Transport and magnetoresistance effect in an oxygen-deficient $SrTiO_3/La_{0.67}Sr_{0.33}MnO_3$ heterojunction*

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An oxygen-deficient $SrTiO_3/La_{0.67}Sr_{0.33}MnO_3$ heterojunction is fabricated on an $SrTiO_3$ (001) substrate by a pulsed laser deposition method. The electrical characteristics of the heterojunction are studied systematically in a temperature range from 80 K to 300 K. The transport mechanism follows $I \propto \exp(eV/nkT)$ under small forward bias, while it becomes space charge limited and follows $I \propto V^{m(T)}$ with $1.49 < m < 1.99$ under high bias. Such a heterojunction also exhibits magnetoresistance (MR) effect. The absolute value of negative MR monotonically increases with temperature decreasing and reaches 26.7% at 80 K under $H = 0.7$ T. Various factors, such as strain and oxygen deficiency play dominant roles in the characteristics.

Keywords: semiconductors, multilayer structure, electrical properties, magnetoresistance

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1. Introduction

Strontium titanate ($SrTiO_3$-STO) is an attractive perovskite dielectric material which has a wide range of applications for its desirable structure and properties.[1–6] The electrical properties of STO can be changed from insulator to metallic conductivity through increasing oxygen vacancies[2–4] or impurity doping.[5,6] Recently, we noted that most of the previous studies focused on the doped $SrTiO_3$ and manganite oxides ($A_{1-x}B_xMnO_3$, A = La, Pr, B = Ca, Sr, and Ba),[7–10] $SrTiO_{3-\delta}$ and silicon.[11] The transport mechanism between $SrTiO_{3-\delta}$ and the doped manganite oxides has not yet been reported on. However, these results are important for next generation complementary metal–oxide–semiconductor devices. Oxygen vacancies are the most common defects, and exist in almost all oxide thin films.[12] The oxygen-deficient $SrTiO_{3-\delta}$ is an n-type semiconductor, and the $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) displays a rich phase diagram as a function of temperature, magnetic field, and shows ferromagnetic metallic with a metal–insulator transition.[13] The carrier concentration in the heterojunction system comprised of $SrTiO_{3-\delta}$ and $La_{0.67}Sr_{0.33}MnO_3$ could be modulated by applying the external bias and magnetic field.

In the present work, we design an oxygen-deficient $SrTiO_3$/LSMO heterojunction by a pulsed laser deposition (PLD) method, and carefully investigate the transport properties at different temperatures and magnetic fields. The transport mechanism and magnetoresistance effect are discussed in detail.

2. Experiment

For this study, the pure $SrTiO_3$ target was prepared by conventional mixed–oxide solid state reaction technique, and the $La_{0.67}Sr_{0.33}MnO_3$ target was prepared by sol–gel process with analytically pure oxides powder. The $SrTiO_{3-\delta}$/LSMO heterojunction was successively deposited by the PLD method with a KrF (λ = 248 nm) laser. The bottom layer $La_{0.67}Sr_{0.33}MnO_3$ (with a thickness of about 106 nm) was grown at 750 °C on the $SrTiO_3$ (001) substrate at an oxygen pressure of 0.5 Pa, and annealed under a flow of oxygen in order to reduce the oxygen-deficient. Then the $SrTiO_{3-\delta}$ layer (with a thickness of about 126 nm) was deposited quickly at the same substrate temperature and an oxygen partial pressure of 5×10^{-4} Pa.

The X-ray diffraction (XRD) patterns were measured by grazing incidence XRD with Göbel Mirror (RigakuD/max-2400, Cu K_α radiation). Electrical propieties were measured using Keithley 2400 SourceMeter. The In electrodes were placed on the surfaces of the STO and LSMO, forming Ohmic contacts. The schematic diagram of the heterostructure is shown in Fig. 1. The temperature-dependent I–V characteristics were investigated in a temperature range from 80 K to 300 K. To study the magnetoresistance (MR) effect, a magnetic field was provided by an ordinary electromagnet, which was perpendicularly applied to the heterostructure.

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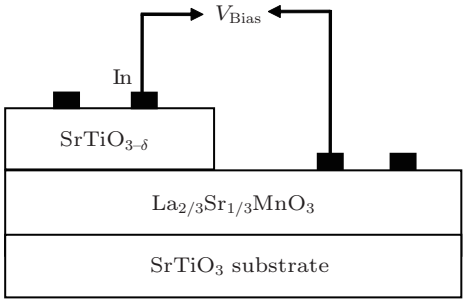


Fig. 1. Schematic diagram of the $SrTiO_{3-\delta}$/LSMO heterostructure.

3. Results and discussion

The $SrTiO_{3-\delta}$/LSMO heterostructure is characterized by X-ray diffraction and shown in Fig. 2. The adjacent double diffraction peaks of the junction for each order indicate that the grown films have good crystallized structures and each of them has an orientation with the c axis perpendicular to the substrate surface. Ohmic contacts were prepared by evaporating In electrodes on surfaces, which are shown in the inset of Fig. 2.

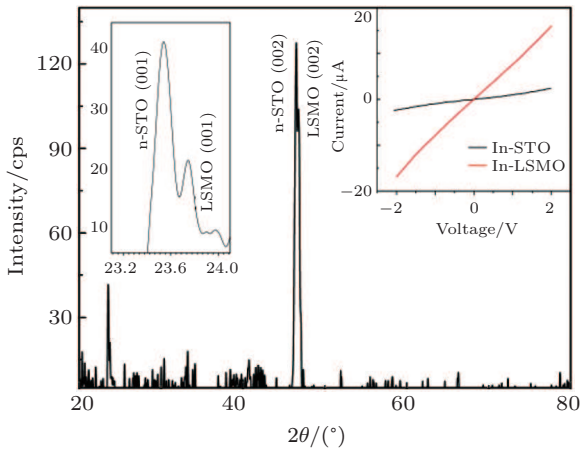


Fig. 2. (color online) XRD pattern of the heterojunction. The inset shows the Ohmic contacts prepared by evaporating In electrodes.

Figure 3 shows temperature dependences of LSMO and STO resistivity. As temperature decreases, the resistivity of STO increases slowly and then very quickly at temperatures lower than 150 K, and it has semi-conductive transport characteristic. Previous studies also suggested that oxygen content has a great influence on magnetic and transport properties of LSMO.

The current–voltage (I–V) characteristics across the $SrTiO_{3-\delta}$/LSMO junction are asymmetric, which indicates that this junction exhibits a visible rectifying behavior as shown in Fig. 4. It is clearly noticed that the diffusion potential ($V_{\rm D}$) decreases almost linearly with the increase of temperature. The $V_{\rm D}$ is in a range from 0.737 V (80 K) to 0.336 V (300 K). Similar characteristics are observed in LSMO/NSTO junction.[14]

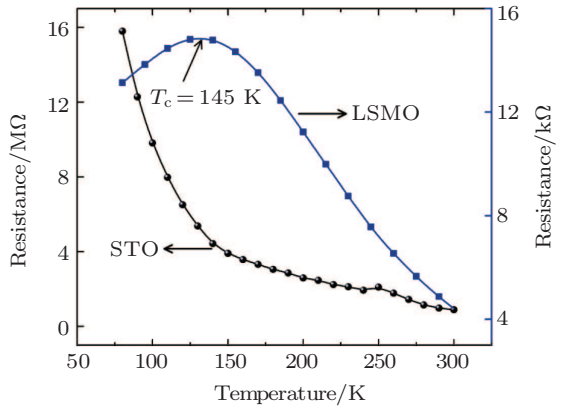


Fig. 3. (color online) Typical temperature dependences of resistivity of LSMO and STO.

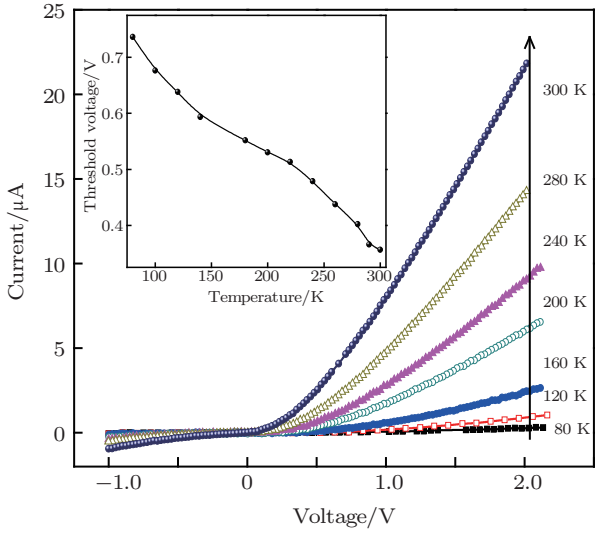


Fig. 4. (color online) Temperature dependences of current–voltage (I–V) curves of the heterojunction, with the inset showing temperature dependence of V_D.

To explain the above phenomena, we invoked the band structure of the STO/LSMO heterojunction, which is constructed by Anderson model.[15] It can be understood that the depletion layer in p–n junction becomes thinner with the increase of temperature due to thermal diffusion. In addition, the diffusion potential should be dominated by the carrier behavior of the p- and n-type compositions and the band gap of p-type semiconductor.[16] In the hole-doped manganite, the $e_g\uparrow$–$e_g\downarrow$ band-gap is expected to vary with temperature. When the spins of the Mn^{4+} ions deviate from a fully ferromagnetic alignment, an exactly parallel or antiparallel arrangement between the spins of the e_g electrons and the Mn^{4+} ions is impossible. This leads to a reduction in energy cost for the e_g electron to reverse its direction. Therefore, with the increase in temperature, the energy gap between e_g bands decreases. As a result, the diffusion potential decreases with temperature increasing.

For a deep understanding of the experimental results, considering the effect of the interface state, such as carrier emission, recombination, and tunneling at the interface, the

current increases exponentially following the standard diode equation[17]

$$I \propto \exp\left(\frac{eV}{nkT}\right), \tag{1}$$

where V is the bias forward voltage, k is the Boltzmann constant, and T is the absolute temperature. The ideality factor n can be evaluated by fitting experiment data using Eq. (1) as shown in Fig. 5(a). We obtain the values of $n = 1.57$ and 34.8 at 300 K in low and high bias voltage regions, respectively.

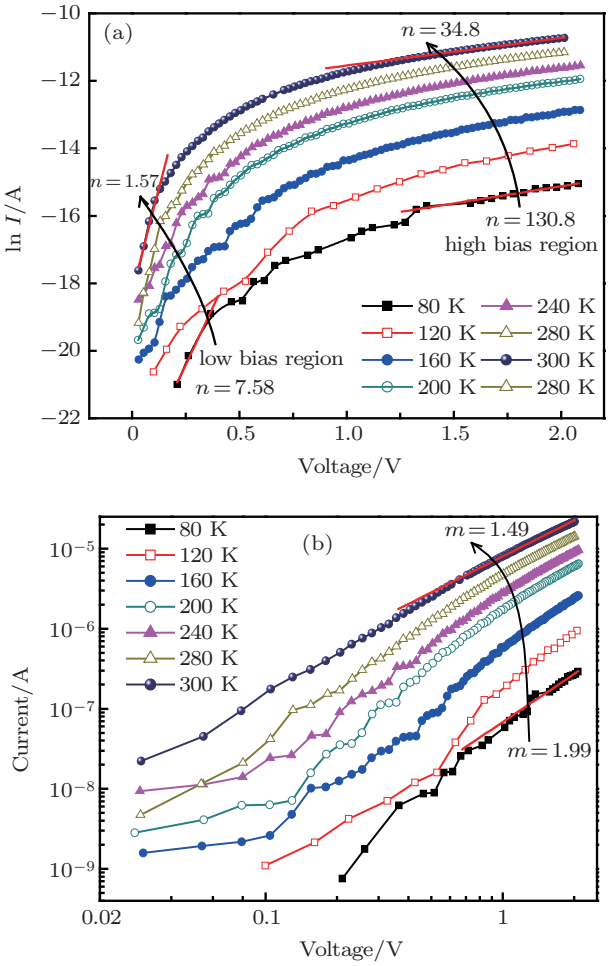


Fig. 5. (color online) (a) The ln(I)–V relation under forward bias in a temperature range from 80 K to 300 K. (b) The variation of current bias voltage.

As is well known, the value of $n = 34.8$ is too large for fitting the Sah–Noyce–Shockley theory.[8] In order to identify the dominating current transport mechanism through the junction under high forward-bias, the I–V curve is plotted in log–log scale, which is shown in Fig. 5(b). We find that the current transport follows the dependence of function $I(V,T) \propto V^{m(T)}$ with the $1.49 < m(T) < 1.99$ in the high bias region, which is described with commonly accepted space charge limited current (SCLC) conduction.[19] As is well known, density, location, and capture across sections of the trapping states have an influence on the characteristic and the magnitude of the space charge limit. For thin films, the key role of lattice distortion has been observed.[11,20] LSMO has an orthorhombic (*Pnma*) crystal structure with $a = 0.552$ nm, $b = 0.556$ nm, and $c = 0.6777$ nm.[21] STO has a tetragonal structure with lattice parameters: $a = b = 0.5522$ nm and $c = 0.3905$ nm.[22] If LSMO grows epitaxially with c axis normal to a–b plane of STO, LSMO films will be slightly compressive strained. Calculated from XRD, the lattice parameter of LSMO is 0.386 nm. This value is slightly smaller than $a/\sqrt{2}$ or $b/\sqrt{2}$, implying that the grown film may be slightly strained. Moreover, the growth conditions, such as oxygen background pressure and the substrate temperature, have great influences on the carrier densities and microstructures of STO and LSMO films.

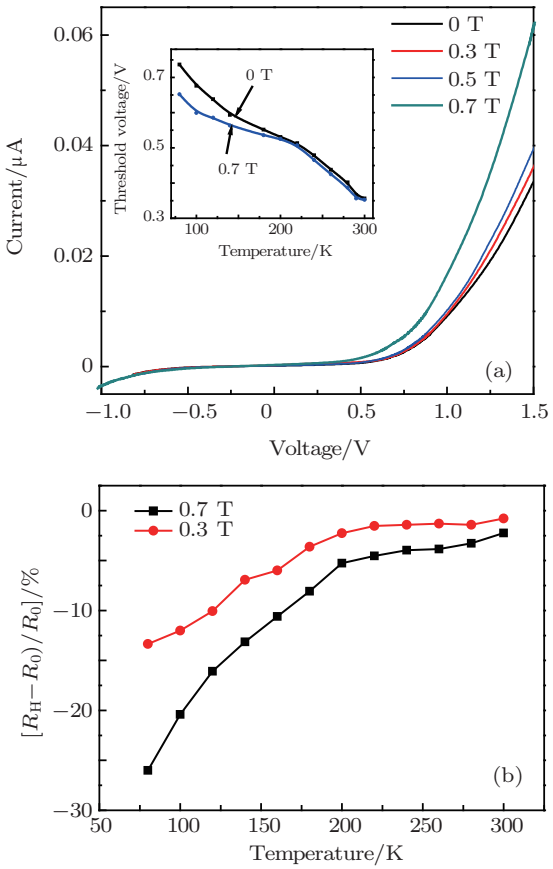


Fig. 6. (color online) (a) The I–V curves of the heterojunction under different applied magnetic fields at $T = 80$ K. The inset shows V_D–T curves under different applied magnetic fields. (b) MR ratio dependences on temperature at $H = 0.3$ T and 0.7 T in zero field.

To investigate the effect of magnetic field on I–V curve, the heterojunction is cooled down to 80 K, and the I–V curve in zero field is measured when temperature is kept unchanged. Then a magnetic field is applied and I–V curve is measured again, and the results are shown in Fig. 6(a). We notice that the applied magnetic field leads to an increase in current at the same voltage and a decrease in diffusion potential as shown in the inset of Fig. 6(a). We define $\mathrm{MR} = \Delta R/R_0 = (R_H - R_0)/R_0$, where R_H is the resistance under the applied magnetic field and R_0 is the resistance without magnetic field. Figure 6(b) shows the negative MR ratios dependent on temperature at $H = 0.3$ T and 0.7 T for the bias voltage (1.0 V).

We can clearly find that the absolute values of the MR are also monotonically reduced. It is reported that the MR of $SrTiO_{3-\delta}$ film is very small and can be seen only under a large magnetic field (>9 T).[23] Hence we can conclude that it is impossible to produce the large MR effect at a low temperature. According to the present scenario, we speculate that the MR phenomenon of our heterojunction is related to oxygen-deficient LSMO thin film and the interface. Oxygen deficiency in LSMO layer leads to a negative electric charge deficiency region which is compensated by reducing Mn^{4+} to keep electrical neutrality. Meanwhile, a large electronic imbalance and local lattice distortion are caused by the oxygen vacancies which are accompanied with inhomogeneous electronic and magnetic phases.[24] Enhanced MR at low temperatures has been found by Li *et al.*[25] because the inhomogeneous electronic and magnetic phases occurred in manganite films, which are sensitive to the external magnetic field. The interface resistance of the heterojunction could be attributed to the lattice mismatch between STO and LSMO.

4. Conclusions

In the present study, a p–n heterojunction is fabricated by depositing $SrTiO_3$ and $La_{0.67}Sr_{0.33}MnO_3$ on $SrTiO_3$ substrates using the PLD method. The asymmetric *I–V* curves show the transport proprieties follow $I \propto \exp(eV/nkT)$ under small forward bias, while they become space charge limited and follow $I \propto V^{m(T)}$ with $1.49 < m < 1.99$ under high bias. This structure also exhibits negative MR effect. The absolute value of MR monotonically increases with temperature decreasing, and it rises up to 26.7% at 80 K under 0.67 T. Various factors, such as strain and oxygen deficiency play dominant roles.

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