrapolation shows that ε_2 will be 20–30 for 1 wt % Nb. On the analogy of these results, we can safely say that the permittivity of STON could not exceed that of $SrTiO_3$ in LCMO/STON. This implies that the results shown in Fig. 4 may be the upper bound of the depletion thickness. These analyses demonstrate the feasibility of charge tunneling in LCMO/STON.

It may be easier for the charge carriers to tunnel through than surmount the interfacial barrier. A direct calculation indicates that the junction resistance of LCMO/STON is $\sim 4\times 10^5\ \Omega$ (in the zero-bias limit) near the ambient temperature. This value is similar to that of the $La_{0.85}Sr_{0.15}MnO_3/SrTiO_3/La_{0.05}Sr_{0.95}TiO_3$ diode with a thin intermediate layer, for which a tunneling-dominated process has been detected.[14]

There is a possibility to release trapped holes by applying a magnetic field, which can improve the spin alignment of Mn ions, therefore enhance the double exchange. This actually implies a possibility to tune charge tunneling by magnetic field noting the relation between hole concentration and depletion width. Based on the results shown in Fig. 4, either positive or negative magnetoresistance (MR) effect is possible, depending on the content of mobile holes. Negative MR is expected to appear when x or ε_2 is small. In this case, the depletion width, therefore the junction resistance, is very sensitive to hole concentration.

Negative MR is indeed observed in LCMO/STON. As shown in Fig. 5, a visible increase in current is observed after the application of a field of 5 T, resulting in an obvious declining of the log *I-V* curves. This effect is especially strong at low temperatures. The relative variation of the log *I-V* slope increases from ~0.87% for $T=220$ K to ~4% for $T=120$ K (inset in Fig. 5). The corresponding MR effect is rather strong, and the maximum MR ratio $[1-\rho(H)/\rho(0)]$ can be as high as ~45% (not shown).

If the tunneling model is applicable, the relative change of the log *I-V* slope will be approximately equivalent to $\Delta t/t$ $(t=t_1+t_2)$ noting the fact that β is a parameter proportional to depletion width.[9,10] This result reveals a variation of a few percent of the depletion width under magnetic field. To produce such an effect, the required variation of hole concentration is $\Delta x \sim 10^{-2}$ to 10^{-3} holes/Mn. The field-induced change of the hole content can be estimated based on the resistive data. In fact, there is a simple relation between log ρ and x, $\Delta(\log \rho)=7.99\Delta x$, for the $La_{0.67}Sr_{0.33}MnO_{3-\delta}$ films.[15,16] If the same relation holds for the LCMO family, the variation of hole content under a field of 5 T will be $\Delta x \sim 0.008$ at $T=230$ K (the resistivities of the LCMO film are 3.255 and 2.775 Ω cm for $H=0$ T and $H=5$ T, respectively). Although Δx is small, the resulted change of t could be significant, especially when the initial x is small. Taking the typical case of $\varepsilon_2=300$ as an example, we found that $\Delta t/t \approx 8\%$ when hole concentration increases from 0.0056 to 0.015. $\Delta t/t$ can be even larger if ε_2 is lower. As discussed above, it is possible for the LCMO film to exhibit a hole concentration much lower than the nominal value, which has been confirmed by the presence of the insulating dead layer in the manganite films.

The *I-V* relations become complex below 140 K, which could be a consequence of the electric bias dependence of the permittivity of STON. Charge tunneling may also be depressed in the low temperature range because of the increase of the permittivity of STON. As a supplement we would like to point out that charge tunneling may prefer to appear in the manganite junctions with a heavily electron-doped $SrTiO_3$, which has a thin depletion layer. The depletion width will become thicker as the content of Nb decreases. In this case, a positive electric bias may be required for significant charge tunneling.

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