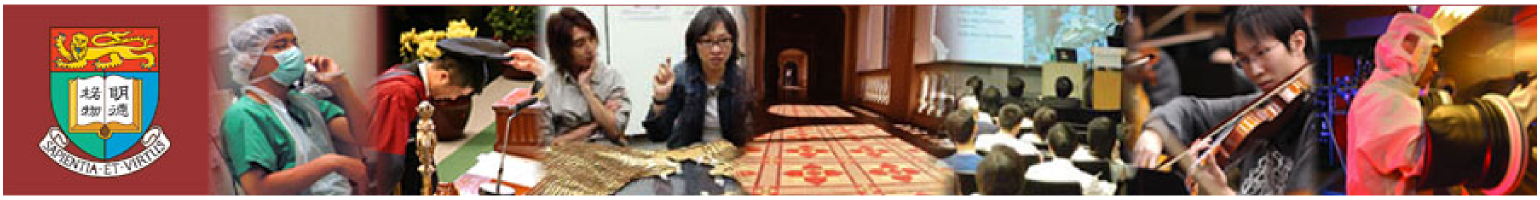

Good rectifying characteristic in $p-n$ junctions composed of $La_{0.67}Ca_{0.33}MnO_{3-\delta}$/Nb–0.7 wt%-doped $SrTiO_3$

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Simple $p-n$ junctions have been fabricated using a simple heteroepitaxial structure of $La_{0.67}Ca_{0.33}MnO_{3-\delta}$/Nb-doped $SrTiO_3$. In such junctions, the $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ exhibits semiconductor behavior due to oxygen deficiency, whereas the Nb–0.7 wt%-doped $SrTiO_3$ shows a metal behavior. These junctions demonstrate good rectifying characteristic in a wide temperature range from 5 to 350 K. An intriguing observation is that the rectifying behavior is nearly independent of temperature. [DOI: 10.1063/1.1606098]

It has been known that the $p-n$ junction has been widely used as a basic element in various semiconductor devices. Compared to the conventional semiconductor $p-n$ junctions, the ones composed of manganese oxides could be expected to exhibit characteristics, such as magnetic, electric, or light controlled behavior, considering the high sensitivity of electronic and magnetic properties of manganese to external magnetic field, electric field, or light.[1–3] They should be of great interest in view of practical applications. Moreover, $p-n$ junctions made of oxides are expected to work at a high temperature where the conventional $p-n$ junctions may not be competent. Therefore, lots of research interest have been attracted to the development of heteroepitaxial junctions of novel oxide materials.[4–8] Mitra *et al.* reported asymmetric $I-V$ characteristics in $La_{0.7}Ca_{0.3}MnO_3/SrTiO_3/La_{0.7}Ce_{0.3}MnO_3$ trilayers,[4,5] in which the hole-doped $La_{0.7}Ca_{0.3}MnO_3$ was referred as a p-type manganite and the electron-doped $La_{0.7}Ce_{0.3}MnO_3$ presented as the n-type electrode. The inserted insulating $SrTiO_3$ layer is necessary to reduce tunneling current and avoid reactions and diffusions between the p- and n-type layers. Asymmetric $I-V$ characteristics were observed above T_C where both the p- and n-type layers display polaronic semiconducting behavior. At low temperatures below T_C both p- and n-type manganites behave as ferromagnetic metals and the asymmetric $I-V$ characteristics disappear. Recently, rectifying characteristics were reported on simple heterostructures of $La_{0.9}Ba_{0.1}MnO_3$/Nb–0.01 wt%-doped $SrTiO_3$ and $La_{0.9}Ba_{0.1}MnO_3/Sr_{0.99}La_{0.01}TiO_3$,[6,7] in which $La_{0.9}Ba_{0.1}MnO_3$ was referred as p-type oxide which exhibits ferromagnetic metallic behavior below T_C ($\sim$300 K), and the doped $SrTiO_3$ with little Nb or La was used as n-type oxide which behaves like a semiconductor. Remarkable asymmetric $I-V$ characteristics were observed in such a simple junction and the electric field modulation of double exchange ferromagnetism on the basis of a $p-n$ junction was demonstrated.[7] Meanwhile, it was proposed that the bilayer junction is precisely the type of degenerate p^+-n junction below T_C based on a band diagram raised by Kudo,[9] and a $p-n$ one above T_C.[7] It has also been known that the doped $SrTiO_3$ with a little more Nb or La would show a metallic behavior.

In this letter, we report rectifying characteristics in a simple heteroepitaxial junction of $La_{0.67}Ca_{0.33}MnO_{3-\delta}$/Nb–0.7 wt%-doped $SrTiO_3$, in which $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ showing a semiconducting characteristic due to oxygen deficiency is used as the p-type oxide while the Nb–0.7 wt%-doped $SrTiO_3$ as n-type reveals a metal behavior. Good rectifying characteristic, which is nearly independent on temperature, was found in the whole temperature range from 5 to 350 K.

These junctions were fabricated simply by growing a $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ epitaxial thin film on a Nb–0.7 wt%-doped $SrTiO_3$ (STO–Nb) single crystal substrate with a (100) orientation using pulsed laser deposition (PLD) technique. Bulk target of $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) was prepared by the conventional solid-state reaction method. To obtain oxygen-deficient $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ film with suitable semiconductive characteristics, relatively high substrate temperature of 800 °C and low power of pulse laser beam about 50 mJ with frequency 10 Hz were employed. Flowing oxygen with pressure about 20 Pa were used. The growing process was halted when the film thickness was about 400 nm. The experiments of x-ray diffraction reveal sharp peaks of the formed ABO_3 phase with the c-axis perpendicular to the substrate surface. Besides the reflection from substrate and the $(00l)$ peaks of the LCMO, no other peaks are visible, demonstrating that the grown films are of single phase. Flat surface was confirmed through high-resolution atomic force microscope. The average surface roughness was found less than 5 Å in a range of 10 μm. All magnetic and electrical resistance measurements were performed using a superconducting quantum interference device magnetometer equipped with a probe for making four-point electrical resistance measurements.

The measurements of in-plane resistance confirmed semiconducting behavior for such an oxygen-deficient $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ film in the whole measured temperature

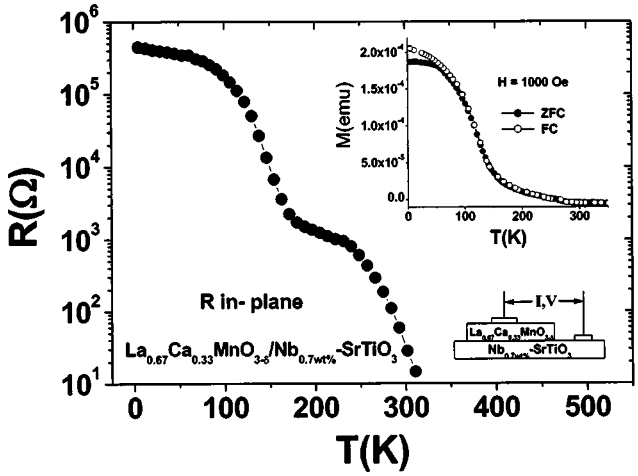

FIG. 1. The temperature dependence of in-plane resistance of oxygen-deficient $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ film. Upper inset is the temperature dependent magnetization measured in ZFC and FC process under a field of 1000 Oe. The lower inset of Fig. 1 is the schematic structure of present $p-n$ junction.

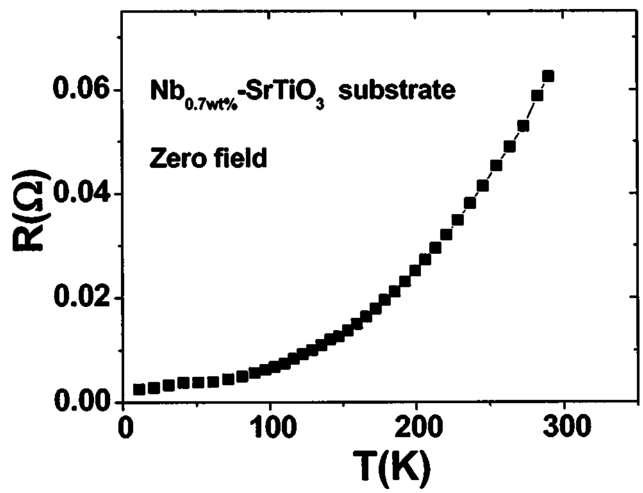

FIG. 2. The temperature dependent resistance of Nb–0.7 wt %-doped $SrTiO_3$ single crystal substrate.

range from 5 to 300 K, as shown in Fig. 1. To exhibit detailed information, resistance R axis in Fig. 1 adopts logarithmic mode. The upper inset of Fig. 1 displays the temperature dependent magnetization of present junction measured in zero-field-cooled (ZFC) and field-cooled (FC) process under a field of 1000 Oe. The appeared ferromagnetic property comes from the $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ layer as the STO–Nb substrate is diamagnetic. In ZFC–FC process, good reversibility is maintained until a low temperature about 70 K, below which an obvious difference between ZFC and FC magnetization appeared. This phenomenon might be relative to the appearance of frozen ferromagnetic clusters or induced ferromagnetic phase by a magnetic field in a picture of phase separation. Compared to the stoichiometric $La_{0.67}Ca_{0.33}MnO_3$, the oxygen-deficient $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ shows reduced Mn^{4+} iron concentration. The reduction of hole concentration weakens the ferromagnetic double exchange interaction, leading to a decrease of ferromagnetic transition temperature T_C and an increase of resistance.[10,11] The metal–insulator transition could even disappear at a critical oxygen content, and semiconducting or insulative behavior appears in whole temperature range.[10,11] The appearance of T_C at a low temperature (~120 K) in the $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ film indicates the existence of considerable hole concentration, which is required for forming a $p-n$ junction. The lower inset of Fig. 1 is the schematic structure of present $p-n$ junction.

Shown in Fig. 2 is the temperature dependent resistance of STO–Nb single crystal substrate, exhibiting metal behavior in the whole measured temperature range. According to a band diagram for an oxide heterostructure as a degerate semiconductor, proposed by Kudo *et al.*,[9] these junctions composed of semiconducting $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ and metallic STO–Nb should be the type of degerate $p-n$ junction.

The current–voltage characteristics ($I-V$ curve) of presented junctions, measured by using a current source, show a good rectifying behavior in a wide temperature range from 5 to 350 K, as shown in Fig. 3(a). To indicate the developing behavior of the $p-n$ junction in a larger expanding scale of applied voltage, the inset of Fig. 3(b) gives the $I-V$ curve specially measured in a wider current scope at room temperature. It is fascinating that the shape of the all $I-V$ curves is very similar to that of $p-n$ junction made of conventional semiconductor and nearly independent on temperature except for the variance of diffusion potential. When a reverse voltage below -2 V is applied, current I slightly decreases in a nearly same slow rate for different temperatures, indicating the large reverse resistance remains nearly a constant with temperature. In the case that the forward voltage is ap-

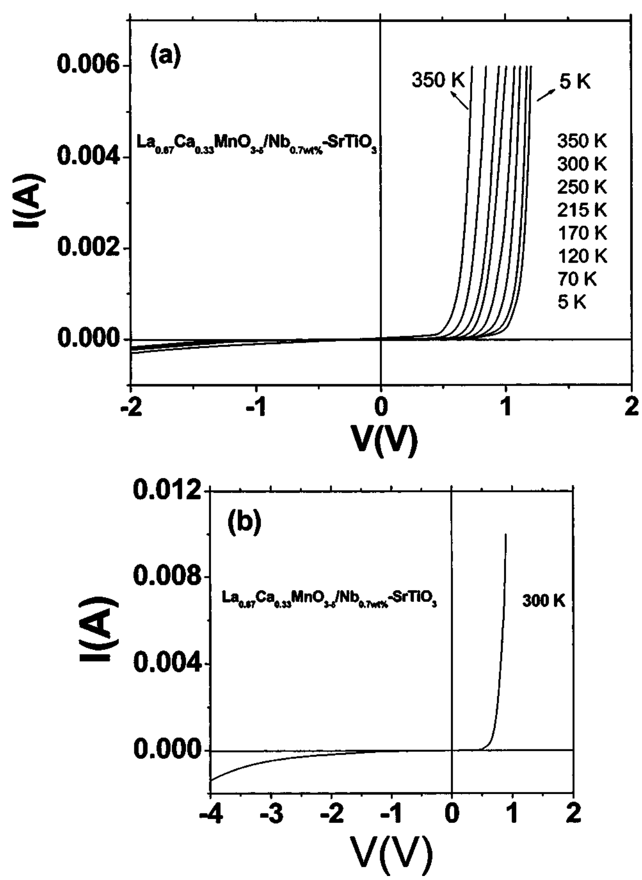

FIG. 3. (a) The current to voltage ($I-V$) curves of junction $La_{0.67}Ca_{0.33}MnO_{3-\delta}$/Nb–0.7 wt %-doped $SrTiO_3$ in a wide temperature range from 5 to 350 K. (b) The $I-V$ curve specially measured in an expanding scale of applied voltage at 300 K.

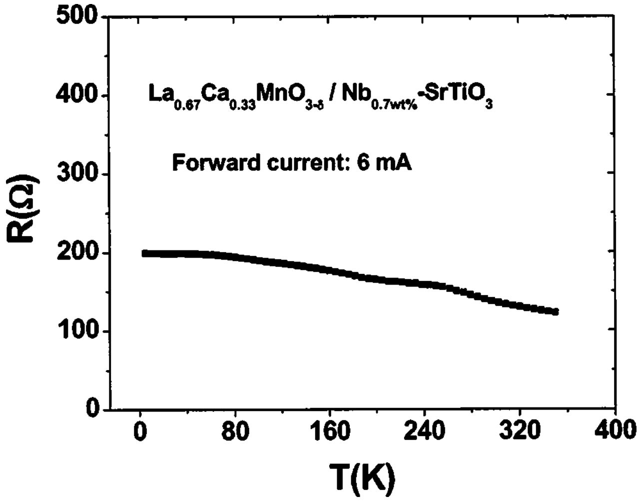

FIG. 4. The temperature dependence of junction conductive resistance under an application of a large forward current ~6 mA.

plied, the $I-V$ curves at different temperatures could be nearly copied one by one on the condition that the applied noncontact bias voltage is as large as diffusion potential for individual one. The sharp increase of current with voltage, when voltage exceeds diffusion potential, indicates the conductive resistance is small. Figure 4 shows the temperature dependent resistance measured under an application of a large forward current ~6 mA without any noncontact bias voltage. One may notice the slight decease of the conductive resistance with temperature.

The diffusion potential, at which point current I starts to increase as a result of applying a bias voltage, decreases nearly linearly with increasing temperature. It can be understood by considering a picture that depletion layer in $p-n$ junction becomes thinner with increasing temperature due to thermal diffusion, similar to the case of conventional $p-n$ junction. As for the presented $p-n$ junction, when the applied positive bias voltage reaches diffusion potential, the $p-n$ junction is conductive and shows small resistance. More important is that the conductive resistance is nearly independent on temperature. This characteristic is much favorable to practical applications. Previous reported $p-n$ junctions with bi-layer structure of oxides also show good rectifying behavior.[6,7] However, not only a series of rigor conditions are required to form a $p-n$ junction with good $I-V$ characteristics but also the conductive resistance of the obtained $p-n$ junction under a contact positive bias voltage is relatively bigger and strongly temperature dependent.[6] It increases notably with increasing temperature.

The different behaviors between our junctions and the previous ones may be qualitatively understood by analyzing the carrier behaviors of each one. According to the band diagram proposed by Kudo *et al.*,[7,9] both the divalent ion doped $La_{1-x}M_xMnO_3$ compounds and Nb- or La-doped $SrTiO_3$ should be regarded as degenerated semiconductor with an extremely high hole or electron concentration. The characteristic of $p-n$ junction should be dominated by the carrier behavior of the p- and n-type composition. In the case of $La_{0.9}Ba_{0.1}MnO_3$/little Nb- or La-doped $SrTiO_3$, previous reported $p-n$ junctions, the n-type Nb- or La-doped $SrTiO_3$ exhibited strict semiconducting behavior in the whole measured temperature scale (5–350 K) but the p-type $La_{0.9}Ba_{0.1}MnO_3$ behaves metalic below T_C and changes to semiconductor above T_C. Although $La_{0.9}Ba_{0.1}MnO_3$ has a high hole concentration (an order of 10^{21} cm^{-3}), the conductive eletrons are strongly correlated by eletron repulsion and dynamic Jahn–Teller efect. Therefore, the conductive eletrons would be signicantly localized with increasing temperature especialy close to or above T_C. As a result, the conductive resistance of the composed $p-n$ junction increases considerably with increasing temperature upon an application of a contact positive bias voltage. In contrast, $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ and Nb–0.7 wt %-doped $SrTiO_3$ in our junctions show strict semiconducting and metallic behaviors, respectively, in the measured temperature range (5–350 K). The carrier in Nb–0.7 wt %-doped $SrTiO_3$ could not be notably localized, and thus, the composed junction exhibits the nearly temperature independent conductive resistance. Quantitative explanation for different junctions requests detailed band information of each composed layer.

In conclusion, heteroepitaxial $p-n$ junctions with good rectifying characteristic in a wide temperature range from 5 to 350 K was created simply by depositing an oxygen-deficient $La_{0.67}Ca_{0.33}MnO_{3-\delta}$ film on a commercial Nb–0.7 wt %-doped $SrTiO_3$ single crystal substrate using the PLD technique. The nearly temperature independent rectifying characteristic is more favorable for practical applications compared to previously reported $p-n$ juctions. The non-notable localization of carrier in the measured temperature scale in Nb–0.7 wt %-doped $SrTiO_3$ might be responsible for the nearly temperature independent conductive resistance under a contact positive bias voltage. The good rectifying behaviors make these simple $p-n$ junctions promissing for various applications.

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