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Rectifying behaviours of heterojunctions composed of manganites with different resistive properties

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Abstract

Oxide heterojunctions composed of manganite films of different tolerance factors and $SrTiO_3$: Nb are fabricated and their rectifying properties are experimentally studied. The current–voltage characteristics of the junctions are found to be dominated by diffusion current at high temperatures and by tunnelling current at low temperatures. Further analyses on the rectifying behaviours of the junctions indicate the occurrence of a built-in voltage independent of manganites, despite the great resistivity change of the manganites and the metal-to-insulator transition above 350 K (for $La_{0.67}Sr_{0.33}MnO_3$) and ∼87 K (for $La_{0.29}Pr_{0.38}Ca_{0.33}MnO_3$). In contrast, the increase in the Nb content causes a reduction of the built-in voltage by ∼0.2 eV. The presence of the depletion layer insensitive to the phase transition of the manganites is believed to be responsible for the present observations.

Sandwiching a $SrTiO_3$ layer between $La_{0.9}Sr_{0.1}MnO_3$ and $La_{0.05}Sr_{0.95}TiO_3$, Sugiura and collaborators fabricated the first manganite p–i–n junction that shows a satisfactory rectifying property in a wide temperature range [1]. Tanaka *et al* further demonstrated that the intermediate layer was unnecessary and constructed a p–n junction simply using $La_{0.9}Ba_{0.1}MnO_3$ and Nb-doped $SrTiO_3$ [2]. Subsequent studies show that, in addition to the excellent rectifying property, manganite junctions have a lot of amazing properties such as strongly bias-dependent magnetoresistance [2] and temperature-dependent photovoltaic effect [3]. In the scenario of the buildup of a built-in voltage due to the interlayer diffusion of holes and electrons between manganites and n-type doped $SrTiO_3$ and the variation of this potential with external fields, these behaviours can be understood qualitatively.

Several successful attempts have been made for a direct measurement of the energy barrier in manganite junctions. Based on the analysis of the current–voltage dependence, Postma *et al* [4] declared that a Schottky barrier of a height of ∼0.94 eV exists in the $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3$: Nb junction (0.01 wt%Nb). Similar studies were also performed by Sawa and collaborators [5], and the built-in voltage was found to be ∼0.72 eV for $Pr_{0.7}Ca_{0.3}MnO_3/SrTiO_3$: Nb and ∼0.65 eV for $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$: Nb (0.02 at.% Nb), essentially independent of temperature above 150 K.

Because of the absence of a metal–semiconductor transition in the manganites involved in the temperature range concerned, the effects of phase transition on built-in voltage were not studied in previous works. Insensitivity of built-in voltage to resistive transition has been reported for the $NdNiO_3/SrTiO_3$: Nb junction, which has been ascribed to the depression of the structure transition of $NdNiO_3$ [6]. Manganites are different from $NdNiO_3$ in many aspects. In addition to the strong Jahn–Teller effect and phase separation, the presence of an interface layer with localized charge carriers due to substrate-induced lattice distortions has been demonstrated for the manganites by various experiments [7]. It is therefore an interesting issue as to how the junction behaves when the manganite undergoes a great change in magnetic and resistive properties.

We noticed that, despite the intensive work on the rectifying property, studies on the built-in voltage of the manganite junction are very limited. In this paper we will perform a systematic investigation on the effects of phase transition on the built-in voltage of the manganite junction.

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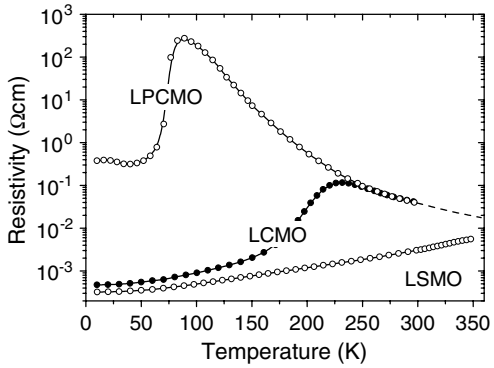

Figure 1. Temperature dependence of the resistivity of the manganite films with different tolerance factors. The dashed line is a guide for the eye.

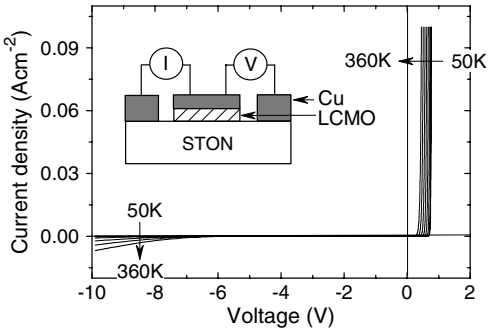

Figure 2. Current–voltage characteristics of the manganite junction LCMO/STON (0.05 wt%Nb) measured under different temperatures below 360 K. Inset plot is a schematic diagram showing the electrode setting.

By adjusting the size mismatch of the rare earth and Mn-site ions, the metal-to-insulator transition was tuned between 87 and 350 K, and the maximum resistivity varied by 5 orders of magnitude. The current–voltage characteristics of the junctions are found to be dominated by thermal current at high temperatures and by tunnelling current at low temperatures. Analysis on the rectifying behaviours of the junction reveal the occurrence of a built-in voltage that is independent of manganites but dependent on $SrTiO_3$: Nb. No visible changes in the rectifying property are observed corresponding to the metal-to-insulator transition of the manganites.

Manganite-based heterojunctions were fabricated by epitaxially growing the $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) and $La_{0.29}Pr_{0.38}Ca_{0.33}MnO_3$ (LPCMO) films (the A-site ionic size decreases from 1.247 to 1.190 Å) of ∼150 nm on Nb-doped $SrTiO_3$ substrates (STON) by the pulsed laser ablation technique. Two substrates, STON(0.05) and STON(0.5), with the doping level of 0.05 wt%Nb and 0.5 wt%Nb were used. The temperature of the substrate was kept at 730 °C and the oxygen pressure at ∼100 Pa during the deposition. To improve crystallinity and oxygen stoichiometry, the resulting samples were annealed at 700 °C for 1 h in an oxygen atmosphere of ∼160 Pa after deposition.

Electric measurements were performed using the cryostat system of a SQUID magnetometer (MPMS-7). We added an external electrical equipment for applying and measuring the bias voltage and for measuring the current through the device. To get a good electric contact and to avoid the effect of current distribution in the junction, three copper electrodes, one on LCMO and the other two on STON, were deposited. The manganite films and electrodes were subsequently patterned into squares of the size of $1 \times 1\,mm^2$ by the conventional photolithography and chemical etching technique. The contacting resistance is lower than 1 Ω/50 Ω between Cu and STON/manganite films, evaluated by comparing the four-point and the two-point results. It is quite small compared with the junction resistance as will be seen below and, therefore, will not affect the quantitative analysis of the rectifying behaviour.

Figure 1 shows the temperature-dependent resistivity of the manganites with various A-site ionic sizes. It shows a metal-to-insulator transition at ∼245 K for LCMO and ∼87 K for LPCMO. No phase transition is observed for LSMO up to the temperature of ∼350 K. Accompanying the low-temperature shift of the metal–semiconductor transition, resistivity of the manganite increases significantly. The maximum resistivity increases from ∼0.005 to ∼138 Ω cm from LSMO to LPCMO, varying by 5 orders of magnitude. These results confirm the great difference in the resistive property of the manganite with different tolerance factors.

As a representative, in figure 2 we show the current–voltage characteristics of LCMO/STON(0.05), measured under different temperatures below 360 K. Excellent rectifying behaviours characterized by strongly asymmetric J–V curves against electric polarity are observed. The current is tiny in the zero-bias limit and remains small as the reverse bias increases, whereas it grows steeply with the voltage bias in the forward direction. The decrease in temperature has no obvious effects except for a nearly rigid shift of the J–V curve along the V-axis. A simple calculation indicates that the junction resistance is extremely high, ∼6 MΩ, in the zero-bias's limit near the ambient temperature, which is a signature of the high quality of the junction. Similar results are obtained for other junctions. An obvious effect of the increase in the Nb content in STON is the depression of the breakdown voltage (not shown).

To obtain information on the built-in voltage, the saturation current, which is expected to vary exponentially against the interfacial barrier, is further analysed. Based on the semiconductor theory, the J–V relation of a p–n junction can be described by the formula $J \approx J_s \exp(qV/nk_BT)$ in the forward direction when $qV \gg nk_BT$ [8]. The prefactor J_s is the saturation current. It varies following the relation $J_s \propto T^{3.5}\exp(-qV_D/k_BT)$ for the thermal diffusion model, where V_D is the effective barrier height, k_B the Boltzmann constant and n the ideality factor ($n = 1$ for a perfect p–n junction). The saturation current can be obtained as the intercept in the J-axis of the extrapolated log J–V relation. It is obvious that the precondition to get reliable J_s is that the log J–V relation should be linear. Figure 3 is a semi-log plot of the J–V curves of LCMO/STON(0.05) and LCMO/STON(0.5). A satisfactorily linear dependence of log J on V is observed in the temperature range 100–360 K for the former and 140–360 K for the latter. The linearity is significantly better than that previously reported for the oxide junctions [4–6]. This is unordinary considering the fact that the doping level in either the manganite or the $SrTiO_3$: Nb is much higher than the conventional semiconductors. The visible deviation from linearity at low temperatures can be ascribed to the increase in

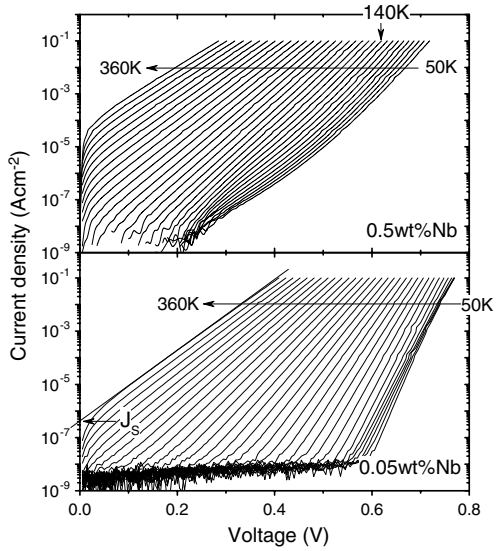

Figure 3. Semi-log plot of the characteristics of LCMO/STON (0.5 wt%Nb) (top panel) and LCMO/STON (0.05 wt%Nb) (bottom panel) measured under different temperatures below 360 K.

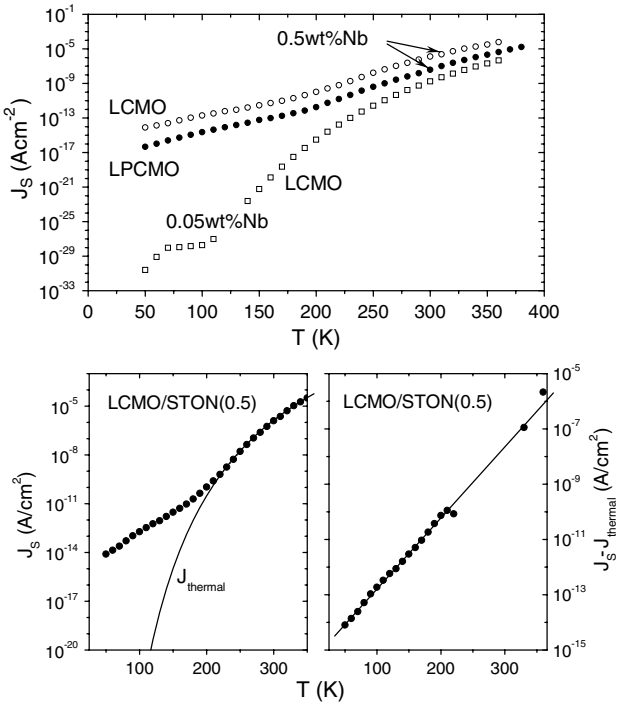

Figure 4. Top panel: temperature dependence of saturation current J_s derived from the current–voltage characteristics of the junctions. Bottom panel: thermal current ($J_{thermal}$) and tunnelling current as functions of temperature. The former is described by the equation $J_s \propto T^{3.5}\exp(-qV_D/k_BT)$ with $V_D = 0.48$ eV, and the latter by $J_S - J_{thermal} \propto \exp(T/T_0)$ with $T_0 \approx 17.24$.

tunnelling current. Electron tunnelling is expected to enhance when the content of Nb in STON increases because of the narrower depletion layer. This analysis is consistent with the observation that the linearity is better for LCMO/STON(0.05) than for LCMO/STON(0.5). Data in the high bias range were used for the derivation of J_s when significant deviation occurs. It is fortunate that such deviation is not so strong as to disturbing the determination of J_s.

The thermionic emission model for the p–n junction has been used for the analysis of the manganite junction that could be a Schottky junction at low temperatures based on the following considerations: at first, the built-in voltage obtained by treating the junction as a p–n one and a Schottky one is very similar [5]. Second, the metallic conduction of the manganite is a bulk behaviour, whereas the interface layer (∼6 nm for LCMO) near STON may remain insulating because of the substrate-induced lattice defects and Jahn-Teller effects [7]. In this case, the p–n model maybe a good approximation.

Figure 4 presents the temperature dependence of saturation current J_s for the junctions LCMO/STON(0.05) LCMO/STON(0.5) and LPCMO/STON(0.5). J_s is quite small even at the ambient temperature, $\sim 0.0017\,\mu$A cm^{-2} for LCMO/STON(0.05) and $\sim 0.6\,\mu$A cm^{-2} for LCMO/STON (0.5), and decreases rapidly with the decrease in temperature. There is a visible inflection near 190 K in the J_s–T curve for the junctions on STON(0.5). This implies a different physical process in the low-temperature range. A careful analysis shows that the saturation current can be well described by the relation $J_s \propto AT^{3.5}\exp(-qV_D/k_BT) + B\exp(T/T_0)$ (A and B are proper parameters). As demonstrated by Newman and others, the second term is the contribution of tunnelling current, [8, 9], which occurs because of the heavy doping of the manganite and the STON substrates. This result indicates that the current across the junction is mainly the thermal current, when the temperature is high, and the tunnelling current, when the temperature is low. A direct calculation based on the formulae $t_1 = \{2N_{D2}\varepsilon_1\varepsilon_2\varepsilon_0 V_D/[qN_{A1}(\varepsilon_1 N_{A1} + \varepsilon_2 N_{D2})]\}^{1/2}$ and $t_2 = \{2N_{A1}\varepsilon_1\varepsilon_2\varepsilon_0 V_D/[qN_{D2}(\varepsilon_1 N_{A1} + \varepsilon_2 N_{D2})]\}^{1/2}$ indicates that the thickness of the depletion layer is ∼9 nm if most of the holes in LCMO are localized by the enhanced lattice distortions (Jahn–Teller effect) near the LCMO–STON interface, where t_1/t_2 is the depletion width in LCMO/STON, $\varepsilon_1/\varepsilon_2$ and N_{A1}/N_{D2} are the permittivity and the hole/electron density of LCMO/$SrTiO_3$, respectively, ε_0 the permittivity of the vacuum, and V_D the diffusion potential. $\varepsilon_1 = 30$, $\varepsilon_2 = 300$, $N_{A1} = 5.6 \times 10^{25}$ m^{-3} (supposing that only 1% of acceptors are effective), $N_{D2} = 5 \times 10^{25}$ m^{-3} and $V_D = 0.5$ eV were adopted for the calculation. Although the dielectric constant of $SrTiO_3$ exhibits a dramatic increase with decreasing temperature, the variation in the depletion width is not large. The dielectric constant of $SrTiO_3$ has been used for the calculation. Considering the fact that the dielectric constant of STON could be smaller due to the presence of Nb, the depletion may be thinner than 9 nm. This result reveals the possibility of electron tunnelling.

Based on the J_s–T relation, a quantitative analysis on the built-in voltage of the junction can be performed, and a simple derivation gives

$$\frac{\mathrm{d}\ln(J_s/T^{3.5})}{\mathrm{d}T^{-1}} = -\frac{qV_D}{k_B} + \frac{Tq}{k_B}\frac{\mathrm{d}V_D}{\mathrm{d}T}. \qquad (1)$$

V_D is nearly temperature-independent in the temperature range above 200 K and can be determined by the $\ln(J_s/T^{3.5})$–$1/T$ slope. Equation (1) can be numerically solved taking the V_D value at 350 K as a boundary condition. Figure 5 presents the built-in voltage and the ideality factor n as functions of

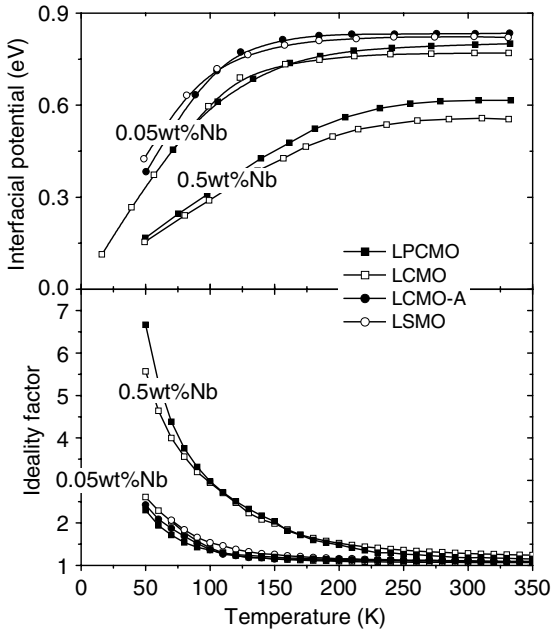

Figure 5. Top panel: built-in voltage as a function of temperature for the manganite junctions with different tolerance factors. Bottom panel: ideality factor of the manganite junctions. LCMO-A denotes the LCMO/STON (0.05 wt%Nb) junction annealed at 600 °C in air for 1 h.

temperature for different junctions. Two remarkable results are obtained. The first one is that the interfacial barrier is nearly constant above ∼200 K for all the samples, despite the metal-to-insulator transition of LCMO, and the second one is that the V_D values of different junctions collapse into two curves corresponding to the two substrates. V_D is essentially the same for all the samples with the same substrate, though the maximum resistivity change is 5 orders of magnitude as the tolerance factor varies (figure 1). From LSMO to LPCMO and to LCMO, V_D decreases from ∼0.82 eV to ∼0.8 and to ∼0.77 eV. The maximum change is ∼0.05 eV. The tolerance factor may not be the main factor affecting V_D considering the fact that the former decreases along a different sequence (from LSMO to LCMO and to LPCMO). The LCMO/STON(0.05) junction is further annealed at 600 °C for 0.5 h in air, and the subsequent study specifies a growth of V_D from ∼0.77 to ∼0.83 eV (marked by LCMO-A in figure 5). The influence of post-annealing on LCMO should be quite weak, and the principle effect is the change in the oxygen stoichiometry of STON. This result indicates that the interfacial structure of the junction and the variation of Nb or the oxygen content in the surface layer of STON could be responsible for the variation of V_D. The increase in Nb content causes an obviously downward shift of the V_D–T curve, and the V_D reduction thus produced is ∼0.22 eV in the temperature range above 200 K. Meanwhile, the ideality factor is close to unity in a wide temperature range, especially for the junctions with a lower Nb content, confirming the high quality of the junctions.

It has been well established that the Jahn–Teller effects can cause a splitting of the e_g band into two sub-bands (e_{g1} and e_{g2}) of the manganites [10, 11], and the built-in potential will be mainly determined by the energy difference of the e_{g1} and e_{g2} sub-bands. As experimentally evidenced, the size mismatch of the A- and B-site ions in manganites enhances the Mn–O–Mn bond bending, therefore the Jahn–Teller distortion of the MnO_6 octahedron. In contrast, the Jahn–Teller effects will be weakened when the film enters into the ferromagnetic state that favours a metallic conduction.

It is obvious that the interfacial barrier of the junction is determined by the band structures of the manganite and STON, and any changes in the electronic structure of the former should have an effect on the built-in potential. The absence of an obvious response of V_D to the resistive transition of the manganite indicates a different process in the interface of the manganite. Unlike the conventional semiconductors, the band structure of the manganite depends strongly on the concentration of charge carriers [12]. A band structure similar to that of $LaMnO_3$ is expected near the interface, where most of the charge carriers are depleted. This actually implies a variation of the band structure of the manganite with the distance from the manganite–STON interface. It is obvious that the resistive transition takes place mainly in the bulk manganite, whereas V_D is exclusively determined by an ultra-thin layer of the manganite films adjacent to STON. The presence of strain, due to lattice mismatch, and carrier depletion, especially the latter, make the interface layer insensitive to phase transition. This explains the nearly constant V_D through the resistive transition.

A typical feature of the manganite is the presence of the interface layer. The interface layer is 60–100 Å in thickness [7], whereas the depletion layer is only a few Angstroms without charge localization. Although the depletion layer can become thicker due to the charge localization near the interface, it is generally thinner than the interface layer. In this case, the effect of the tolerance factor is unimportant because the lattice distortion is mainly determined by the lattice mismatch between the film and the substrate.

The gradual decrease of V_D in the low-temperature range, which was also observed in other manganite junctions [13], has been ascribed to the increase in the dielectric constant of $SrTiO_3$ [5]. This may not be the main reason for the reduction of V_D according to the present work. In fact, a silent assumption for the derivation of V_D from equation (1) is that the current across the junction is thermal current. This is obviously not true at low temperatures, where the tunnelling current is dominant. The involvement of tunnelling current in the derivation of V_D causes an underestimation of V_D. Reducing Nb content in the substrate depresses electron tunnelling. As a result, the V_D anomaly is pushed to low temperatures as observed in LCMO/STON (0.05 wt%Nb).

To summarize, oxide heterojunctions composed of manganite films of different tolerance factors and $SrTiO_3$: Nb are fabricated and their rectifying properties are experimentally studied. The current–voltage characteristics of the junctions are found to be dominated by thermal current at high temperatures and by tunnelling current at low temperatures because of the heavy doping of the manganites and the $SrTiO_3$ substrates. Analyses of the rectifying behaviours of the junction, which can be well described by the Shockley equation, indicate the occurrence of an built-in voltage independent of manganites, despite the great change in resistivity of the manganites as the tolerance factor varies, and the metal-to-insulator transition above ∼350 K (for

$La_{0.67}Sr_{0.33}MnO_3$) and ∼245 K (for $La_{0.67}Ca_{0.33}MnO_3$). In contrast, the increase in the Nb content causes a reduction of the built-in voltage by ∼0.2 eV. The presence of the depletion layer insensitive to the phase transition of the manganites is believed to be responsible for the present observations.

Acknowledgments

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