Effect of charge order transition on tunneling resistance in $Pr_{0.6}Ca_{0.4}MnO_3$/Nb-doped $SrTiO_3$ heterojunction*

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An oxide p–n heterojunction composed of $Pr_{0.6}Ca_{0.4}MnO_3$ film, with a charge order (CO) transition, and 1wt% Nb-doped $SrTiO_3$ substrate is fabricated, and the transport properties of the interface are experimentally studied. The rectifying behavior of the junction, well described by the Newman equation, is observed, indicating that tunneling is the dominant process by which the carriers pass through the interface. Above and below the CO transition temperature, satisfactory linear dependencies of junction resistance on temperature are observed, but the slopes of the two resistance-temperature relations are different. The CO process is believed to be relevant to this difference.

Keywords: manganite, heterojunction, tunneling, charge order transition

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1. Introduction

Compared with conventional semiconductor junctions, manganite-based p–n junctions are expected to exhibit much more powerful functions. Indeed, in addition to the excellent rectifying property, manganite junctions exhibit a lot of interesting properties, such as strongly bias-dependent magnetoresistance,[1,2] a magnetocapacitance effect[3] and a temperature-dependent photovoltaic effect.[4,5] It is obvious that the physical properties of the junction are determined by the interfacial barrier. According to traditional semiconductor theory, the interfacial barrier is controlled by the energy band of the material composing the junction, which means that transport properties of a manganite based heterojunction depend strongly on the transition, while the transition in turn changes the energy band of manganite. However, previous reports show that the transition of a manganite has almost no effect on the transport properties of a manganite based p–n heterojunction when the thermo-emission is the determining process of a carrier surmounting the interfacial barrier.[6,7] In addition, a strong external magnetic field has little effect on such a junction, even if it affects the energy band of the manganite and makes it show a colossal magnetoresistance effect.[8] These results may be ascribed both to the existence of a magnetic field-insensitive layer of the manganite and to the thick depletion layer of the heterojunction,[9] which weakens the effect of the energy band on the interfacial energy structure. On the other hand, it shows the possibility that the transport properties of a junction would be affected by an energy band of the manganite when the interfacial barrier region is much thinner and the tunneling is the dominant way for a carrier to surmount the interfacial barrier. Sun[10] reported that the tunneling current in a manganite based p–n junction, composed of an ultra thin $La_{0.9}Ca_{0.1}MnO_3$ film and 1 wt% Nb doped $SrTiO_3$ substrate, can be strongly affected by an external magnetic field.

In this paper, we report the transport properties of a $Pr_{0.6}Ca_{0.4}MnO_3$ (PCMO)/1 wt% Nb doped $SrTiO_3$ (STON) p–n heterojunction. The PCMO is chosen for two reasons: firstly, the PCMO is a material of charge order (CO) transition with a transition temperature of 210 K, which makes it convenient to study the effect of the CO transition on the transport properties; and secondly, the carrier in PCMO is almost trapped because of the CO, which induces a thinner depletion layer at the interface by reducing the depletion layer at the STON side, which makes it easier for the carriers to surmount the interfacial barrier by tunneling.

2. Experimental details

The PCMO/STON junction was fabricated by epitaxially growing a 200-nm-thick PCMO film on the (001) STON substrate by pulsed-laser deposition. The temperature of the substrate was kept at 750 °C and the oxygen pressure was at 50 Pa during the deposition. The resulting sample was furnace-cooled to room temperature in an oxygen atmosphere of 160 Pa after deposition. To characterize the transport properties of the film, a PCMO film with the same thickness was prepared on $SrTiO_3$ substrates at the same time. All electrical resistance measurements were performed using a superconducting quantum interference device magnetometer equipped with a probe for electrical resistance measurements.

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3. Results

The STON substrate lattice constant a_{STON} is 0.3905 nm. The bulk $Pr_{0.6}Ca_{0.4}MnO_3$ is orthorhombic, with lattice parameters $a \approx b \approx \sqrt{2}a_{STON}$ and $c \approx 2a_{STON}$. Such a pseudocubic orthorhombic film can be accommodated on STON. As shown by the X-ray diffraction data (Fig. 1), only the (001) peaks of the PCMO film and STON substrate are observed, indicating that the PCMO film is clean, single phase, and highly textured. According to the XRD data, the out-of-plane lattice constant of PCMO film is calculated to be 0.758 nm.

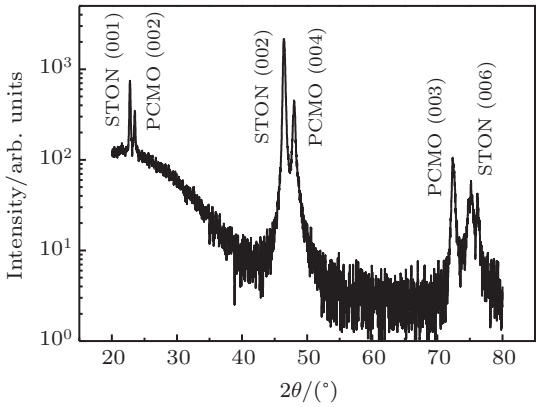


Fig. 1. The X-ray diffraction spectra of the PCMO/STON heterojunction.

The CO transition temperature (T_{CO}) of bulk PCMO is about 235 K,[11] and the resistivity jumps drastically at T_{CO} on the resistivity versus temperature curve. Figure 2(a) shows the resistivity of our PCMO film deposited on the STO substrate, measured by four-probe technology. It can be seen that the resistivity increases monotonously and smoothly with decreasing temperature. No distinct signature of a CO transition can be found; however, it has been proved that the T_{CO} can be extracted from the ρ versus $1/T$ curve.[12] As shown in Fig. 2(b), the resistivity is linear with $1/T$ under higher and lower temperatures, respectively, and the cross of the two lines is at 210 K, which is attributed to the contribution of CO. The CO transition is clearer in the derivative plot of $\mathrm{d}(\ln\rho)/\mathrm{d}(1/T)$, as shown in the inset of Fig. 2(b). The resistivity behavior of the PCMO film is that of a gapped semiconductor, which can be described by the formula $\rho(T) = \rho_0 \exp(\Delta/k_B T)$, where ρ_0 is the resistivity at zero temperature, Δ is the activation energy, and k_B is the Boltzmann constant. For $T > T_{CO}$, the activation energy Δ is 0.11 eV, while it is about 0.16 eV at temperatures below T_{CO}. The activation energy approximates that of a bulk PCMO,[13] indicating the high quality of the PCMO film.

The electrical measurements of the junction were performed in the two-probe configuration. To get a good electric contact, and to avoid the effect of current distribution in the junction,[14] three copper electrodes, one on the PCMO film and two on the STON substrate, were deposited (inset in Fig. 3(a)). The PCMO film and copper electrodes were subsequently patterned into 1 mm×1 mm squares by the conventional photolithography and chemical etching technique. The contact resistance between the electrode and the STON substrate is lower than 1 Ω, and the Cu-PCMO contact resistance is ∼ 10 Ω at room temperature, which are evaluated by comparing the results of four-probe and two-probe measurements. The current-bias (I–V) characteristics of the heterojunction measured under various temperatures are shown in Fig. 3(a). The junction exhibits a satisfactory rectifying property, as demonstrated by the strong asymmetry of the I–V curves against the polarity of the electrical bias. The current is negligibly small and remains tiny in the initial stage of the application of electrical bias in both directions, but it grows rapidly when the bias voltage exceeds a threshold value of direction dependence. In the forward direction, the threshold is lower than 0.3 V. However, the current is still tiny in the reverse direction, until the bias reaches 1 V. With a decrease of temperature, the I–V curve exhibits a simple expansion along the V-axis, just as occurs in conventional p–n junctions.

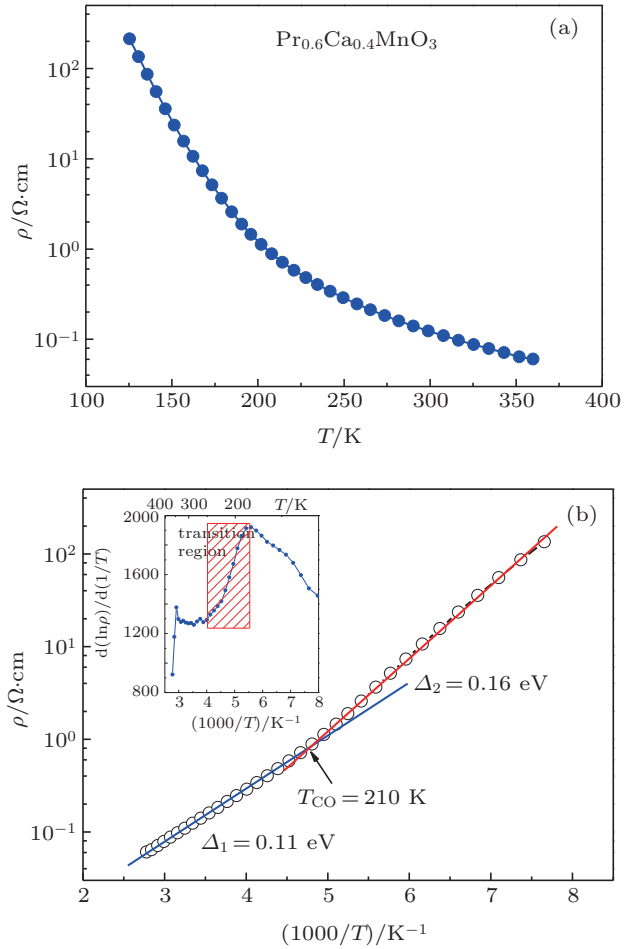


Fig. 2. (color online) The dependence of resistivity of PCMO film on temperature (a) and $1/T$ (b). The CO transition is clearly observable in the derivative plot of resistivity shown in the inset of (b).

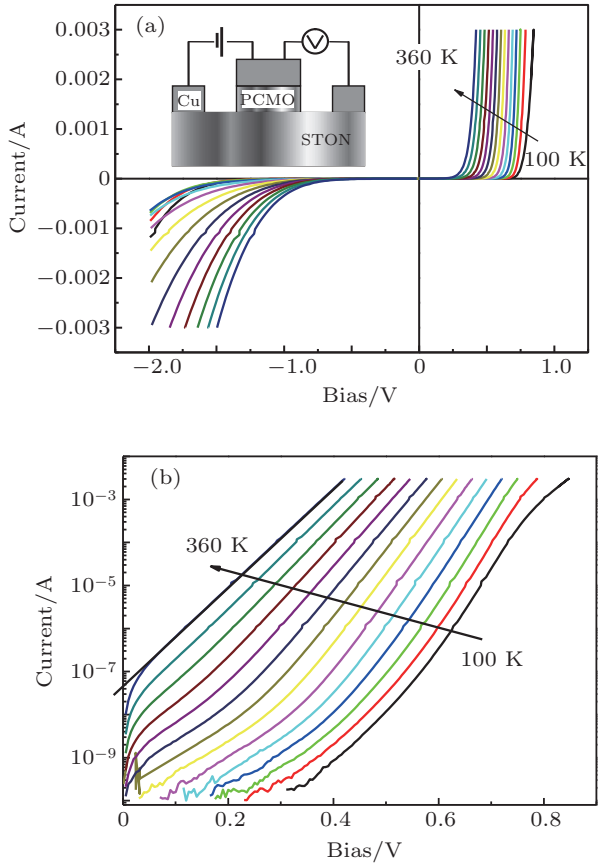


Fig. 3. (color online) Current–voltage characteristics (a) and logarithmic (b) plot of the characteristics of PCMO/STON junctions measured under different temperatures between 100 K and 360 K.

In order to get information on the transport mechanism of the junction, the I–V curves were further analyzed. Figure 3(b) is a semilogarithmic plot of the I–V curves under forward bias. A satisfactory linear relationship between $\log(I)$ and V is observed in the temperature range from 160 K to 360 K. Decreasing the temperature causes a nearly rigid rightward 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 semiconductor theory, the forward current can be either thermal or nonthermal. To produce thermal current, charge carriers have to overcome the potential barrier to cross the junction. In this case, the temperature plays an important role in activating charge carriers and the slope of $\log(I)$–V curve is expected to be proportional to $1/T$. On the other hand, charge carriers can also tunnel through the potential barrier. If the tunneling occurs predominantly, then the current is non-thermal in nature and can be described by Newman's equation[15]

$$I = I_{\rm s}\exp(T/T_0)\exp(V/V_0), \tag{1}$$

where $I_{\rm s}$, T_0, and V_0 are parameters weakly depending on V. This equation predicts a $\log(I)$–V slope that is essentially independent of temperature and a linear decrease of V with temperature if the applied current is fixed. A comparison of the $\log(I)$–V slopes of the thermal and nonthermal processes is shown in Fig. 4. This shows that the temperature dependence of the measured $\log(I)$–V slope is weak, closer to that of the nonthermal one. A roughly linear decrease of V with temperature is also observed under a constant applied current (1 μA for example, inset in Fig. 4). These features are consistent with those predicted by Eq. (1) and suggest the tunneling character of the transport behavior of PCMO/STON heterojunction.[15] The linear decrease of V with increasing temperature indicates that the resistance of the heterojunction also linearly decreases with the temperature. This is a remarkably useful property if the junction is used as a negative temperature coefficient thermistor.

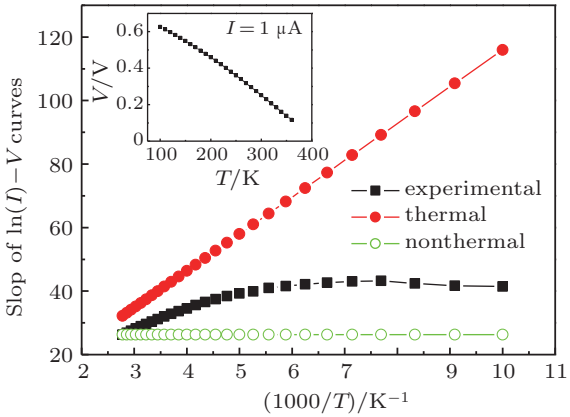


Fig. 4. (color online) Slopes of $\ln(I)$–V curves as functions of temperature. The results of the thermal and nonthermal processes are shown for comparison. Voltage as a function of temperature under a fixed measured current ($I = 1$ μA) is shown in inset.

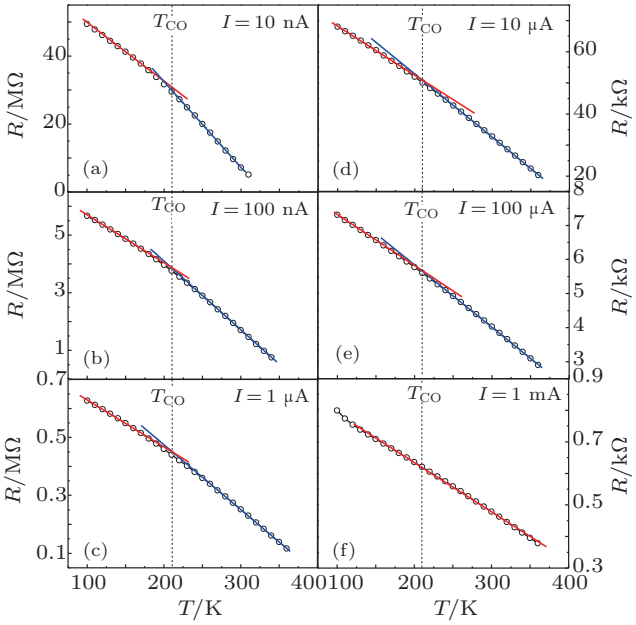


Fig. 5. (color online) The resistance of PCMO/STON heterojunction dependence of temperature measured under fixed current. The current is (a) 10 nA, (b) 100 nA, (c) 1 μA, (d) 10 μA, (e) 100 μA, and (f) 1 mA, respectively.

By carefully analyzing the linear relationship between resistance of the heterojunction and temperature, it can be found that above and below T_{CO}, the linear relation is not consistent, showing that the slopes of the R–T line under the two temperature regions are different from each other. Six R–T curves measured under 10 nA, 100 nA, 1 μA, 10 μA, 100 μA, and 1 mA are shown in Fig. 5. The resistance slowly varies linearly with temperature under low temperature and more rapidly under high temperature. All the transformation temperatures under the various measured current are near the T_{CO} of the PCMO film, which is 210 K, making it reasonable to propose that the transition of resistance of the heterojunction has a close relation with the CO transition of the PCMO film.

According to Eq. (1), the slope of the R–T curve is proportional to V_0/T_0. The parameter V_0 below T_{CO} should be less than that above T_{CO} if the parameter T_0 is a constant. V_0, the effective interfacial barrier, depends on the interfacial energy structure and the thickness of the depletion layer. Based on a simple formula,[16,17] the depletion width of the PCMO/STON junction can be estimated by

$$t_1 = \left(\frac{2N_{D2}\varepsilon_1\varepsilon_2\varepsilon_0(V_0 - V)}{qN_{A1}(\varepsilon_1 N_{A1} + \varepsilon_2 N_{D2})} \right)^{1/2},$$

$$t_2 = \left(\frac{2N_{A1}\varepsilon_1\varepsilon_2\varepsilon_0(V_0 - V)}{qN_{D2}(\varepsilon_1 N_{A1} + \varepsilon_2 N_{D2})} \right)^{1/2},$$

where t_1/t_2 is the depletion layer thickness of PCMO/STON, $\varepsilon_0/\varepsilon_1/\varepsilon_2$ is the permittivity of vacuum/PCMO/STON, N_{A1}/N_{D2} is the hole/electron density in PCMO/STON, and V_0 is the effective interfacial potential. Here, we can simply estimate the thickness of the depletion layer under zero bias by adopting the parameters $\varepsilon_1 = 30/30$ at high/low temperature,[18] $\varepsilon_2 = 306/1500$ at high/low temperature,[19] and $N_{D2} = 3.34 \times 10^{26}$ m^{-3}. The total thickness of the depletion layer is 8.6 nm, postulating that 100% carriers are stimulated when the temperature is above T_{CO} of PCMO. For the temperature below T_{CO}, however, it is more complex. Most of the carriers in the PCMO film are trapped by the CO state, which can also be proven by the fact that the activation energy of the carrier is 0.16 eV, which is much larger than that of 0.11 eV above the T_{CO}. Under such a condition, if only 10%, 5%, or 1% of carriers are stimulated, the calculated depletion layer thickness is 6.6 nm, 5.1 nm, or 4.8 nm, respectively. That is to say that the depletion layer of the PCMO/STON heterojunction below T_{CO} is thinner than that above T_{CO}, providing a possibility for the electrons to tunnel through the depletion layer more easily than when suppressing the effective interfacial potential to a lower level, as shown in Fig. 6. This proposal agrees with Saucke's finding[20] that the effective interfacial barrier of PCMO/STON, measured by electron energy-loss spectroscopy is 0.57 eV at 80 K and 0.65 eV at 300 K.

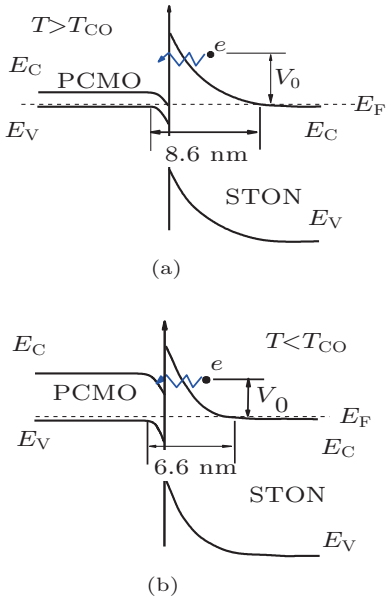


Fig. 6. (color online) Schematic diagrams for the energy band structure of PCMO/STON heterojunction at (a) $T > T_{CO}$ and (b) $T < T_{CO}$.

4. Conclusion

In conclusion, the transport properties of a PCMO/STON heterojunction, which has an excellent rectifying characteristic, are experimentally studied. The rectifying behavior of the junction, which is well described by Newman's equation, is observed, indicating that tunneling is the dominant process by which the carriers pass through the interfacial region. Above and below the CO transition temperature of the PCMO film, satisfactory linear dependencies of junction resistance on temperature are observed, showing that the resistance slowly varies linearly with temperature below T_{CO} and more rapidly above T_{CO}. The CO process, which traps the carriers in the PCMO film, making the depletion layer of the heterojunction thinner and leading to a lower effective interfacial barrier, is believed to be relevant to these results.

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