Available online at www.sciencedirect.com
ScienceDirect
Solid State Communications 143 (2007) 131–135
solid state communications
www.elsevier.com/locate/ssc

Electronic transport and magnetoresistance of a heterojunction composed of $La_{0.7}Ce_{0.3}MnO_3$ and 1 wt% Nb-doped $SrTiO_3$

Y.W. Xie*, D.J. Wang, Y.Z. Chen, S. Liang, W.M. Lü, B.G. Shen, J.R. Sun

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

Received 16 January 2007; received in revised form 31 March 2007; accepted 7 May 2007 by B.-F. Zhu
Available online 22 May 2007

Abstract

We experimentally studied the transport properties and magnetoresistance behavior of a $La_{0.7}Ce_{0.3}MnO_3/SrTiO_3$ (doped by 1 wt% Nb) junction. Based on the analyses of the current–voltage relations and the depletion width, we conclude that the dominant transport mechanism of the junction is tunneling. The magnetoresistance of the junction is negative throughout the whole bias voltage range (from −1 V to 0.4 V) and the whole temperature range (below 300 K). It is believed that the magnetic field depresses the junction resistance by reducing the depletion width of the junction.

PACS: 75.47.Gk; 73.40.Lq; 75.70.Cn

Keywords: A. Heterojunctions; A. Magnetically ordered materials; A. Surfaces and interfaces; A. Thin films

1. Introduction

The successful fabrication of p–n junctions based on colossal magnetoresistive (CMR) manganites, $R_{1-x}A_xMnO_3$ (R is a trivalent rare-earth ion and A is a divalent dopant), has evoked tremendous interest for its potential in applications [1–5]. By changing the doping concentration, doping type, and/or oxygen content, the physical properties of manganites exhibit a surprisingly wide variety, from being completely insulating for $Pr_{0.7}Ca_{0.3}MnO_3$ to completely metallic (below room temperature) for $La_{0.67}Sr_{0.33}MnO_3$ [6]. Many of these manganites are sensitive to external perturbations, such as magnetic field and light. Utilizing these manganites, it is promising to be able to obtain multi-functional junctions that can be controlled simultaneously by electric bias, magnetic field, and light.

Such multi-functions have been partly realized in a $La_{0.7}Ce_{0.3}MnO_3$-based junction. Recently, Sun et al. found a significant photovoltaic effect in a junction composed of $La_{0.7}Ce_{0.3}MnO_3$ and Nb-doped $SrTiO_3$ [4], and subsequent research by Sheng et al. showed that the photovoltaic effect can be effectively modulated by an external magnetic field [7]. To explain these interesting observations, understanding the fundamental transport mechanism of the junction is necessary.

Although there is a lot of work on manganite junctions, researches on the transport mechanisms are still scarce. Based on the conventional semiconductor theory [8,9], the transport mechanism of a junction can be derived from its current–voltage (I–V) relations. Postma et al. [10] may be the first researchers who undertook a quantitative analysis on the current–voltage characteristics of manganite junctions, and they found that the transport behavior of $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3$:Nb (0.1 wt% and 0.01 wt% Nb) can be well described by the thermionic emission model. For a similar junction, $Pr_{0.7}Ca_{0.3}MnO_3/SrTi_{0.9998}Nb_{0.0002}O_3$, Sawa et al. [11] concluded that the thermal diffusion process was dominative. However, it seems that not all of the transport behaviors of the manganite junctions can be explained based on these models. In fact, the depletion width in heavily doped junctions is thin, and thus a tunneling mechanism is also possible.

In this work, we studied the transport properties and magnetoresistance (MR) of a junction composed of a $La_{0.7}Ce_{0.3}MnO_3$ film (LCMO) and a 1 wt% Nb-doped $SrTiO_3$ (STON) substrate. The two-probe method was adopted to measure its I–V

* Corresponding author. Tel.: +86 10 82649261; fax: +86 10 82649485.
E-mail address: xieyanwu@g203.iphy.ac.cn (Y.W. Xie).

0038-1098/$ - see front matter
doi:10.1016/j.ssc.2007.05.007

relations [12]. The most important results of the present work are the discovery of a tunneling-dominated mechanism and the striking and negative MR throughout the whole bias range (from −1 V to 0.4 V) and the whole temperature range (below 300 K). It is believed that a magnetic field depresses the junction resistance by reducing the depletion width.

2. Experimental

The LCMO/STON junction was fabricated by growing the LCMO film on a (001) STON substrate by the pulsed laser ablation technique. During the deposition, the substrate was kept at ∼720 °C, and the O_2 pressure was kept at ∼100 Pa. The film thickness is ∼100 nm, controlled by the deposition time. The size of the junction area is 1×1 mm^2; it is fabricated by the conventional photolithography and chemical etching technique. The contact resistance between Ag and STON is smaller than 10 Ω [13]; and the contact resistance between Ag and LCMO, evaluated by comparing the results of four- and two-probe measurements, is less than 50 Ω. These resistances are small compared with the resistance of the junction, as will be seen below, and would not affect the quantitative analysis of the transport properties.

3. Results and discussion

In previous research we have examined the quality of an LCMO film and its interface with a $SrTiO_3$ substrate by X-ray diffraction and cross-sectional high-resolution transmission electron microscopy [14,15]. Epitaxial growth with c-axis orientation and sharp interface were confirmed. Ce-rich nanoclusters, which also grew epitaxially, were also observed in the film. Though earlier work reported that the major carriers in LCMO are electrons, more and more studies revealed that its major carriers are actually holes, which are introduced by the formation of Ce-rich nanoclusters and the excess of oxygen content [14,16,17]. Thus the LCMO/STON junction is of p–n type. Considering that the LCMO film is inhomogeneous in structure, in an LCMO/STON junction, there are cation-deficient regions and Ce-rich regions in contact with STON, respectively. Since the Ce-rich regions are of bad conduction, the transport behavior of the junction is mainly determined by the cation-deficient regions in the LCMO film to form many p–n junctions in parallel. In this case, the behavior of the LCMO/STON junction is similar to that of a junction based on typical manganites.

Fig. 1 shows the temperature dependence of the in-plane resistivity and MR, for the LCMO film. An insulator-to-metal transition occurs, at $T_P = 233$ K. Below T_P, the resistivity increases again with the decrease of temperature at ∼140 K, which is a common phenomenon in oxygen-deficient or under-doped manganites [18]. A 5 T magnetic field shifts the T_P to higher temperature, and meanwhile decreases the resistivity of the film, producing an MR $[\rho(5\text{ T})/\rho(0\text{ T}) - 1]$ which can be as high as −75%. These characteristics are similar to those of typical CMR manganites.

Fig. 2(a) shows the selected I–V relations for the LCMO/STON junction, at various temperatures, and a

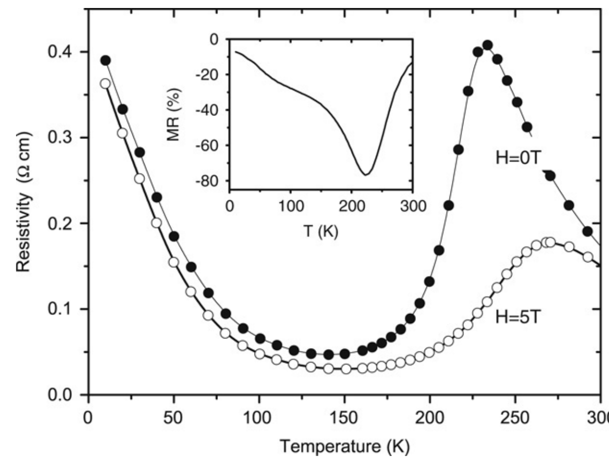

Fig. 1. Temperature dependence of the in-plane resistivities for a $La_{0.7}Ce_{0.3}MnO_3$ film, measured with $H = 0$ and $H = 5$ T field. In the inset is the temperature dependence of MR $[\rho(5\text{ T})/\rho(0\text{ T}) - 1]$ for the film.

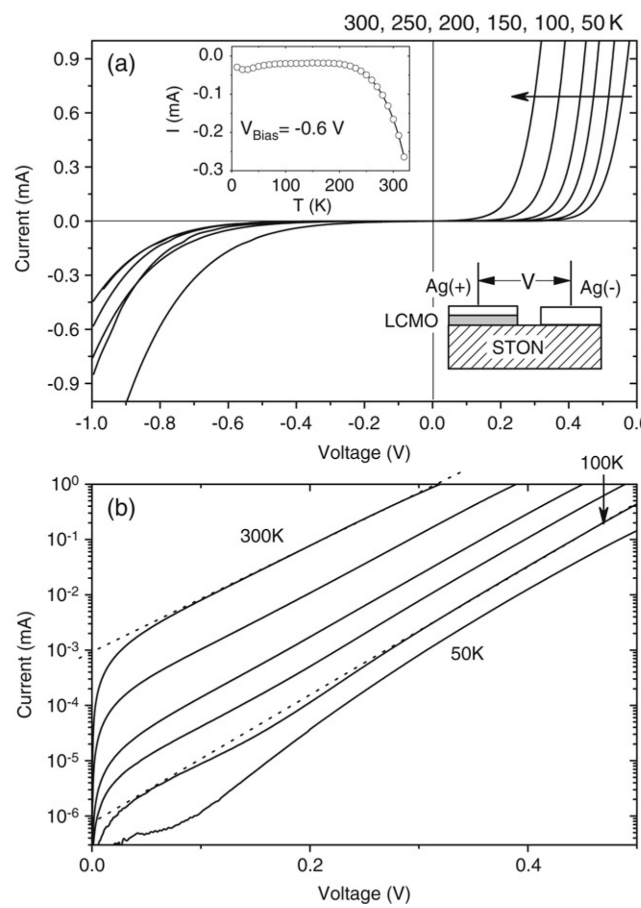

Fig. 2. (a) Selected current–voltage relations for a $La_{0.7}Ce_{0.3}MnO_3$/1 wt% Nb-doped $SrTiO_3$ junction. The interval of temperature is 50 K. The upper inset shows the temperature dependence of current at a constant voltage, −0.6 V. The lower inset shows a schematic view of the junction. (b) Forward characteristics plotted in semi-logarithm coordinates. The dashed lines are guides for the eye. The excellent linear relation of log I–V curves indicates the good quality of the junction.

schematic view for the configuration is given in the lower inset. The junction exhibits fairly good rectifying behaviors, characterized by the strongly asymmetric I–V curves. The forward-bias characteristics can be described by a shift to lower voltage with increasing temperature, while the reverse-bias characteristics vary complexly with temperature. To give an intuitionistic impression, in the upper inset of Fig. 2(a) we show the temperature dependence of current at −0.6 V; an evident transition at ∼220 K is observed. This transition temperature is consistent with the T_P of the LCMO film, indicating their inherent correlation. It is possible that the resistive transition in the bulk LCMO film, due to the proximity effect, induces a transition in the depleted LCMO layer near the interface.

To obtain information on the transport mechanism of the junction, the I–V curves were further analyzed. Fig. 2(b) depicts the forward characteristics in a semi-logarithmic plot. An excellent linear relation between $\log I$ and V is observed above 100 K, which is a phenomenon hardly observed in a p^+–n^+ diode, which usually suffers from significant creepage (at low bias a typical p^+–n^+ diode has large current density and shows no rectifying behavior) [8]. The excellent linear relation confirms that the junction is of good quality, and also confirms that the contact resistances/barriers have negligible effect on the transport properties, as stated above.

According to the semiconductor theory [8,9], the forward current can be either thermal (diffusion, thermal emission) or non-thermal (tunneling). To produce thermal current, charge carriers have to surmount the potential barrier to cross the junction. In this case, the I–V relation can be written in empirical form as

$$I = I_0 \exp(qV/nk_BT) \quad (1)$$

where $I_0 = A\exp(-qV_{B0}/nk_BT)$, A is a parameter weakly depending on temperature, V_{B0} is the barrier at zero applied voltage, q is the unit charge carrier, k_B is the Boltzmann constant, and n is the ideality factor, which has a value between 1 and 2. Charge carriers can also tunnel through the potential barrier. If the tunneling occurs predominantly at the base of the potential barrier, the current is non-thermal in nature, and can be described by the Newman equation

$$I = I_s \exp(\alpha T)\exp(\beta V) \quad (2)$$

where I_s, α, and β are parameters weakly depending on V. Although both Eqs. (1) and (2) predict a linear relation between $\ln I$ and V, from Eq. (1) the slope of $\ln I$–V is expected to vary with $1/T$, and the temperature plays an important role in activating charge carriers; in contrast, from Eq. (2) the slope of $\ln I$–V is expected to be independent of temperature.

In order to distinguish the dominant transport mechanism, in Fig. 3(a) we compare the slope of $\ln I$–V observed for the LCMO/STON junction with those expected from the thermal and non-thermal processes. The temperature dependence of the observed slope of $\ln I$–V is quite weak, much closer to that of the non-thermal one. Eq. (2) also predicted an exponential growth of the current with temperature under a constant voltage. This dependence was also confirmed by the experimental results (Fig. 3(b)). Based on above analyses, we strongly suggest that the dominant transport mechanism of LCMO/STON is tunneling.

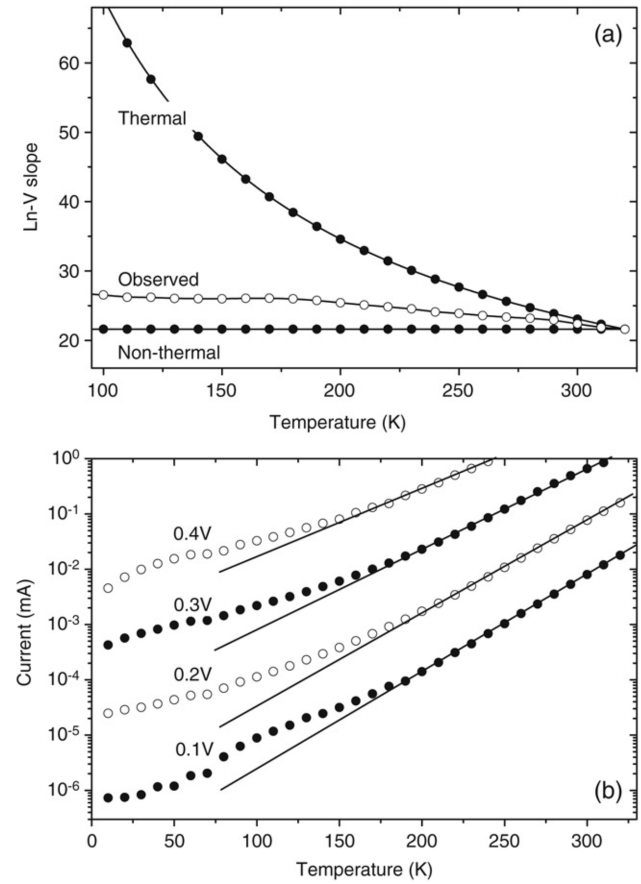

Fig. 3. (a) Temperature dependence of the slopes of $\ln I$–V curves for the thermal and non-thermal processes. Experimental results are shown for comparison. (b) Temperature dependence of current at different bias voltages. Solid lines are guides for the eye.

At low temperatures, the dominant mechanism should still be tunneling. A typical tunneling current is independent of temperature. The weak temperature dependence of current, predicted by Eq. (2), comes from the possible band change with temperature [19]. From Fig. 3(b) we can find that, at low temperatures, $\log I$ has a much weaker dependence on temperature, which may indicate that the band structure of LCMO has a weaker dependence on temperature, and is still consistent with the tunneling mechanism.

To justify tunneling as the dominant transport mechanism, we have analyzed the depletion width of the junction. The depletion width can be estimated based on the formulae [8,9]

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

and

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

where t_1, ε_1, N_{A1} and t_2, ε_2, N_{D2} are the depletion width, dielectric constant and carrier concentration of LCMO and STON respectively, and V_D is the potential barrier. As a manganite, LCMO is very different from conventional semiconductors since its electrons are strongly correlated. Although a simple estimation from doping concentration shows ∼0.3 holes/Mn, the real hole concentration in LCMO could

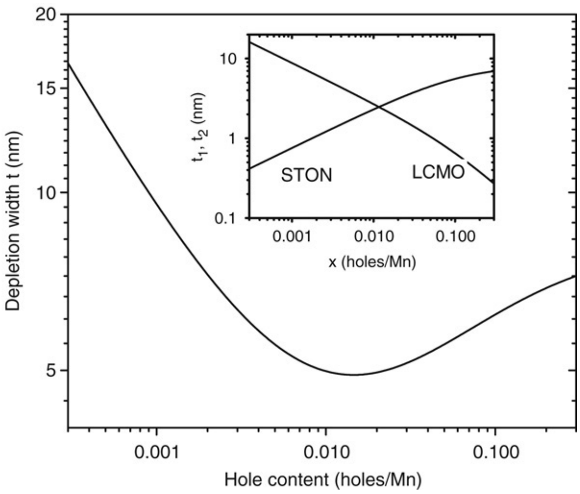

Fig. 4. Depletion width as a function of mobile hole content in the LCMO film. The inset shows the depletion widths of LCMO and STON, respectively.

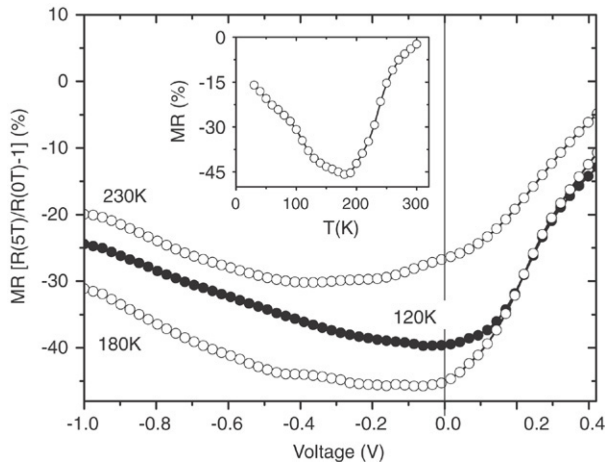

Fig. 5. Bias dependence of MR $[R(5\ \mathrm{T})/R(0\ \mathrm{T})-1]$ for the $La_{0.7}Ce_{0.3}MnO_3$/1 wt% Nb-doped $SrTiO_3$ junction at various temperatures. At each temperature, the maximal value of MR appears near 0 V bias. In the inset is the temperature dependence of the maximal MR for the junction.

be much smaller, owing to the strong localization by the Jahn–Teller effect, strain, etc. Fig. 4 illustrates the depletion width as a function of the hole concentration (x) of LCMO, adopting the parameters of $\varepsilon_1 = 10\varepsilon_0$ (ε_0 is the permittivity in vacuum) [20], $\varepsilon_2 = 300\varepsilon_0$ [21], $N_{D2} = 1.98 \times 10^{26}/\mathrm{m}^3$, and $V_D = 0.4$ eV [22] for the calculation. When varying x in an extremely large range, from 0.3 to 0.001, we found the total width of the depletion layer is in a narrow range, about several nanometers. The minimum thickness is ∼4.9 nm, appearing at $x \approx 0.0145$ holes/Mn ($N_{A1} \approx 2.5 \times 10^{26}/\mathrm{m}^3$). This result showed that the depletion layer of the LCMO/STON junction is relatively thin, and thus the tunneling effect should be important, consistent with the analysis based on the I–V relations.

The junction exhibits striking MR $[R(5\ \mathrm{T})/R(0\ \mathrm{T}) - 1]$. In Fig. 5 we show the bias voltage dependence of the MR, which is negative in all the bias range. At each temperature the largest MR appears near the zero bias. In the forward bias region the MR decreases sharply with increasing voltage, while in the reverse bias region the MR retains a large value, which only decreases slightly with increasing voltage. In the inset of Fig. 5 we give the temperature dependence of the maximal MR at each temperature. The MR is negative throughout the whole temperature range, and has a largest value, ∼−45%, at ∼190 K, a temperature smaller than the T_P of LCMO. It is obvious that the LCMO layer near the interface has a determinative role on the properties of the junction. This layer is mostly strained by the lattice mismatch, which will cause a decrease of magnetic order and thus of T_P. The bias and temperature dependence of MR of the present junction is different from the previous result [23], which may originate from the different measuring configurations used in the present and the previous studies [12].

The observed MR behaviors can be explained using the tunneling model. In a tunneling model, the resistance is proportional to the depletion width. Applying a magnetic field will delocalize the holes by rearranging local spins and depressing the Jahn–Teller effect [6], and thus will increase the hole concentration. From Fig. 4 we can see that the increase of hole concentration can either increase or decrease the depletion width, depending on the starting hole concentration and the extent of the increase. If the starting concentration is small, the increase of the hole concentration will decrease the depletion width, and thus decrease the resistance of the junction, producing a negative MR. The fact that the MR is negative implies that the free hole concentration of LCMO is less than 0.0145 holes/Mn (Fig. 4), much smaller than that estimated from the doping concentration. However, our estimation is consistent with the previous results on underdoped manganites studied by angle-resolved photoemission spectroscopy and X-ray absorption spectroscopy [6].

4. Conclusions

We experimentally studied the transport properties and MR behavior of a LCMO/STON junction. Based on the analyses of the I–V relations and the depletion width, we found that tunneling is the dominant transport mechanism of the junction. The MR of the junction is negative throughout the whole bias range and the whole temperature range. We believe that the origin of the MR is the modulation of depletion width by applying a magnetic field. Further, our results indicate that the analyses of the transport properties and MR of a manganite junction can be an effective way to estimate the free carrier concentration of the manganite.

Acknowledgments

This work has been supported by the National Natural Science Foundation of China and the National Fundamental Research of China.

References

[1] M. Sugiura, K. Uragou, M. Noda, M. Tachiki, T. Kobayashi, Japan J. Appl. Phys., Part 1 38 (1999) 2675.

[2] H. Tanaka, J. Zhang, T. Kawai, Phys. Rev. Lett. 88 (2002) 027204.
[3] J.R. Sun, C.M. Xiong, T.Y. Zhao, S.Y. Zhang, Y.F. Chen, B.G. Shen, Appl. Phys. Lett. 84 (2004) 1528.
[4] J.R. Sun, B.G. Shen, H.F. Tian, J.Q. Li, Y.X. Weng, Appl. Phys. Lett. 87 (2005) 202502.
[5] C. Mitra, P. Raychaudhuri, G. Köbernik, K. Dörr, K.H. Müller, L. Schultz, R. Pinto, Appl. Phys. Lett. 79 (2001) 2408.
[6] For a review, see Y. Tokura, Colossal Magnetoresistive Oxides, Gordon & Breach, London, 1999.
[7] Z.G. Sheng, B.C. Zhao, W.H. Song, Y.P. Sun, J.R. Sun, B.G. Shen, Appl. Phys. Lett. 87 (2005) 242501.
[8] S.M. Sze, Physics of Semiconductor Devices, 2nd ed., Wiley, New York, 1981.
[9] B.L. Sharma, R.K. Purohit, Semiconductor Heterojunctions, Pergamon Press, New York, 1974.
[10] F.M. Postma, R. Ramaneti, T. Banerjee, H. Gokcan, E. Haq, D.H.A. Blank, R. Jansen, J.C. Lodder, J. Appl. Lett. 95 (2004) 7324.
[11] A. Sawa, T. Fujii, M. Kawasaki, Y. Tokura, Appl. Phys. Lett. 86 (2005) 112508.
[12] D.J. Wang, Y.W. Xie, C.M. Xiong, B.G. Shen, J.R. Sun, Europhys. Lett. 73 (2006) 401.
[13] A Schottky barrier exists between Ag and STON, and it has been broken by applying a proper electric pulse to obtain an ohmic contact.
[14] D.J. Wang, J.R. Sun, S.Y. Zhang, G.J. Liu, B.G. Shen, H.F. Tian, J.Q. Li, Phys. Rev. B 73 (2006) 144403.
[15] D.J. Wang, C.M. Xiong, G.J. Liu, Y.W. Xie, B.G. Shen, J.R. Sun, Physica B 371 (2006) 187.
[16] Takeshi Yanagida, Teruo Kanki, Bertrand Vilquin, Hidekazu Tanaka, Tomoji Kawai, Phys. Rev. B 70 (2004) 184437.
[17] W.J. Chang, J.Y. Tsai, H.T. Jeng, J.Y. Lin, Kenneth Y.J. Zhang, H.L. Liu, J.M. Lee, J.M. Chen, K.H. Wu, T.M. Uen, Y.S. Gou, J.Y. Juang, Phys. Rev. B 72 (2005) 132410.
[18] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitru, G. Kido, Y. Tokura, Phys. Rev. B 51 (1995) 14103.
[19] A.R. Riben, D.L. Feucht, Solid-State Electron. 9 (1966) 1055.
[20] L.M. Wang, C.C. Liu, H.C. Yang, H.E. Horng, J. Appl. Phys. 95 (2004) 4928.
[21] T. Tomio, H. Miki, H. Tabata, T. Kawai, S. Kawai, J. Appl. Phys. 76 (1994) 5886.
[22] The diffusion potential of the manganite/$SrTiO_3$:Nb junction is a function of the content of Nb. The V_D values corresponding to the Nb content of 0.01 wt%, 0.05 wt%, 0.1 wt% have been published in the literature. $V_D = 0.4$ eV is a simple extrapolation of the above results to 1 wt%. N_{D2} was calibrated by Hall measurement.
[23] Z.G. Sheng, W.H. Song, Y.P. Sun, J.R. Sun, B.G. Shen, Appl. Phys. Lett. 87 (2005) 032501.