

Interfacial potential in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3/\text{SrTiO}_3:\text{Nb}$ junctions with different Ca contents

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Manganite-based heterojunctions $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3/\text{SrTiO}_3:\text{Nb}$ (0.05 wt %) with $x=0.1, 0.2, 0.33, 0.65, 0.75,$ and 1 have been fabricated, and the effects of Ca content on the interfacial potential are experimentally studied. Rectifying behavior well described by the Shockley equation is observed, and the interfacial potential (V_D) is obtained for all of the junctions based on an analysis of the current-voltage characteristics. The most remarkable result of the present work is the strong dependence of the interfacial potential on the carrier content of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ films: V_D increases monotonously from ~ 0.6 to ~ 1.1 V as x sweeps from 0.1 to 1. Influence on V_D of the Fermi energy and Jahn–Teller effect in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ films are discussed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2841643]

Manganite-based heterojunctions have attracted much attention in recent years.^{1–3} In addition to the excellent rectifying behavior, manganite junctions exhibit a lot of abnormal properties such as strongly bias-dependent magnetoresistance,² magnetic-field-tunable photovoltaic effects,³ etc. Although the detailed mechanisms are not very clear, modification of the interfacial potential by magnetic field is believed to be the underlying reason for these phenomena.

In analogy with the conventional junction, an energy barrier could be formed near the interface of the manganite junction due to the difference of the Fermi energies of the two materials forming the junction. Presence of the interfacial potential has been experimentally proved. Based on an analysis of the current-voltage relation, Postma *et al.*⁴ revealed the appearance of a Schottky barrier of ~ 0.94 eV in the $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{SrTiO}_3:\text{Nb}$ junction (0.01 wt % Nb). Similar analyses were also performed by Sawa *et al.*,⁵ and the energy barrier was found to be ~ 0.72 eV for $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{SrTiO}_3:\text{Nb}$ and ~ 0.65 eV for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{SrTiO}_3:\text{Nb}$ (0.02 at. % Nb).

Based on the semiconductor theory, any changes in the band structure of either constituent of the junction can affect the energy barrier. This has been verified for the conventional p - n junctions, the properties of which can easily be tuned by the doping level and electric field. There are also attempts to modify the band structure of the manganites by magnetic field. The effects are unfortunately not obvious. However, it was found that the Fermi energy can be effectively controlled by the content of charge carrier in manganites, and its shift can be as high as ~ 0.8 eV.^{6,7} This provides us an opportunity to modulate the properties of manganite junctions. We noticed that most of the previous works concentrated on the junctions composed of nearly optimally hole-doped manganites, and the effects of carrier concentration on the interfacial potential have not been taken into consideration. We have performed a study on the built-in potential of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3/\text{SrTiO}_3:\text{Nb}$ (0.5 wt %) junction

with $x=0, 0.33,$ and 1.⁸ However, the method used there is simplistic: V_D was obtained by extrapolating the current-voltage (J - V) curve in the first quadrant directly to the V axis. It was afterward found that different V_D could be obtained using different segments of the I - V curve for the extrapolation. This makes the comparison of the interfacial potentials in different junctions inadequate. As a result, a systematic study on the interfacial potential and its variation under different conditions, which is helpful for a thorough understanding of the amazing properties of the manganite junction, is still lacking. Based on these considerations, in this letter, we performed a systematic study on the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3/\text{SrTiO}_3:\text{Nb}$ junctions with different Ca contents; special attention has been paid to the effects of carrier content of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ on the interfacial potential. This is of particular importance noting the presence of suspicions about the applicability of the conventional semiconductor theory to manganites, the typical strong electron correlated systems.

Manganite junctions were fabricated by growing the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO) ($x=0.1, 0.2, 0.33, 0.65, 0.75,$ and 1) films on the 0.05 wt % Nb-doped (001) SrTiO_3 (STON) substrates using the pulsed laser ablation technique. The substrate temperature was kept at 720 °C during the deposition. An oxygen pressure between 50 and 100 Pa, depending on the content of Ca, was adopted. The film thickness is ~ 150 nm, controlled by deposition time.

To get good electric contacts, two Cu electrodes on the $\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$ film and the STON substrate were prepared. The contact resistances are ~ 15 Ω between Cu and STON and 200 Ω between Cu and LCMO at the ambient temperature. The lateral size of the junction is 1×1 mm². Resistive measurements were performed using a superconducting quantum interference device magnetometer equipped with an electric measure unit.

X-ray diffraction spectra confirm the epitaxial growth of the LCMO films. The full width at half maximum of the rocking curve of the (002) peak varies from 0.4° to 0.8° as x increases, which is comparable to that of the STON single crystal (0.4°). The in-plane resistivity of selected LCMO films, for clarity, is shown in Fig. 1. A semiconductorlike

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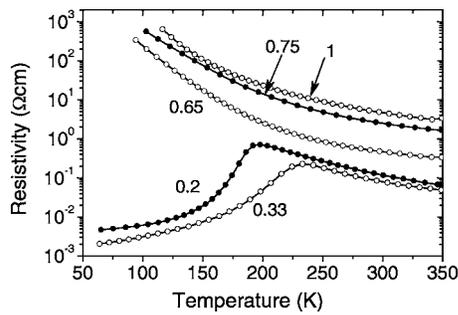


FIG. 1. Temperature dependence of the resistivity of the LCMO films with different Ca contents.

behavior is observed in the whole temperature range investigated for the films of $x=0.65$, 0.75 , and 1 , with a monotonic increase of the resistivity from $x=0.65$ to 1 . A metal-to-insulator transition occurs in the nearly optimally doped films, and the critical temperatures are ~ 200 K for $x=0.2$ and ~ 230 K for $x=0.33$. These phenomena are similar to those of the bulk LCMO and confirm the change of the electronic structure of the LCMO films with Ca content.

Figure 2 presents the current-voltage (J - V) curves measured in the temperature range below 350 K for a selected sample $x=0.75$. The junction shows an excellent rectifying behavior, as demonstrated by the strong asymmetry of the J - V curves against the polarity of the electric bias. The current is negligibly small in the negative direction up to the bias voltage of -7 V, while it grows rapidly in the positive direction when the bias voltage exceeds a threshold value. Decrease in temperature produces a nearly rigid shift of the J - V curves along the V axis. Similar behavior is observed in other junctions except for the difference of threshold voltage. A simple calculation indicates that the zero-bias junction resistance increases from $\sim 6.2 \times 10^6$ to $\sim 5.4 \times 10^8 \Omega$ as x goes from 0.1 to 1 .

To obtain the information on the interfacial potential, the saturation current, which is expected to vary exponentially against the interfacial barrier, is further analyzed. Based on the semiconductor theory, the J - V relation of a p - n junction can be described by the formula $J \approx J_s \exp(qV/nk_B T)$ in the forward direction when $qV \gg nk_B T$,⁹ where J_s is the saturation current, k_B the Boltzmann constant, and n the ideality factor ($n=1$ for an idealized p - n diode). The saturation current can be obtained as the intercept in the J axis of the extrapolated $\log J$ - V curve. It is obvious that the precondition to get a reliable J_s is that the $\log J$ - V dependence should be

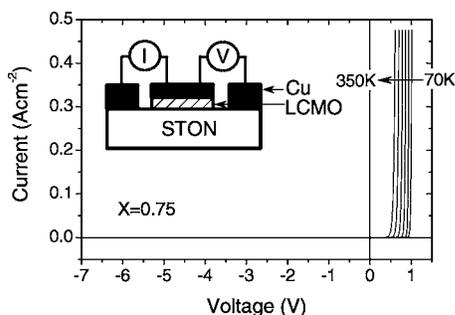


FIG. 2. Current-voltage characteristics of the LCMO/STON junction ($x=0.75$) measured under different temperatures below 350 K. Inset plot is a schematic diagram showing the electrode setting for the resistive measurements.

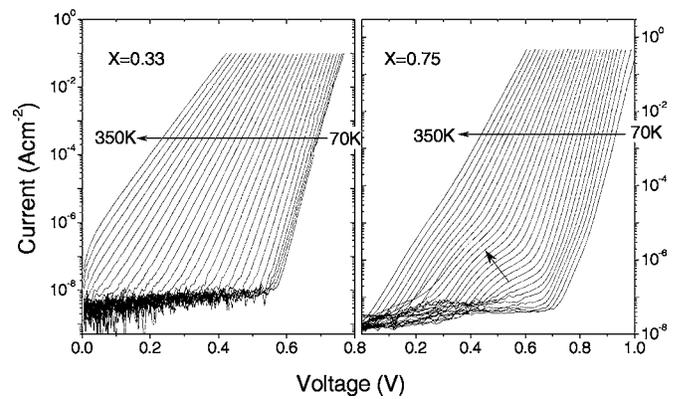


FIG. 3. Semilog plot of the characteristics of LCMO/STON for $x=0.33$ (left panel) and $x=0.75$ (right panel) measured under different temperatures below 350 K. The arrow marks the inflection that mediates the two electronic processes.

exactly linear. Figure 3 is the $\log J$ - V plots for selected junctions with $x=0.33$ and 0.75 . Fortunately, satisfactorily linear relations between $\log J$ and V are observed for most of the samples in the temperature range from 100 to 350 K. Although a close view of the J - V curves indicates the occurrence of two electronic processes in the junctions with $x \geq 0.75$, which is a phenomenon deserving further study, it is fortunate that such a deviation is not as strong as disturbing the determination of J_s . In this case, the data in the high bias range were used to calculate J_s .

Figure 4 shows the temperature dependence of the saturation current J_s (top panel) and the interfacial potential derived from J_s based on the relation $J_s \propto T^2 \exp(-qV_D/k_B T)$ (bottom panel). Leakage or tunneling current will affect the determination of V_D in the low temperature range and, therefore, only the data above 150 K are shown here. The most remarkable observation of the present work is the strong dependence of the interfacial potential on the Ca content in the LCMO films. V_D is ~ 0.6 V for $x=0.1$ and grows rapidly from ~ 0.6 to ~ 0.82 V as x increases from 0.1 to 0.33 . Further increase in x produces minor effects until $x \approx 0.75$, above which a rapid increase of V_D reappears. The maximum

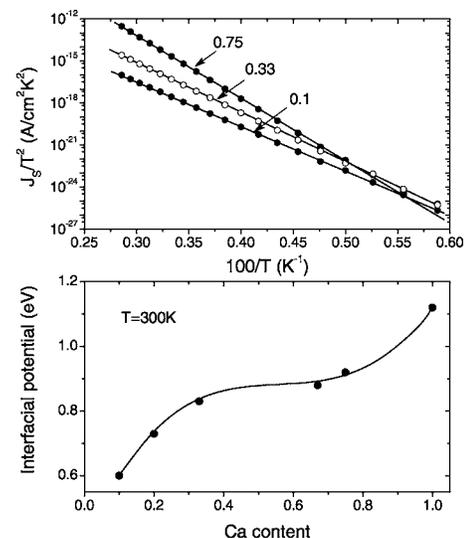


FIG. 4. Saturation current as a function of temperature (top panel) and the Ca content dependence of the interfacial potential obtained at the room temperature (bottom panel). Solid lines are guides for the eyes.

V_D is ~ 1.1 V, obtained in the junction $\text{CaMnO}_3/\text{STON}$. We failed to obtain the energy barrier for the junction of $x=0$. However, the V_D - x relation for $x \leq 0.7$ can be described satisfactorily by a third order polynomial (not shown). Based on this result, the V_D will be ~ 0.4 V for $x=0$. Therefore, V_D experiences a complex variation as x increases, and the total increase of V_D would be ~ 0.7 V from $x=0$ to 1.

In the above analyses, the same model for the p - n junction has been used for the junction that could be a Schottky diode based on the considerations. First, the interfacial potential 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 behavior, whereas the interface layer (~ 6 nm for LCMO) near STON may remain insulating because of the substrate-induced lattice defects and Jahn–Teller effect.¹⁰ In this case, the p - n model maybe a good approximation.

As is well known,¹¹ in the hole-doped manganites, three Mn $3d$ electrons form the localized t_{2g} band, and the remaining $3d$ electrons occupy two e_g bands ($e_{g\uparrow}$ and $e_{g\downarrow}$, classified according to spin orientation) that are energetically higher than the t_{2g} band. Because of the strong cooperative Jahn–Teller distortion of the MnO_6 octahedra, the $e_{g\uparrow}$ band will further split into two subbands $e_{g1\uparrow}$ and $e_{g2\uparrow}$, each about 1 eV in width, with an indirect gap of the order of ~ 0.1 eV. The lower $e_{g1\uparrow}$ band of LaMnO_3 is fully occupied and the others completely empty. In contrast, there are only two e_g subbands of different spin orientations in CMO, and both are unoccupied. As a result, the conduction and valence bands of CMO will be mainly of the $e_{g\uparrow}$ and $t_{2g\uparrow}$ characters, respectively. Photoemission/absorption experiments indicate that the Fermi level of the manganite locates below the $e_{g2\uparrow}$ band, with a separation that is essentially independent of x . Based on the angle-resolved photoemission experiments performed by Park *et al.*,⁶ the Fermi energy (E_F) of LCMO experiences a downward shift with x , and the total change is ~ 0.72 eV as x sweeps from 0 to 1. When a LCMO film is deposited on STON, an energy barrier (eV_D) will be established to prevent the charge diffusion between STON and LCMO. Positive V_D indicates that the Fermi level of STON is higher than that of LCMO. The tendency of electron migration from STON to LCMO would be enhanced as the content of Ca increases because of the decrease of the Fermi level of LCMO. This actually implies an increase of V_D with x . In this picture, we can understand the correlation between E_F and V_D , the latter rises as the former lowers, and the coincidence of $e\Delta V_D$ (~ 0.7 eV) with ΔE_F (~ 0.72 eV). Figure 5 is a schematic plot showing the variation of the band structure of the LCMO/STON junctions with Ca content.

However, the correspondence between the V_D - x and E_F - x relations is obviously not as simple and direct as expected. As reported by Park *et al.*,⁶ E_F exhibits a simple and monotonic decrease with x in the whole doping range, whereas V_D is nearly constant between $x=0.33$ and 0.7

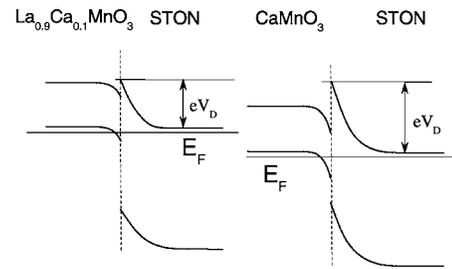


FIG. 5. Schematic band structures of the LCMO/STON junction demonstrating the effects of Ca content.

(Fig. 4). This implies the presence of extra factors affecting the interfacial potential. A possible reason could be the occurrence of phase separation. It has been well known that the interfacial electronic state usually differs from that of the bulk for the manganite, which can lead to the coexistence of two phases. Alternatively, the Fermi level pinning by interface states can also result in a complex variation of V_D , as occurred in conventional semiconductor junctions. Further studies are obviously required to elucidate the physics for the complex behavior of V_D .

As a supplement, we would like to point out that although the charge carrier in the LCMO films of $x > 0.5$ are electronlike in character, as confirmed by the Hall effect study, similar rectifying behavior as the ordinary p - n junctions is observed. This could be a difference between the manganite and the conventional semiconductor.

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