Effects of lattice strains on the interfacial potential in $La_{0.67}Ca_{0.33}MnO_3/SrTiO_3$:Nb heterojunctions

D. J. Wang,[1,2,a)] J. R. Sun,[2] Y. W. Xie,[2,3] Y. B. Li,[1] L. G. Zhang,[1] R. W. Wang,[1] and B. G. Shen[2]

[1]*Department of Applied Physics, Wuhan University of Science and Technology, Wuhan 430081, People's Republic of China*

[2]*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*

[3]*State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, People's Republic of China*

(Received 5 August 2010; accepted 24 October 2010; published online 10 November 2010)

Oxide p-n heterojunctions composed of $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) films with different thickness and $SrTiO_3$:Nb 0.1 wt % are fabricated and the effects of thickness on the interfacial potential are experimentally studied. Excellent rectifying behavior of the junctions well described by the Shockley equation is observed and the interfacial potential eV_D is obtained for all of the junctions based on an analysis of the current-voltage characteristics. The remarkable result of the present work is the strong dependence of the interfacial potential on the thickness of LCMO films: eV_D increases from 0.5 to 0.72 eV as the thickness increase from 3.6 to 33 nm. The strain in the LCMO film, which affects the carrier density through modulating the Jahn–Teller effect, is believed to be responsible for the observation. © *2010 American Institute of Physics*. [doi:10.1063/1.3515905]

By sandwiching a $SrTiO_3$ layer between $La_{0.9}Sr_{0.1}MnO_3$ and $La_{0.05}Sr_{0.95}TiO_3$, Sugiura[1] fabricated the first manganite p-n junction that shows a satisfactory rectifying property in a wide temperature range, which stimulated the intensive research on manganite p-n junction in the past decade. Compared with the conventional semiconductor junction, 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 and temperature-dependent photovoltaic effect.[2–4] It is obvious that the physical properties of the junction is mainly determined by an interfacial barrier. The direct information about the interfacial potential is therefore highly desired, especially for the manganite junctions that show emergent phenomena. Based on the thermionic emission model for the Schottky diode, Postma *et al.*[5] analyzed the current-voltage characteristics of the $(La,Sr)MnO_3/SrTiO_3$:Nb junction and obtained a Schottky barrier of ~0.65 eV, where $(La,Sr)MnO_3$ is treated as a metal. Alternatively, Sawa[6] studied the $Pr_{0.6}Ca_{0.4}MnO_3/SrTiO_3$:Nb junction in the frame of the conventional semiconductor theory and obtained a similar value (~0.70 eV) for the interfacial barrier. Subsequent work by Lu *et al.*[7] and Wang *et al.*[8] show that the interfacial barrier can be tuned by hole content for the $La_{1-x}Ca_xMnO_3/SrTiO_3$:Nb junctions, whereas it is insensitive to the metal-to-insulator transition and the change in resistivity due to the variation of tolerance factor.

According to the semiconductor theory, the interfacial potential is mainly determined by the carrier density near the interface. As is well known, a distinctive feature of manganite is the strong charge-phonon correlation or the charge-lattice coupling. Therefore, the lattice distortion near the interface of the junction may have a visible effect on interfacial potential for the manganite junction. In this paper, we performed a systematic study on the rectifying properties of the $La_{0.67}Ca_{0.33}MnO_3$ (LCMO)/0.1 wt % Nb-doped $SrTiO_3$ (STON) p-n heterojunctions with different LCMO thickness. The interfacial barrier is found to grow significantly with the increase of film thickness when the latter is below 33 nm. The strain relaxation in the LCMO film is believed to be responsible for the increase of the energy barrier.

The LCMO/STON junctions were fabricated by growing LCMO films of the thickness of $t=3.6$, 11, 33, 100, and 300 nm on the (001) STON substrates by the pulsed-laser deposition technique. The temperature of the substrate was kept at 700 °C and the oxygen pressure at 100 Pa during the deposition. The resulting sample was furnace-cooled to room temperature in an oxygen atmosphere of 160 Pa after deposition. As shown by the x-ray diffraction data, the LCMO films are clean single phase and highly textured. The out-of-plane lattice constant shows a monotonic increase with the increase of film thickness. Assuming a constant cell volume for the films of different thickness, we can calculate the in-plane lattice constant a. Figure 1 shows the c/a ratio thus obtained. The c/a ratio shows a monotonic growth with t and

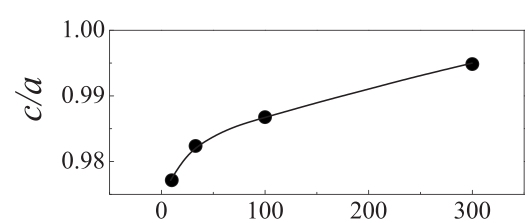

FIG. 1. Lattice constant c/a of LCMO films dependence of the film thickness. The solid line is a guide for the eye.

[a)]Author to whom correspondence should be addressed. Electronic mail: d.j.wang@163.com.

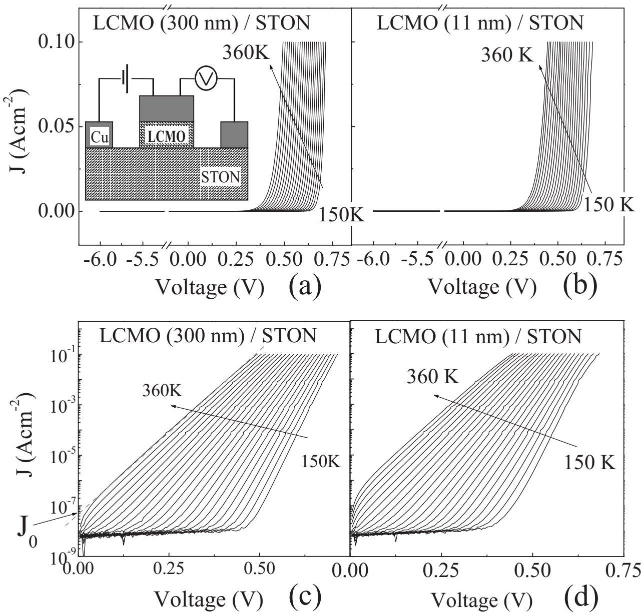

FIG. 2. Current-voltage characteristics and semilogarithmic plot of the characteristics of LCMO/STON junctions measured under different temperatures between 150 and 360 K. LCMO thickness is [(a) and (c)] 300 and [(b) and (d)] 11 nm.

the most rapid relaxation takes place below 50 nm. The maximal change is 2% for the film thickness from 0 to 300 nm. This result clearly indicates the relaxation of lattice strains in thick films.

The current-voltage (*J-V*) characteristics of the junction were measured in the two-probe configuration. To get good electric contact and to avoid the effect of current distribution in the junction,[4] three copper electrodes, one on the LCMO film and two on the STON substrate, were deposited. The LCMO film and copper electrodes were subsequently patterned into squares with the size of 1×1 mm^2 by the conventional photolithography and chemical etching technique. As representatives, in Fig. 2 we show the *J-V* curves of LCMO (300 nm)/STON and LCMO (11 nm)/STON, measured in the temperature range from 150 to 360 K. Excellent rectifying behaviors 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 voltage bias in the forward direction. The increase in temperature has no obvious effects except for a nearly rigid shift of the *J-V* curve along the v-axis.

To obtain the information about interfacial potential, a further analysis on the temperature dependence of the saturation current, which is expected to vary exponentially against the interfacial barrier, is required. Based on the semiconductor theory, the *J-V* relation of an ideal p-n junction can be described by the formula $J\approx J_0\exp(eV/nk_BT)$ (Refs. 9 and 10) for $eV>nk_BT$ in the forward direction. The prefactor J_0 is the reverse saturation current and it varies following the relation $J_0\propto T^{3+\gamma/2}\exp(-eV_D/k_BT)$, where eV_D parametrizes the interfacial potential, k_B is the Boltzmann's constant, n is the ideality factor, and γ is a constant determined by $D/\tau=T^{\gamma}$ (D is the diffusion coefficient and τ the lifetime of the minority carrier). The saturation current can be obtained as the intercept in the y-axis of the extrapolated log *J-V* relation. It is obvious that the precondition to get a reliable J_0 is that the log *J-V* relation should be linear. Fortunately, this condition is satisfied by the present junctions. As shown in Figs. 2(c) and 2(d), an excellent linear dependence of log J on bias voltage is observed in the whole temperature ranges studied.

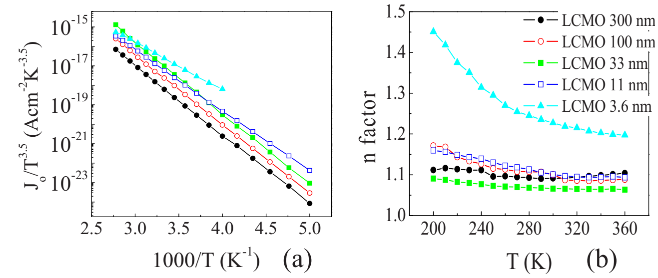

FIG. 3. (Color online) The (a) temperature-dependent saturation current and (b) ideality factor for all the samples with five typical thicknesses.

Figure 3 shows the temperature dependence of the saturation current J_0 and the ideality factor n on temperature, where n is determined by the slope of the log *J-V* curve. The saturation current is quite small, indicating the high quality of the junction. This is consistent with the fact that the ideality factor is pretty small, varying between 1.0 and 1.5, when the temperature changes between 200 and 360 K (n is expected to be unity for an ideal p-n junction). Especially, for the junction with 33 nm LCMO, n varies from 1.07 to 1.1.

Based on the J_0-T relation, a quantitative analysis on the interfacial potential of the junction can be performed. A simple calculation shows that $\ln(J_0/T^{3+\gamma/2})/(1/T)=-eV_D/k_B$. Based on this equation, eV_D can be directly derived from the slope of the $ln(J_0/T^{3+\gamma/2})-1/T$ curve if it is independent of temperature, which is the case occurring above 200 K ($1/T<0.005$ K^{-1}) as shown in Fig. 3(a). The interfacial potential thus obtained is shown in Fig. 4 as a function of film thickness. It can be seen that the interfacial potential strongly depends on the thickness of LCMO films: eV_D increases from 0.5 to 0.72 eV for the thickness from 3.6 to 33 nm. It should be pointed out that the parameter γ is set to unity without significantly affecting the final result (the prefactor $T^{3+\gamma/2}$ is unimportant compared to the exponential term).

It has been believed that the lattice strain has a strong effect on the manganite films. The in-plane strain can enhance the Jahn–Teller effect, reducing the density of mobile carriers in the manganite film. As a result, the resistivity grows and the magnetization decreases. Both the theoretical and experimental studies show that the strain effect plays a dominant role when the thickness of the manganite film is less than 30 nm.[11–13] It is interesting to note that this is ex-

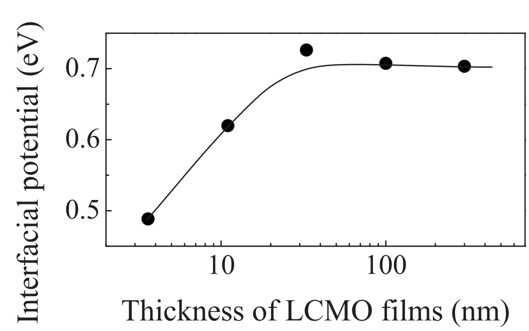

FIG. 4. Interfacial potential of the LCMO/STON junctions as a function of the LCMO thickness. The solid line is a guide for the eye.

actly the critical thickness observer in our experiments. It is therefore reasonable to propose that the variation of the interfacial barrier here has a close relation with the lattice strains in the LCMO films. According to the semiconductor theory, the interfacial potential is determined by the difference of Fermi levels of LCMO and STON. In fact, the thickness of the depletion layer of the junction can also affect the apparent interracial barrier. Electrons can only overcome the barrier by thermal activation if the depletion width is thick enough, whereas they can tunnel through the depletion layer when the latter is thin enough. Electron tunneling causes a reduction of the effective interfacial barrier. Based on the simple formula, the depletion width of the LCMO/STON junction can be estimated[14]

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

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

where t_1/t_2 is the depletion layer thickness of LCMO/STON, $\varepsilon_0/\varepsilon_1/\varepsilon_2$ is the permittivity of vacuum/LCMO/STON, N_{A1}/N_{D2} the hole/electron density in LCMO/STON, and V_D the interfacial potential. In a previous work, Xie[15] had studied the dependence of the depletion width on the hole content in LCMO for the LCMO/STON junctions. Here we can estimate the thickness of the depletion layer by adopting the parameters $\varepsilon_1=30$, $\varepsilon_2=300$, and $N_{D2}=3.25\times 10^{26}$ m^{-3}. The total thickness of the depletion layer is 26 nm for the heterojunction with 300 nm LCMO film, postulating that 100% carriers are stimulated under weak Jahn–Teller effect ($N_{A1}=5.34\times 10^{27}$ m^{-3}). For the junction with 11 nm LCMO film, however, it is more complex. If there are only 10%, 3%, 1%, and 0.3% carriers stimulated under the strong Jahn–Teller effect,[16,17] the calculated depletion layer thickness is 22, 18, 15, and 14 nm, respectively. That is to say that the depletion thickness of the LCMO/STON heterojunctions decreases with the stronger Jahn–Teller effect in LCMO film, providing a possibility for the electrons to tunnel through the depletion layer of LCMO/STON heterojunctions easier, then leading up the effective interfacial potential to the lower. Such a conclusion can be proved by the ideal factor n shown in Fig. 3(b). For the LCMO (300 nm)/STON junction, n approximately equals unity, implying that the depletion is very thick and the electrons pass through the interface only by overcoming the interfacial barrier. Also, the n of LCMO (3.6 nm)/STON junction, between 1.2 and 1.5, indicates that the depletion is not thick enough so that a part of the electrons can go through the interface by tunneling. It should be pointed out that when the carrier density of LCMO film decreases further, the total calculated depletion layer will increase. However, this is meaningless when the depletion layer in the LCMO side exceeds film thickness.

In conclusion, the transport properties of LCMO/STON heterojunctions with various LCMO thickness, which are of excellent rectifying characteristic, are experimentally studied. The interfacial potential of the junctions is evaluated using the model of conventional p-n junction, which has a great dependence on the thickness of LCMO films while the thickness of the film is lower than 33 nm: eV_D increases from 0.5 to 0.72 eV as the thickness enhances from 3.6 to 33 nm and it is a constant of 0.72 eV as the thickness of film further increases. The strain in the LCMO film, affecting the carrier density by modulating the Jahn–Teller effect, is believed to be responsible for the observation. The present work shows that the transport properties of a manganite-based heterojunction can be modulated by changing the thickness of the manganite layer.

This work has been supported by the National Basic Research of China, the National Natural Science Foundation of China, the Knowledge Innovation Project of the Chinese Academy of Science, and the Beijing Municipal Nature Science Foundation.

[1]M. Sugiura, K. Uragou, M. Noda, M. Tachiki, and T. Kobayashi, Jpn. J. Appl. Phys., Part 1 **38**, 2675 (1999).
[2]M. Ziese, A. Setzer, I. Vrejoiu, B. I. Birajdar, B. J. Rodriguez, and D. Hesse, J. Appl. Phys. **104**, 063908 (2008).
[3]J. R. Sun, B. G. Shen, Z. G. Sheng, and Y. P. Sun, Appl. Phys. Lett. **85**, 3375 (2004).
[4]D. J. Wang, J. R. Sun, Y. W. Xie, W. M. Lü, S. Liang, T. Y. Zhao, and B. G. Shen, Appl. Phys. Lett. **91**, 062503 (2007).
[5]F. M. Postma, R. Ramaneti, T. Banerjee, H. Gokcan, E. Haq, D. H. A. Blank, R. Jansen, and J. C. Lodder, J. Appl. Phys. **95**, 7324 (2004).
[6]A. Sawa, T. Fujii, M. Kawasaki, and Y. Tokura, Appl. Phys. Lett. **86**, 112508 (2005).
[7]W. M. Lü, J. R. Sun, D. J. Wang, Y. W. Xie, S. Liang, Y. Z. Chen, and B. G. Shen, Appl. Phys. Lett. **92**, 062503 (2008).
[8]D. J. Wang, J. R. Sun, W. M. Lue, Y. W. Xie, S. Liang, and B. G. She, J. Phys. D: Appl. Phys. **40**, 5075 (2007).
[9]S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981).
[10]R. L. Anderson, Solid-State Electron. **5**, 341 (1962).
[11]R. Zhang and R. F. Willis, Phys. Rev. Lett. **86**, 2665 (2001).
[12]C. A. Perroni, V. Cataudella, G. De Filippis, G. Iadonisi, V. Marigliano Ramaglia, and F. Ventriglia, Phys. Rev. B **68**, 224424 (2003).
[13]C. M. Xiong, J. R. Sun, D. J. Wang, and B. G. Shen, Acta Phys. Sin. **53**, 3909 (2004).
[14]P. C. Newman, Electron. Lett. **1**, 265 (1965).
[15]Y. W. Xie, J. R. Sun, D. J. Wang, S. Liang, W. M. Lü, and B. G. Shen, Appl. Phys. Lett. **90**, 192903 (2007).
[16]The resistivity dependence on the thickness of LCMO films is studied. As the thickness of the film was decreased, the resistivity increased and the 11-nm-thick LCMO film showed a semiconducting behavior, which is about 0.2 Ω cm at room temperature, much larger than that of 300-nm-thick LCMO (~0.02 Ω cm), and increases rapidly with the decrement of temperature. According to the work of Liang (Ref. 17), the thickness of the magnetic and conductive dead layer is ~10 nm. When the film thickness is thinner than 10 nm, the carrier concentration could be very low. So it is reasonable to postulate that the carriers in LCMO of 11 nm are almost localized.
[17]S. Liang, J. R. Sun, J. Wang, and B. G. Shen, Appl. Phys. Lett. **95**, 182509 (2009).