Magnetically and electrically tunable transport property of the heterojunction composed of $La_{0.9}Ca_{0.1}MnO_{3+\delta}$ and Nb-doped $SrTiO_3$

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Magnetically and electrically tunable transport property of the heterojunction composed of $La_{0.9}Ca_{0.1}MnO_{3+\delta}$ and Nb-doped $SrTiO_3$

Y W Xie, J R Sun[1], D J Wang, S Liang, W M Lü and B G Shen

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

E-mail: jrsun@g203.iphy.ac.cn

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Abstract
A manganite-based heterojunction composed of an oxygen-rich $La_{0.9}Ca_{0.1}$ $MnO_{3+\delta}$ film and a $SrTiO_3$ substrate doped by 1 wt% Nb has been fabricated, and its transport behaviours were experimentally studied. The junction resistance shows a metal-to-insulator transition at a critical temperature that varies with applied magnetic field. In contrast, bias current does not affect the transition temperature, although it depresses the junction resistance significantly. The junction resistance decreases with magnetic field, and the maximum magnetoresistance is $\sim -60\%$ under a field of 5 T, appearing at $T \approx 220$ K. The magnetoresistance gets its maximum value in the zero electric bias limit, and drops rapidly when bias voltage exceeds a threshold of 0.1–0.2 V, varying with temperature.

1. Introduction

By sandwiching a $SrTiO_3$ layer between a $La_{0.9}Sr_{0.1}MnO_3$ and a $La_{0.05}Sr_{0.95}TiO_3$ layer, Sugiura and collaborators fabricated the first manganite 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]. In addition to the excellent rectifying property, the most important discovery of Tanaka *et al* is the significant dependence of the transport behaviours of the junction on electric field. It was found that the metal-to-insulator transition of the junction resistance could be modified by electric field, and the transition temperature increases considerably with bias voltage. A similar phenomenon was also observed in a $La_{0.7}Sr_{0.3}MnO_3$/ZnO junction [3]. To explain this phenomenon, the injection of charge carriers

[1] Author to whom any correspondence should be addressed.

into the manganite layer has been postulated. This effect is interesting in the sense that it suggests a possibility for the electric modification of the magnetism of the manganite. However, different results were obtained by Lang and collaborators for a p–i–n junction composed of $La_{0.7}Ca_{0.3}MnO_3$, YSZ and Si [4]. The resistive transition of the junction resistance was found to shift to low temperatures with the increase of bias voltage. Meanwhile, the maximum magnetoresistance (MR) of the junction occurs near the temperature where the resistive transition happens. Changes of the depletion layer under electric/magnetic field, which may affect the tunnelling of charge carriers across the junction, are believed to be responsible for these observations.

These results indicate that the magnetic/electric field effects in manganite junctions could be very different. To capture the underlying physics, a full exploration of the diverse behaviours of the manganite junction is obviously desired. Based on this consideration, we performed a systematic study on the magnetic/electric field effects for a p–n junction composed of an oxygen-rich $La_{0.9}Ca_{0.1}MnO_{3+\delta}$ (LCMO) film and a $SrTiO_3$ substrate doped by 1 wt% Nb (STON). Although the stoichiometric $La_{0.9}Ca_{0.1}MnO_3$ is completely insulating below room temperature, the LCMO film shows a metal-to-insulator transition because of the excessive oxygen introduced [5]. This is different from $La_{0.9}Ba_{0.1}MnO_3$, for which lattice strain is believed to be the reason for the metal-to-insulator transition [6]. Based on our previous research on the effects of oxygen content [7], δ in LCMO was estimated to be $\sim$0.1. One of the most important observations of the present work is that the transport behaviour of the LCMO/STON junction is similar to that of the LCMO film. The junction resistance shows a metal-to-insulator transition at a critical temperature that varies with applied magnetic field. In contrast, bias current does not affect the transition temperature, although it depresses the junction resistance significantly. The second important observation is the significant MR of the junction. The maximum MR is $\sim -60\%$ under a field of 5 T, appearing at $T \approx 220$ K. The MR gets its maximum value in the zero electric bias limit, and drops rapidly when bias voltage exceeds a threshold of 0.1–0.2 V, varying with temperature. These behaviours can be qualitatively understood by assuming the change of the band structure of the junction.

2. Experimental details

The LCMO/STON junction was fabricated by growing the LCMO film on a (001) STON substrate of size $\sim 3 \times 5$ mm^2 by the pulsed laser ablation technique. The substrate was kept at 750 °C and the O_2 pressure at 100 Pa during the deposition. The film thickness is $\sim$150 nm, controlled by deposition time.

The phase purity and crystal structure of the sample were studied by powder x-ray diffraction performed on a Rigaku x-ray diffractometer with a rotating anode and Cu Kα radiation. A Quantum Design SQUID magnetometer (MPMS-7) was used for the magnetic measurements.

3. Results and discussion

X-ray diffraction has been performed for the LCMO films to check their crystal quality, and only the peaks of the $SrTiO_3$ substrate are observed (figure 1). It is possible that the reflections of the LCMO film coincide with those of the $SrTiO_3$ substrate, noting the fact that the lattice constant is $\sim$0.389 nm [8] for LCMO and 0.3905 nm for $SrTiO_3$. In contrast, the LCMO film grown on $LaAlO_3$ shows only the (00l) peaks, indicating the same orientation of the LCMO and the $LaAlO_3$ substrate. These results reveal that the LCMO films are of single phase and highly textured.

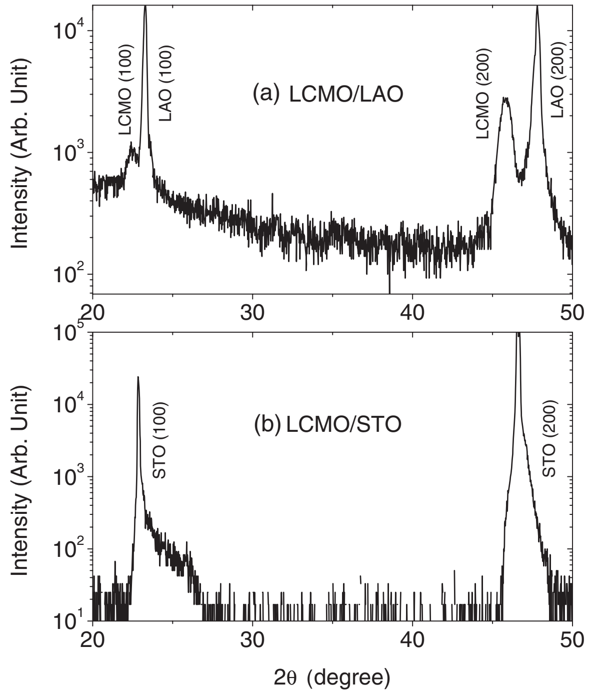

Figure 1. Typical x-ray diffraction spectra of the LCMO films grown on (a) (001) $LaAlO_3$ (LAO) and (b) (001) $SrTiO_3$ (STO) substrates.

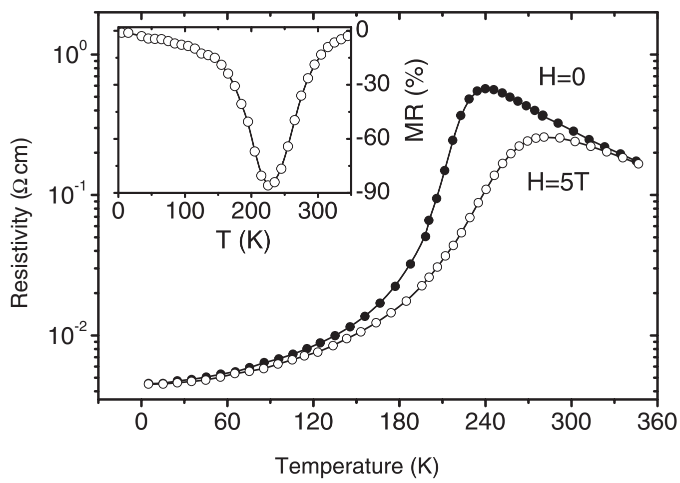

Figure 2. Temperature-dependent resistivity of the LCMO film measured under $H = 0$ and 5 T. The inset plot displays the magnetoresistance of the film obtained under a field of 5 T.

The in-plane resistivity of the LCMO film was measured by the four-probe technique under different magnetic fields, and the typical results are shown in figure 2. As expected, a metal-to-insulator transition takes place as the temperature decreases. This transition shifts from ∼231

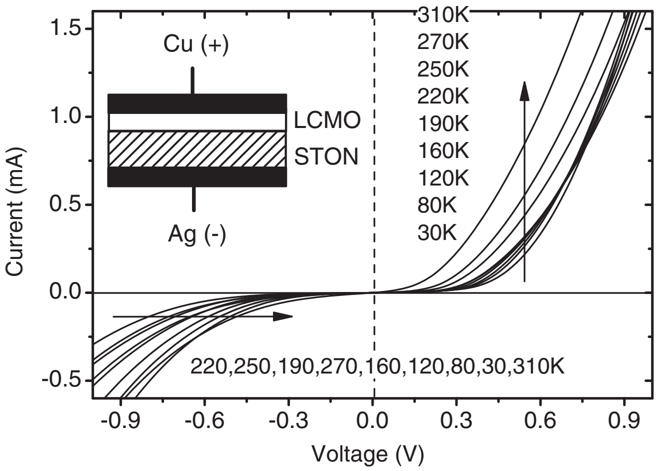

Figure 3. Current–voltage characteristics of the LCMO/STON junction measured under different temperatures. Inset is a schematic diagram of the configuration of the junction.

to ~267 K when the magnetic field increases from 0 to 5 T. The MR thus resulting is as high as ~85% ($\rho(H)/\rho(0) - 1$) (inset in figure 2). These results confirm the change of the electronic structure of the LCMO film as temperature or magnetic field varies.

The electric measurements of the junction were conducted in the two-probe configuration. To get a good electric contact and to avoid the current distribution [9] in the junction, a Cu pad and an Ag pad ~300 nm in thickness were deposited, as electrodes, on the top of the LCMO film and on the bottom of the STON substrate, respectively. The maximum contacting resistance is 10 Ω between Ag and STON and 50 Ω between Cu and the LCMO film in the temperature range below[2] 310 K, evaluated by comparing the results of four- and two-probe measurements. The contacting resistance is much smaller than the junction resistance as will be seen below and, therefore, would not affect the quantitative analysis of the rectifying behaviour. To depress the possible self-heating effect, the junction was mounted on a copper radiator with silver paste, and electric pulses of the duration of ~300 ms were used for the measurements. Data obtained at different measuring speeds were essentially the same, indicating that the effects of self-heating are negligible.

Figure 3 presents the current–voltage (I–V) relation measured by tuning bias voltage under different temperatures below 310 K. The junction exhibits a fairly good rectifying behaviour as demonstrated by the considerable asymmetry of the I–V curves against the electric polarity. The accelerated current increase under large bias voltage specifies the weakening (breakdown) of interfacial potential. Different from other manganite junctions [2, 4, 10], for which the I–V curves exhibit a simple expansion along the V-axis with the decrease of temperature, the variation of the I–V dependence of LCMO/STON is complex, which reveals a complex variation of junction resistance with temperature.

To obtain further knowledge about the junction, the junction resistance was subsequently measured under different currents and magnetic fields. As shown in figure 4, the most remarkable observations are the occurrence of a resistive transition and the independence of this transition from electric bias. When cooled below room temperature, the junction exhibits

[2] A Schottky barrier exists between Ag and STON, and it has been broken by applying a proper electric pulse to obtain an ohmic contact.

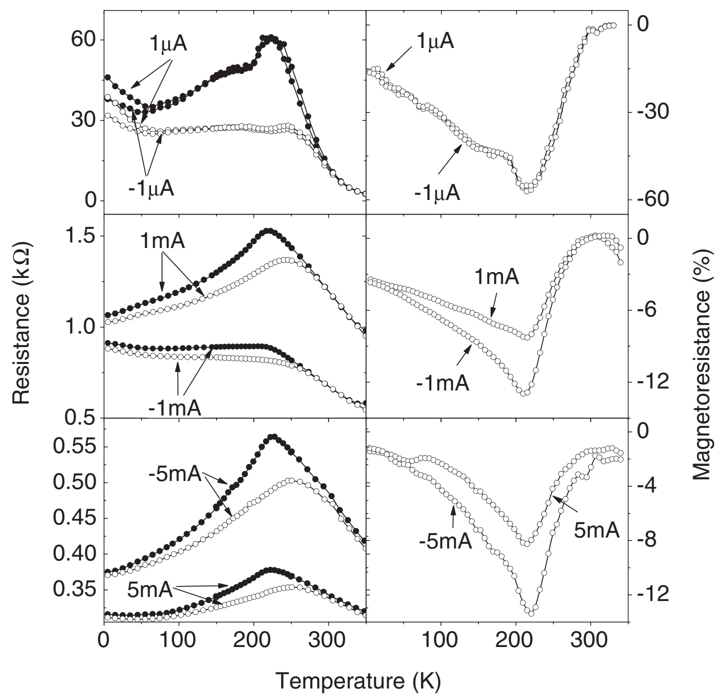

Figure 4. Temperature dependence of junction resistance measured under the fields of 0 and 5 T (left panel) and the corresponding magnetoresistance (right panel). Black and white symbols correspond to the results obtained without and with magnetic field, respectively. The current used for the resistive measurements is also given in the figure.

a semiconductive conduction until a critical temperature $T_C \approx 220$ K, at which a resistive transition that leads to metallic (or weakly semiconductive) conduction takes place. The increase of bias current depresses junction resistance greatly, which decreases from ~60 kΩ for $I = 1$ μA to ~0.4 kΩ for $I = 5$ mA. However, the transition temperature remains unaffected. Similar results are obtained when the bias voltage, instead of current, is fixed (not shown). To ensure that the obtained results are reliable, the experiments were repeated for several samples and similar behaviours were observed.

Different from electric field, magnetic field pushes the resistive transition to high temperatures, in the meantime depressing junction resistance. The transition temperature increases from ~220 to ~252 K as the field increases from $H = 0$ to 5 T. As a result of the upward shift of the resistive transition, significant MR $(R(H)/R(0) - 1)$ appears in the temperature range adjacent to and below T_C. The maximum MR can be as high as 60%, occurring in the zero bias limit. This is a value comparable to that of the LCMO film.

A simple analysis indicates the similarity of the transport behaviours of LCMO/STON and LCMO, including the occurrence of the resistive transition and the MR around this transition, except that the transition temperature and the MR value are somewhat lower in the former system (figures 2 and 4). However, differences between the two systems are also obvious. Compared with the LCMO film, the resistance of the junction depends strongly on electric bias.

Figure 5 shows the MR of the junction obtained under different bias voltages. Two special features different from other manganite junctions can be identified from figure 5 [2, 4, 11, 12]. The first one is the appearance of the maximum MR in the zero bias limit, and the second one

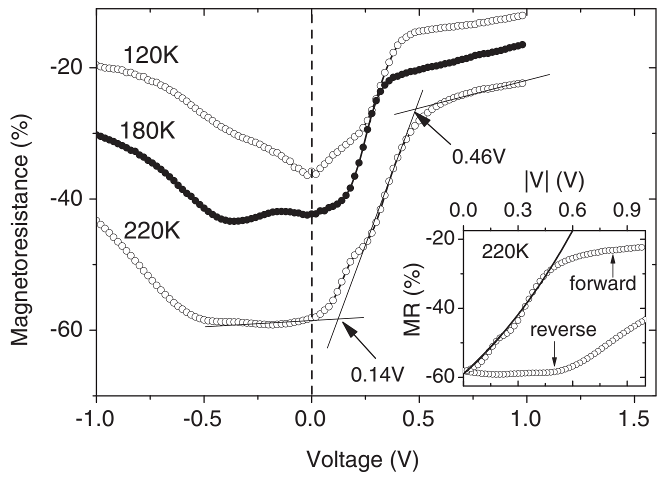

Figure 5. Electric bias dependence of the magnetoresistance of the LCMO/STON junction obtained under a field of 5 T. The inset plot is a comparison for the results corresponding to the forward and backward electric bias (symbol); the calculated results (solid line) using $\mathrm{MR}(V) = f(V)\exp(-e\Delta V_D/k_B T) - 1$ are also shown.

is the existence of a critical bias voltage above which the MR rapidly drops. Take the data collected at $T = 220$ K as an example. The MR is ~59% in the zero bias limit, and reduces from ~59% to ~26% as the bias voltage increases from ~0.14 to ~0.46 V. When the electric bias exceeds 0.46 V, a clear turn appears in the MR–V curve, signifying the weakening of the electric field effect. In contrast, the variation of the MR against the reverse electric bias is much smoother (inset in figure 5).

This bias dependence of MR is different from that of the magnetic tunnel junction, for which the MR–V curve is symmetric for the forward and reverse bias [13]. This implies the different mechanisms for the MR in the magnetic tunnel junction and the manganite junction. For the former, the MR appears when magnetic field modifies the spin orientation in the top and the bottom magnetic layers. However, it is obvious that the change in spin direction will not affect the junction resistance of LCMO/STON.

It is easy to estimate that the out-of-plane resistances of the LCMO film and the STON substrate are ~0.0001 Ω and 0.01 Ω, respectively, whereas the maximum junction resistance is ~60 kΩ. Therefore, the interfacial potential must play a dominative role in determining the electronic process across the junction. It is the variation of the electronic structure of the LCMO film that affects this potential, which explains the apparent correspondence between the transport behaviours of the LCMO/STON junction and the LCMO film (figures 2 and 4).

As shown in figure 6 and the inset plot, in hole-doped manganites, three of the Mn-3d electrons form the t_{2g} band, and the remaining electrons occupy the e_g band, which is energetically higher than the t_{2g} band [14]. Due to the Jahn–Teller effect, the e_g band further splits into two sub-bands, e_{g1} and e_{g2}, with an energy difference of ~1.2 eV [14, 15]. Two changes can be produced by the metallic transition of the LCMO film. The first one is the expansion of the band width considering that the hopping probability of the e_g electrons will affect the band width according to the double-exchange theory, and the second one is the reduction of the e_{g1}–e_{g2} bandgap due to the weakening of the Jahn–Teller effects [14]. A rough estimate indicates that the bandgap may change from ~0.5 to ~0.1 eV when the LCMO film enters the metallic state. This actually implies a decrease of diffusion potential in the junction,

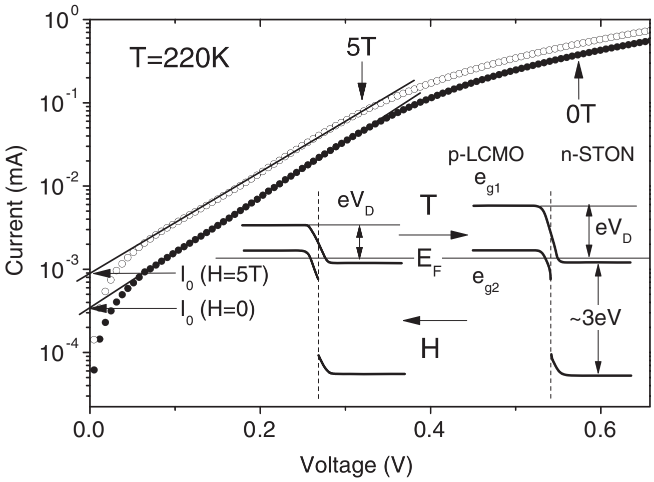

Figure 6. Effects of magnetic field on the current–voltage characteristics of the LCMO/STON junction. Inset is a schematic diagram of the band structure change of the junction against magnetic field or temperature. Solid lines are guides for the eye.

noting the fact that the band structure of STON will remain unaffected across the resistive transition of the LCMO film.

Based on the standard semiconductor theory [16], the forward current–voltage relation for a p–n junction can be described by the empirical equation

$$I = I_0 \exp(eV/mk_BT), \tag{1}$$

where $I_0 \propto \exp(-eV_D/k_BT)$, k_B is the Boltzmann's constant, V_D the diffusion potential, and m a factor describing the ideality of the junction. It is obvious that if the bandgap closes up, or the diffusion potential reduces, at a speed higher than the decrease of temperature, a metal-like conduction of the junction can occur.

In fact, the resistive transition of the junction implies a transition of the depleted LCMO layer near the LCMO/STON interface. This could be due to a proximity effect, i.e., the phase transition in bulk LCMO film induces the phase transition in the depletion layer. This is possible considering the fact that the depletion layer is very thin for the present junction because of the high carrier concentration in STON and LCMO. The similarity of the two transition temperatures of LCMO/STON and LCMO indicates that this effect is quite strong. In this case, the effect of electric bias will be weak because of the determinative role of the strong coupling between the depletion layer and the bulk LCMO film in determining the resistive transition in the former. In the junction with a thick depletion layer, the proximity effect works only after the depletion layer is depressed by electric bias. This implies an electric bias dependence of the resistive transition in the junction. This may be the case studied by Tanaka *et al* [2].

Magnetic field can depress the Jahn–Teller effects by improving the ferromagnetic order of the LCMO film [14]. This actually implies a reduction of junction resistance, which explains the MR of the junction. The largest MR of the junction takes place near T_C, where it is easy for an external field to modify the spin arrangement of the LCMO film. A simple derivation indicates that the MR of the junction will have the form

$$MR(V) = I(0)/I(H) - 1 = f(V)\exp(e\Delta V_D/k_BT) - 1,$$

if equation (1) is applicable, where $f(V) = \exp[(1/m_0 - 1/m_H)\ eV/k_BT]$, ΔV_D is the variation of V_D under magnetic field, and m_0 and m_H are the ideality factors without and with magnetic field, respectively. In the zero bias limit, $f(V)$ is equal to unity. In this case an MR of $\sim-60\%$ requires only a change of ~-0.017 V in V_D. A direct calculation based on the analysis of the log I–V slope, which gives the $I_0[\propto \exp(-eV_D/k_BT)]$ value (the intercept in the I-axis for $V = 0$), confirms that a field of 5 T causes a reduction of the diffusion potential by $\Delta V_D = (k_BT/e)\ln[I_0(H = 0)/I_0(H = 5\ \mathrm{T})] \approx -0.018$ V at $T = 220$ K (figure 6). This result is consistent with the above analysis.

From the slope of the log I–V curves in figure 6, the ideality factor is 3.42 for $H = 0$ and 3.7 for $H = 5$ T. For a typical p–n junction, m takes a value between 1 and 2. The large m of our junction could be a consequence of the high doping level in LCMO and STON. As Sze [16] has pointed out, m is very close to unity for a low doping level and deviates substantially from unity when the doping level is high. In the depletion layer of LCMO, carriers are strongly localized because of the presence of Jahn–Teller effects, lattice strain, and structure defects such as anion or cation vacancies. Applied field can depress the Jahn–Teller effects, resulting in an increase of the concentration of the effective charge carriers. This may explain the increase of m under magnetic field. By substituting the ideality factor m of 0 and 5 T into the above equation for MR(V), the bias dependence of MR can be calculated. The inset of figure 5 shows the calculated MR–V curve (solid line) at 220 K, which is very close to the measured results when V_{bias} is below 0.4 V.

The MR dependence on the reverse bias cannot be well explained yet. If the junction is completely ideal, the reverse current will saturate at $-I_0$ and the MR should be nearly independent of electric bias. However, for the LCMO/STON, the reverse current increases with bias without saturation (figure 3). The accelerated increase of the reverse current with bias may be caused by the large leakage current due to, for example, charge tunnelling, interface defects and the generation–recombination of charge carriers in the depletion region. This makes the MR behaviour for the reverse bias much more complex and it cannot be expressed using a simple equation such as that for the forward bias.

It is obvious that the transport behaviours of the LCMO/STON junction are significantly different from those of the LCMO film. The resistivity of the junction can be tuned by not only magnetic field but also electric field. This feature can be used to design devices working under different conditions. For example, a sensor with different sensitivity to magnetic field can be obtained by adjusting bias current. The compensation of the effects of increasing bias current by decreasing magnetic field makes the junction resistance essentially independent of electric bias, which is useful when significant change in junction resistance is undesired.

4. Summary

In summary, we studied the magnetic/electric field effects for a LCMO/STON junction. The independence of resistive transition on electric bias may imply that the magnetism of the LCMO is not modified by the electric field. The transport of the junction can be strongly modulated by an external magnetic field, which shifts the resistive transition to a high temperature and produces a pronounced negative MR which is strongly dependent on the electric bias. Based on the analysis with conventional semiconductor theory, these behaviours can be qualitatively understood by assuming the change of the band structure of the junction with temperature, electric bias and magnetic field.

Acknowledgments

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