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Bias-dependent rectifying properties of n - n manganite heterojunctions $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3/\text{SrTiO}_3:\text{Nb}$ ($x=0.65-1$)

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The transport property of n - n type manganite heterojunctions, composed of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ films ($x=0.6, 0.75, 0.85, \text{ and } 1$) and 0.05 wt % Nb-doped SrTiO_3 , has been experimentally studied. Different from p - n junctions, the rectifying behavior of which is either thermionic emission/diffusion-dominated or tunneling-dominated; the electronic process in the n - n junction undergoes a nonthermal to thermal transition as bias voltage increases, which is a feature emerging when Ca content exceeds $x=0.75$ and developing with the increase in x . The two processes can be well described by the Shockley equation and the Newman equation, respectively. Possible mechanisms for this phenomenon are discussed. © 2008 American Institute of Physics.
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Manganite-based heterojunctions have attracted much attention in recent years because of their abnormal properties such as excellent rectifying behavior,¹ strongly bias-dependent magnetoresistance,² and magnetic field-tunable photovoltaic effect.³ On the analogy of the conventional junction, an energy barrier could be formed due to the difference in the Fermi energies of manganites and $\text{SrTiO}_3:\text{Nb}$. Although detailed mechanisms are not very clear at present, variation in interfacial potential with magnetic field/temperature is believed to be the underlying reason for the abundant properties of manganite junctions.

It is fortunate that the rectifying behaviors observed in manganite junctions can be well described by the Shockley equation that has been proposed for conventional p - n junctions:^{4,5} The current shows an exponential increase with both the bias voltage and reciprocal temperature, which is a feature appearing when charge carriers surmount interfacial barrier with the assistance of thermal energy,⁶ and the information on interfacial potential can be obtained from the current (I)-voltage (V) characteristics.⁴⁻⁷ However, when the carrier concentration in $\text{SrTiO}_3:\text{Nb}$ is high, a completely different rectifying behavior appears. The current grows exponentially with either bias voltage or temperature, instead of reciprocal temperature. This is a character of electron tunneling and, as shown by Xie *et al.*,⁸ can be described by the so-called Newman equation. It occurs when the depletion layer is thin enough for electrons to tunnel through.

In general, the rectifying property of the p - n manganite junction is either thermionic emission/diffusion-dominated or tunneling-dominated, depending on the carrier concentration in $\text{SrTiO}_3:\text{Nb}$. In this letter, however, we report on an evolution from the latter to the former as bias voltage increases in the n - n junctions $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO)/ $\text{SrTiO}_3:\text{Nb}$. This phenomenon appears when x exceeds ~ 0.75 and develops with the increase in Ca content.

Manganite junctions were fabricated by growing $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x=0.65, 0.75, 0.85, \text{ and } 1$) films on 0.05 wt % Nb-doped (001) SrTiO_3 (STON) substrates using

the pulsed laser ablation technique. During the deposition, the substrate temperature was kept at 720 °C and the oxygen pressure between 50 and 80 Pa (increasing with the content of Ca). The film thickness is ~ 150 nm, controlled by deposition time.

The lateral size of the junction is 1×1 mm², patterned by the conventional photolithographic and chemical etching technique. Two Cu electrodes were deposited, respectively, on the LCMO film and the STON substrate. The electric contacts are Ohmic with the contact resistance of ~ 15 Ω between Cu and STON and ~ 200 Ω between Cu and LCMO at the ambient temperature. The current-voltage characteristics were measured by a superconducting quantum interference device magnetometer equipped with a resistance measurement unit.

X-ray diffraction analyses reveal a linear decrease in lattice constant with Ca content (except for $x=1$), which is a result in quantitative agreement with those reported by other groups (not shown). This result is an indicator of the near stoichiometry of the Mn^{4+} content in our samples and suggests the electronlike character of the charge carriers in the LCMO films ($x \geq 0.65$), noting the electron-doped behaviors of the LCMO film for $x=0.5$ and 0.67 as proved by the Hall study.⁹ As determined by the four-probe technique, the LCMO films (grown on the SrTiO_3 substrate for comparison study) are semiconducting in the whole temperature range investigated, with a monotonic increase in resistivity as x grows from 0.65 to 1 (not shown). These behaviors are similar to those of bulk LCMO.

Excellent rectifying behaviors are observed in all of the junctions. The current is extremely small for the backward bias up to the voltage of -7 V, while grows rapidly in the opposite direction when the bias voltage exceeds a threshold value (not shown). This asymmetry develops with the decrease in temperature due to the asymmetric expansion of the I - V curves along the V -axis. The zero-bias junction resistance is of the order of 10^7 Ω at the temperature of 350 K. These are actually the typical behaviors of the p - n manganite junctions,^{5,6} although LCMO/STON is nominally an n - n one when $x \geq 0.65$. Compared with the p - n junction, however, the I - V relations of the n - n junctions are much more com-

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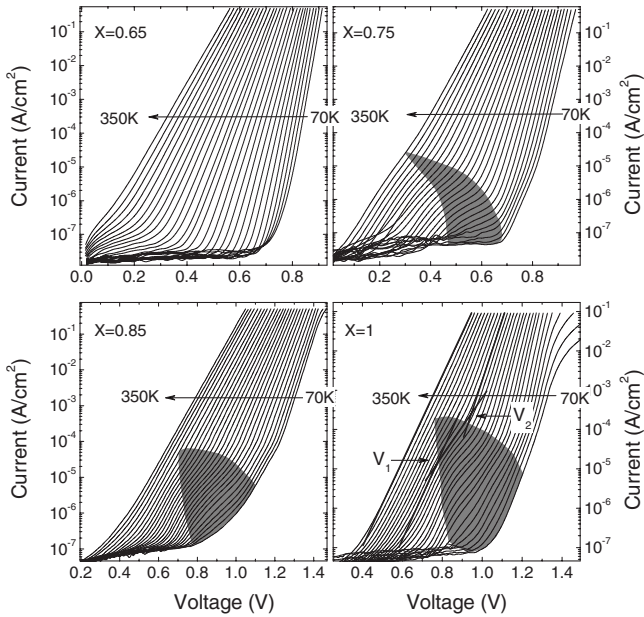


FIG. 1. Semilogarithmic plot of the characteristics of LCMO/STON (right panel). Straight lines in the right panel show the log I - V relations of two electronic processes. Hatched areas mark the regions for the electronic evolution.

plex. Figure 1 presents the I - V curves, in semilogarithmic scale, of LCMO/STON recorded in the temperature range of 70–350 K. A linear variation in $\log I$ versus V with a slope varying against $1/T$, as will be shown later, is observed when bias voltage is large. The ideality factor n , defined by the Shockley equation $I \approx I_0 \exp(eV/nk_B T)$, varies from ~ 1.3 for $T=350$ K to ~ 1.5 for $T=150$ K for the sample of $x=1$, nearly constant in a wide temperature range, where I_0 is the saturation current and k_B the Boltzmann constant. According to the semiconductor theory, n will be 1, when thermal current is dominative, or 2, when recombination current prevails. An ideality factor between 1 and 2 means a combined contribution of the two currents.¹⁰ These results, which are similar to those obtained by Sawa *et al.*⁵ for $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{SrTi}_{0.9998}\text{Nb}_{0.0002}\text{O}_3$ and by Wang *et al.*¹¹ for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3/\text{STON}$, reveal the occurrence of thermionic emission/diffusion in the present junctions under high biases.

A different electronic process appears at low biases. An electronic evolution that proceeds in a wide bias range (marked by the hatched areas in Fig. 1), which is particularly obvious in the intermediate temperature range, takes place with the decrease in bias voltage, and parallel log I - V curves are resulted. For a further analysis of the two electronic processes, the log I - V slope in the high (κ_{high}) and low (κ_{low}) bias ranges of the sample $x=1$ is presented in Fig. 2 (top panel). κ_{high} displays a linear increase with $1/T$ (solid line), whereas κ_{low} is nearly independent of temperature ($\sim 25.1 \log(\text{A cm}^{-2})/\text{V}$). The other two distinctive features of the low bias process are the exponential current growth with temperature, if bias voltage is fixed at a value below 0.75 V, and the parallelism of the log I - T curves obtained at different biases (bottom panel of Fig. 2). The log I - T slope is $\sim 0.0456 \log(\text{A cm}^{-2})/\text{K}$. Similar features are observed in samples with $x=0.75$ and 0.85. According to the semiconductor theory, an alternative approach for the charge carriers to go across the junction is quantum tunneling. If

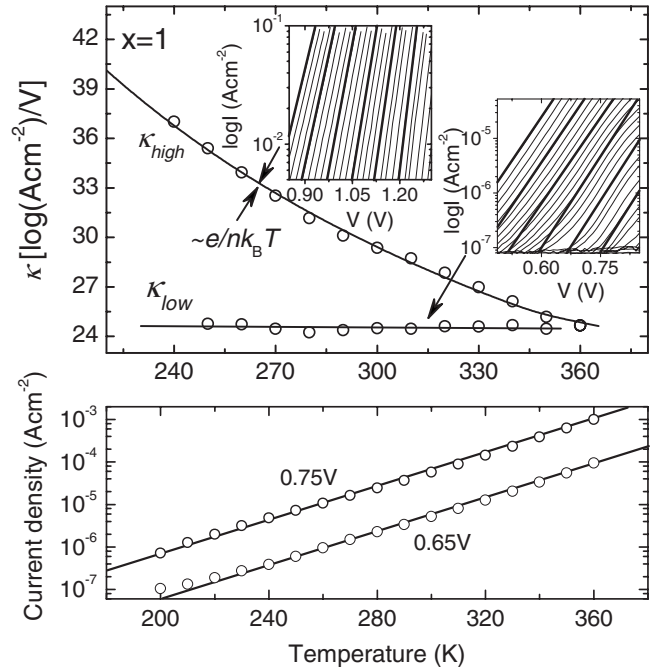


FIG. 2. The log I - V slopes of the thermal and nonthermal processes as functions of temperature (top panel) and the linear log I - T relations of the nonthermal process under two typical biases (bottom panel) for the LCMO/STON junction with $x=1$. Inset plots are close views of the I - V curves of the thermal and nonthermal processes. Thick solid lines are guides for the eyes.

the tunneling occurs predominantly at the base of the potential barrier, the current is nonthermal in nature and can be described by the empirical Newman equation, $I \propto \exp(\alpha T) \exp(\beta V)$, where α and β are parameters approximately independent of V and T .¹² It means that both the log I - T and log I - V relations are linear with the slopes of α and β , respectively. Electron tunneling has been observed by Xie *et al.*⁸ in $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3/\text{SrTiO}_3$: 1 wt % Nb, which exhibits a rather thin depletion layer because of the heavy doping levels, and the deduced parameters there are $d \log I/dT \approx 0.0448 \log(\text{A cm}^{-2})/\text{K}$ and $d \log I/dV \approx 25.0 \log(\text{A cm}^{-2})/\text{V}$. It is obvious that all of the features predicted by the Newman equation can be identified from the data presented in Fig. 2. Similarities between LCMO/STON ($x=1$) and $\text{La}_{0.9}\text{Ca}_{0.1}\text{MnO}_3/\text{SrTiO}_3$: 1 wt % Nb are also obvious (~ 0.0456 versus ~ 0.0448 and ~ 25.1 versus ~ 25.0). These results strongly suggest the occurrence of electron tunneling in the present junction when bias voltage and temperatures are low.

As a representation, Fig. 3 (left panel) shows the temperature dependence of the threshold voltages for the cross-over between the two processes for the junction $x=1$. The voltage that triggers the electronic evolution (V_1) is insensitive to temperature, whereas the one (V_2) required to stabilize the thermal process grows rapidly as temperature decreases. This result shows the preference of the junction for the tunneling process at low temperatures. A monotonic decrease in V_2 with Ca content was also observed when temperature was kept constant, and no electronic transition is observed down to the current of 10^{-10} A (the lower limit of our ammeter) in the junction of $x=0.65$ (not shown). As shown by the right panel of Fig. 3, V_2 would vanish if x is lower than ~ 0.65 for $T=210$ K. These results imply that the electronic transformation takes place only in n - n junctions.

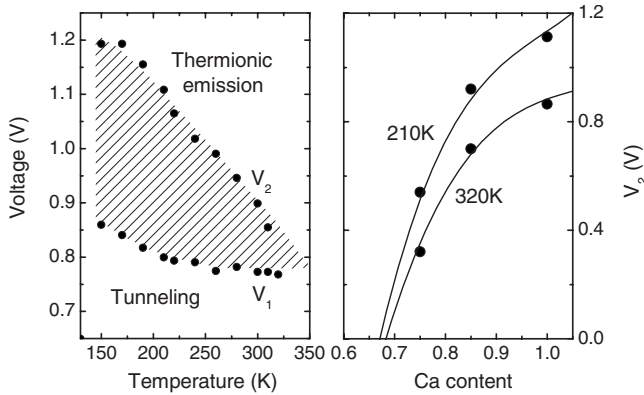


FIG. 3. Left panel: temperature-dependent characteristic voltage for the evolution between different electronic processes in junction LCMO/STON ($x=1$). Right panel: the threshold voltage for the thermionic emission process as a function of Ca content. Hatched area marks the transition region. Solid lines are the results of third-order polynomial fittings of the experiment data.

Variation in built-in potential with Ca content has been studied in a previous paper.¹³ The focus of the present study is the evolution of the electronic process as bias voltage grows. In general, the thermionic emission process prevails in the junctions composed of hole-doped manganites if the carrier density in SrTiO₃:Nb is low, and the tunneling-dominated behavior appears only when Nb content is so high that the depletion width is thin enough. The carrier concentration in the STON substrate used here is $\sim 1 \times 10^{19}/\text{cm}^3$, and the depletion layer will be ~ 36 nm for a manganite p - n junction adopting the permittivity of 300 for STON and the hole concentration of $\sim 1.7 \times 10^{21}/\text{cm}^3$ for LCMO. Cases could be somewhat different for the n - n junctions. To get the information on interfacial state, the capacitance (C) of LCMO/STON was further studied. Negative bias voltages were applied to avoid the damage of the junction. Well linear $1/C^2$ - V relations are obtained for all of the junctions (not shown), which is a feature predicted by semiconductor theory. As shown by Fig. 4, the capacitance of LCMO/STON, recorded under the frequency of 200 kHz at the temperature of 140 K, exhibits a gradual decrease with Ca content, and the typical capacitance is ~ 27.8 nF/mm² for $x=0.65$ and ~ 17.9 nF/mm² for $x=1$. Based on the capacitance data, the effective thickness of the depletion layer

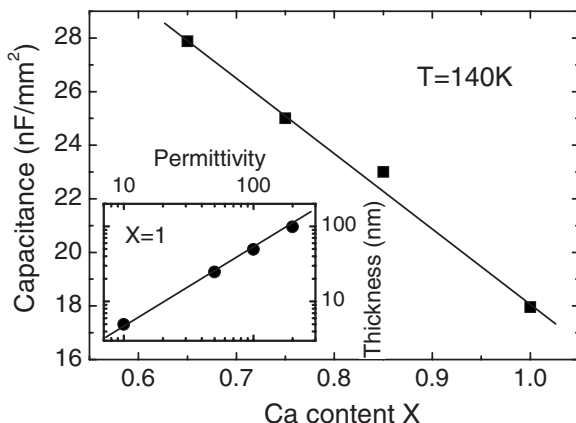


FIG. 4. Zero-bias capacitance of LCMO/STON as a function of Ca content, measured under the frequency of 200 kHz at $T=140$ K. Inset plot shows the depletion width corresponding to different permittivity for the junction $x=1$.

($\sim \epsilon_0 \epsilon / C$) can be estimated, and it is ~ 16 and ~ 24 nm for $x=0.65$ and 1, respectively, adopting the same permittivity of $\epsilon=50$ for STON.

As is well known, the LCMO film is generally oxygen deficient when Ca content is high, especially as x approaches unity. It may therefore display a tendency to strip oxygen from neighboring STON. This is expected to enhance the electron concentration in STON, causing a decrease in permittivity. As reported, the permittivity of STON can decrease from ~ 210 to ~ 20 as the electron concentration grows from $\sim 10^{17}/\text{cm}^3$ to $\sim 10^{20}/\text{cm}^3$.¹⁴ A direct calculation shows that the depletion width will be ~ 5 nm when $\epsilon=10$ (inset in Fig. 4). This is a thickness allowing electron tunneling. Considerable oxygen migration may occur only around the imperfections on the surface of STON (the presence of which has been experimentally proved¹⁵). As a consequence, the rectifying behavior characterized by a large area thermionic emission/diffusion in parallel with a small area charge tunneling emerges. The latter process, which prevails at low biases, can be attenuated at moderate bias by a large series spreading resistance due to its small area, which may explain the curvature of the log I - V curves toward the ones determined by thermal diffusion. Imperfection-induced leakage current occurring near defects has been observed in conventional p - n junctions,¹⁶ although the electronic process there is somewhat different from that observed here.

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