Manipulation of reverse bias transport by photocarrier injection in $Pr_{0.7}Ca_{0.3}MnO_{3-\delta}/SiO_2/Si$ heterojunction

2009 J. Phys. D: Appl. Phys. 42 085002

(http://iopscience.iop.org/0022-3727/42/8/085002)

IOP Publishing Journal of Physics D: Applied Physics

J. Phys. D: Appl. Phys. **42** (2009) 085002 (5pp) doi:10.1088/0022-3727/42/8/085002

Manipulation of reverse bias transport by photocarrier injection in $Pr_{0.7}Ca_{0.3}MnO_{3-\delta}/SiO_2/Si$ heterojunction

Z G Sheng, Y P Sun, J M Dai, X B Zhu, W H Song and Z R Yang

Key Laboratory of Materials Physics, Institute of Solid State Physics, Hefei High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

E-mail: ypsun@issp.ac.cn

Received 17 September 2008, in final form 4 March 2009
Published 26 March 2009
Online at stacks.iop.org/JPhysD/42/085002

Abstract

A $Pr_{0.7}Ca_{0.3}MnO_{3-\delta}/SiO_2/Si$ heterojunction with good rectifying property is fabricated. An interesting phenomenon observed in these heterojunctions is that electrical transport under reverse bias is sensitive to light illumination, while that under forward bias is insensitive. The photoinduced resistance ratio can even reach ∼93.8% with a reverse bias $I = 0.04\,\mu A$ and is always over 75% within the whole measured current range as the light power density $P = 0.3\,mW\,cm^{-2}$ at $T = 200\,K$. The observed phenomenon is discussed according to the effect of photocarrier injection to the junction under different direction bias voltages.

(Some figures in this article are in colour only in the electronic version)

Many efforts have been recently devoted to exploring quantum functional properties and verifying new device concepts based on manganese oxides. Tanaka *et al* reported the electrical modulation of double-exchange ferromagnetism in the $La_{0.9}Ba_{0.1}MnO_3$/Nb-doped $SrTiO_3$ p–n junction [1]. Mitra *et al* observed a large positive magnetoresistance (MR) in a $La_{0.7}Ca_{0.3}MnO_3/SrTiO_3/La_{0.7}Ce_{0.3}MnO_3$ tunnel junction [2]. From the point of view of device integration, grown manganites on silicon substrates are very important because silicon is one of the most important substrates in modern semiconductor technology. In order to combine the functional properties of oxides with Si electronics, several manganese oxide films, such as $La_{0.67}Sr_{0.33}MnO_{3-\delta}$ [3], $La_{0.67}Ba_{0.33}MnO_3$ [4] and $La_{0.9}Ca_{0.1}MnO_3$ films [5], were successfully deposited on Si substrates. More recently, a $La_{0.67}Ca_{0.33}MnO_3$/yttrium-stabilized zirconia/Si heterojunction with MR and good rectifying properties was fabricated by Zhang *et al* [6].

As is well known, photoinduced effects, such as photoconductivity and photoinduced metal-to-insulator transition, are especially interesting from the viewpoint of applications. With regard to optical effects on manganite-based heterojunctions, Sun *et al* observed an obvious photovoltaic effect in the $La_{1-x}Pr_xCa_{0.33}MnO_3/SrNb_{0.005}Ti_{0.995}O_3$ p–n junction when the $La_{1-x}Pr_xCa_{0.33}MnO_3$ film in the junction was irradiated by a 532 nm laser pulse with 10 ns duration or a 632.8 nm He–Ne laser [7, 8]. In our previous work, it is also found that there is a photovoltaic effect in $La_{0.7}Ce_{0.3}MnO_3/SrNb_{0.005}Ti_{0.995}O_3$ and the photovoltage can be changed by the applied magnetic fields [9]. Recently, Pardhan and co-workers reported junction characteristics in $SrTiO_3$ or $BaTiO_3$ on p-Si and photocarrier injection effects in $La_{0.7}Sr_{0.3}MnO_3$ on ZnO or n-Si p–n junctions [10, 11]. Up to now, all these previous works were focused on the photoinduced effect on the p–n junction; no study has been reported for the photoinduced effect on manganite-based semiconductor–insulator–semiconductor structure (SIS) junctions. In this paper, we report the photocarrier injection effect in the SIS junction constituted by a $Pr_{0.7}Ca_{0.3}MnO_{3-\delta}/SiO_2/Si$ heterojunction. An interesting phenomenon is observed in this SIS junction, namely, the electrical transport under reverse bias is sensitive to light illumination, while that under forward bias is almost independent of light illumination.

$Pr_{0.7}Ca_{0.3}MnO_{3-\delta}/SiO_2/Si$ heterojunctions used in this experiment were fabricated by growing $Pr_{0.7}Ca_{0.3}MnO_{3-\delta}$ (PCMO) films on heated n-type Si (0 0 1) wafers by the off-axis dc-magnetron sputtering technique with a substrate temperature of 750 °C. Before sputtering, the Si wafers were kept at 750 °C with oxygen pressure of 5 Pa for 20 min to grow SiO_2 on Si. The thickness calibrations of the SiO_2 layer (∼3 nm) were carried out using *ex situ* spectroscopic ellipsometry. The PCMO films were ∼200 nm in thickness measured by a field emission scanning electron microscope (FESEM). The in-plane resistance of the PCMO film was measured by the four-probe method. To provide ohmic contact, Ag electrodes are deposited on the PCMO and Si surface by mask evaporation. The temperature dependence of the resistance of the PCMO film under zero and 5 T magnetic fields measured by the Quantum Design Physical Property Measurement System (PPMS) exhibits semiconductor-like behaviour in the whole measured temperature range and a very small negative MR (not shown here). For the photoinduced effect measurement, the sample was mounted in a vacuum room which was sealed by a double quartz glass window; a He–Ne laser of wavelength $\lambda = 632.8$ nm with variable power density was used to illuminate the PCMO film surface perpendicularly through the window. The magnetization of the sample was measured on a Quantum Design Superconducting Quantum Interference Device (SQUID) MPMS system ($1.9\,K \leqslant T \leqslant 400\,K$, $0\,T \leqslant H \leqslant 5\,T$) and the Curie temperature of the PCMO film is 65 K determined by field-cooled magnetization measurement (not shown here).

The I–V characteristic curves measured (by using a current source) at different temperatures are shown in figure 1. The inset shows a schematic illustration for the current and voltage contact configuration for the I–V measurement with respect to the illuminated region. The positive bias was defined as the current flows through the heterojunction from the PCMO film to the n-type Si substrate. To minimize the heating effect at a low temperature, the measuring current was kept below 1 μA. Sufficient rectifying behaviour was observed in our PCMO/SiO_2/Si junctions. For the sake of clarity, we have plotted the I–V curves at $T = 150, 175, 200, 225$ K only. The SIS junction exhibits excellent rectifying behaviour and high resistance, which implies high quality of the insulator barrier SiO_2. The rectifying behaviour was observed throughout the whole temperature range of our study ($130\,K < T < 300\,K$). Figure 1 shows that the current increases sharply with the forward voltage as the voltage exceeds the diffusion potential (V_d), implying that the forward conductive resistance is small. From figure 1, V_d of the SIS junction is determined to be ∼0.6 V and ∼1.02 V at 200 K and 150 K, respectively. Moreover, the results indicate that V_d decreases with increasing temperature, which is similar to the results of previous works [12, 13]. It can be understood by considering that the forward current is proportional to $\exp(-1/T)$ in SIS junctions which will be discussed below.

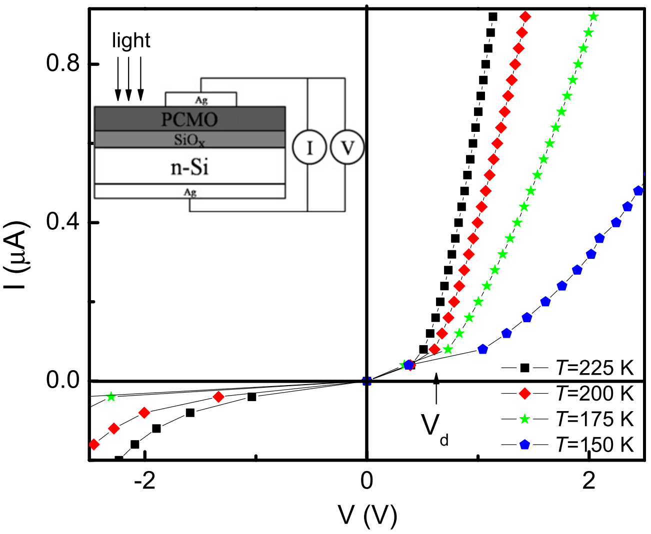


Figure 1. (Colour online) I–V characteristics of the PCMO/SiO_2/Si SIS junction measured at selected temperatures between 150 and 225 K. The inset shows the schematic illustration for the current and voltage contact configuration for I–V measurement with respect to the illuminated region.

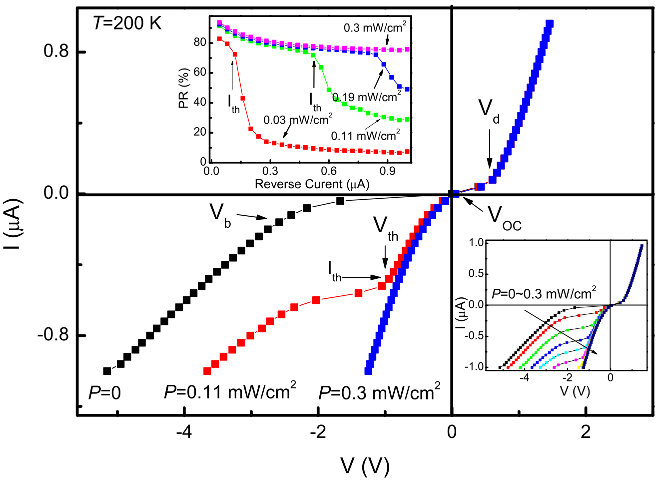


Figure 2. (Colour online) I–V characteristics with and without light illumination of the PCMO/SiO_2/Si SIS junction measured at $T = 200$ K. The upper inset shows the PR as functions of the reverse current bias with selected power density $P = 0.03\,\mathrm{mW\,cm^{-2}}$, $0.11\,\mathrm{mW\,cm^{-2}}$, $0.19\,\mathrm{mW\,cm^{-2}}$ and $0.3\,\mathrm{mW\,cm^{-2}}$, respectively, at 200 K. The right lower inset presents the I–V characteristics with different laser power densities at 200 K.

To test whether the observed rectifying behaviour in the PCMO/SiO_2/Si heterojunction can be influenced by the illumination of light, the PCMO film of the heterojunction is illuminated by a He–Ne laser with different light power densities. Typical I–V curves at 200 K are shown in figure 2. It is observed that the I–V curve shows good rectifying behaviour with $V_d = 0.6$ V and breakdown voltage $V_b = -2.58$ V without light illumination. However, as a very weak light of $0.3\,\mathrm{mW\,cm^{-2}}$ illuminates the junction, the I–V curve of the SIS junction exhibits a remarkable change. The change includes two aspects. The first one is that the I–V curve with light illumination does not pass through the point of origin of coordinates. That is to say there exists a photovoltaic effect in this SIS junction with open-circuit voltage $V_{OC} = 0.06$ V and short-circuit current $I_{SC} = 0.01\,\mu$A at a temperature of 200 K with a light power of $0.3\,\mathrm{mW\,cm^{-2}}$. The second one is that the photoinduced effects on electrical transport are different under forward and reverse bias. As shown in figure 2, the I–V

curves under forward bias hardly change and V_d does not shift with the light illumination, meaning that the electrical transport under forward bias is insensitive to the light illumination. In contrast, for the reverse bias condition, the I–V curves show a very sensitive characteristic to the light illumination. As seen from figure 2, the V_b of the heterojunction decreases sharply from −2.58 V down to −0.37 V as a weak power light of $P = 0.3\,\mathrm{mW\,cm^{-2}}$ is irradiated on the junction at 200 K. In addition, as the light power density is reduced further, the I–V curve of the junction under reverse bias manifests a complex shape. For example, for $P = 0.11\,\mathrm{mW\,cm^{-2}}$, the shape of the I–V curve is similar to that of the I–V curve for $P \geqslant 0.3\,\mathrm{mW\,cm^{-2}}$ as the reverse bias voltage is below a threshold V_{th}, i.e. $V < V_{th}$, while, as $V > V_{th}$, the shape of the I–V curve behaves similarly to that of the I–V curve without light illumination as shown in the main panel of figure 2. The similar I–V curve variation of the junction under light illumination with different power densities at $T = 200$ K is shown in the right lower inset of figure 2. Moreover, the I–V curve variation can be repeatedly observed in the temperature range of 125–300 K (not shown here).

To analyse the variation of the junction resistance R_j under light illumination quantitatively, we defined the junction resistance R_j as V/I, and the upper inset of figure 2 shows the photoinduced resistance (PR) (defined as $\lfloor R_j(0) - R_j(L)\rfloor / R_j(0)$) as functions of the reverse current bias with selected power density $P = 0.03\,\mathrm{mW\,cm^{-2}}$, $0.11\,\mathrm{mW\,cm^{-2}}$, $0.19\,\mathrm{mW\,cm^{-2}}$ and $0.3\,\mathrm{mW\,cm^{-2}}$, respectively, at 200 K. It displays that the PR ratio increases with increasing light power density and drops sharply as the current bias exceeds the threshold reverse current I_{th} at a fixed temperature. Moreover, the PR ratio is as large as 93.8% with $I = 0.04\,\mu$A and is always over 75% within the whole measured current range as the light power density $P = 0.3\,\mathrm{mW\,cm^{-2}}$ at $T = 200$ K. This large PR under reverse bias may be of worth in potential applications of new generation of data storage and sensing devices.

In order to test whether the observed variation of the I–V curve induced by light illumination is universal to similar manganite-based heterojunctions, we also perform the same measurements in $La_{0.67}Sr_{0.33}MnO_{3-\delta}/SiO_2/Si$ heterojunctions. The results show that the above similar phenomenon can also be observed, implying that the manipulation of reverse electrical transport by light illumination may be a common feature of manganite/SiO_2/Si junctions.

As for the possible origin of the observed phenomenon in the studied junction, one possible hypothesis is that change in the magnetic disorder of the junction is caused by light illumination because the studied junction is of magnetic characteristic. To verify this hypothesis, the I–V characteristics of the heterojunction under zero and 5 T magnetic fields in the temperature range 125–325 K were measured by PPMS. Almost no variation of the I–V curves under the magnetic field is observed (not shown here), meaning that the suppression of magnetic disorder of the heterojunction is not the primary origin of the photoinduced variation of the I–V curves. That is to say, the photoinduced effect observed is independent of the change in the magnetic state of the heterojunction.

Different photoinduced effects of I–V characteristics under forward and reverse bias may originate from different electrical transport mechanisms. In the framework of traditional semiconductor theory [14], the ideal current–voltage relation of diodes is given by

$$J = \left[\frac{qD_p p_{no}}{L_p} + \frac{qD_n n_{po}}{L_n}\right] \times [\exp(qV/k_B T) - 1], \qquad (1)$$

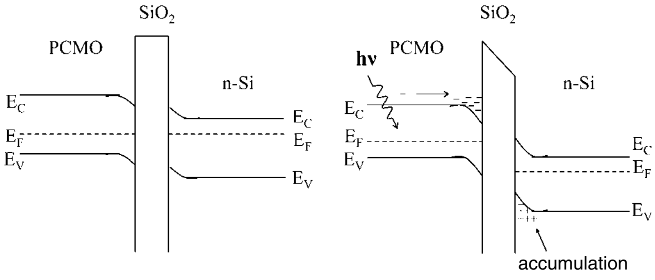
where D_p and D_n are diffusion coefficients of holes and electrons respectively, L_p and L_n are diffusion lengths of holes and electrons, respectively, p_{no} and n_{po} are the concentrations of holes in the depletion layer on the n-type Si side and of electrons in the depletion layer on p-type PCMO, respectively, and k_B is the Boltzmann constant. In the forward direction (positive bias on PCMO), for $V \gg k_B T/q$ and small concentration of p_{no} and n_{po} near the insulator barrier, the forward current–voltage relation can be given by

$$J_F \propto \exp\lfloor -(E_g - qV)/k_B T\rfloor, \qquad (2)$$

where J_F is the forward direction current density, E_g presents the energy-band gap and V is an applied bias voltage. Based on equation (2), it can be deduced that the effect on electrical transport under forward bias by light illumination is negligible because the photoexcited carriers driven by the applied voltage have little contribution to enhance the concentration of minority carriers p_{no} and n_{po} near the insulator barrier. As for the reverse direction (negative bias on PCMO) for $\exp(qV/k_B T) \ll 1$ ($V < 0$), the reverse current can be written by

$$|J_R| \approx J_s \equiv \frac{qD_p p_{no}}{L_p} + \frac{qD_n n_{po}}{L_n}, \qquad (3)$$

where J_R is the reverse direction current density and J_s is the saturation current density. Without light illumination, the reverse current density in the ideal junction increases with a small voltage bias and keeps a constant value J_s until breakdown of the junction. Moreover, for an artificial SIS junction, the surface space charge region contributes to reverse electrical transport of the junction. As $V = 0$, the band of junction remains constant in the semiconductor as shown in figure 3(*a*). However, the top of the valence band of PCMO bends downwards and the band of n-type Si bends upwards closer to the Fermi level when a reverse bias voltage is applied on the junction as shown in figure 3(*b*). Since the carrier density depends exponentially on the energy difference ($E_F - E_V$), this band bending causes an accumulation of minority carriers (holes in n-type Si and electrons in PCMO) near the semiconductor surface. This is the so called 'accumulation' case and the accumulation of minority carriers in the surface space charge region is helpful in enhancing the reverse current under a small voltage bias. It can also be understood from equation (3) that the reverse current is proportional to the minority carrier density at the interface of junctions. Therefore, one can anticipate that the tunnelling current will



(a) V=0 (b) V<0

Figure 3. A possible energy-band diagram for PCMO/SiO$_2$/Si SIS junctions with bias voltage $V = 0$ (*a*) and $V < 0$ (*b*).

increase with the accumulation of minority carriers near the semiconductor surface. However, with increasing reverse voltage bias, the energy gap between the two electrodes of the heterojunction $E_g - qV$ ($V < 0$) would increase and the tunnelling of carriers near the insulator barrier becomes more difficult. Furthermore, the state of the junction will change from the 'accumulation' case to 'depletion' and 'inversion' cases in turn with increasing reverse bias voltage. That is to say, the increasing reverse bias would hinder the carriers passing through the barrier then cause the decreasing of reverse current. Interestingly, the injection of photocarriers will influence this process. Based on the study of the optical spectrum [15] and the photoconductivity of manganites [3], electron–hole pairs in PCMO/SiO$_2$/Si can be easily generated by light with a photon energy of 1.96 eV in our experiments. Moreover, the minority carriers generated by light in the electrode will be driven to the interface of the junction by the reverse bias voltage, while the majority carriers will be driven to the opposite direction as shown in figure 3(*b*). With the equilibrium condition, the minority carrier concentration at the edge of the depletion region is only considered to be related to the bias voltage. In our case, the situation is quite different in that there are many extra carriers caused by light illumination existing at the edge of the depletion layer. Thus, the extra carriers contribute to the accumulation process under reverse bias (generally, it is called the inversion process in traditional semiconductor junctions). That is to say the application of light will accelerate the 'accumulation' process under the reverse bias voltage and then increase the reverse current. In this regard, there is a competition of effects on the reverse current between the increase in the reverse voltage bias and the acceleration of the accumulation process by light illumination. This is in accordance with our observations as shown in figure 2. Based on this viewpoint, one can easily deduce that the threshold voltage V_{th} will increase with increasing light power densities. Actually, it has been observed in our experiments as shown in the right lower inset of figure 2. By comparing the photoinduced reverse transport at different temperatures, we found that the threshold voltage V_{th} increased quickly with the decrease in temperatures with the same laser power density. The large temperature dependence of V_{th} implies a large temperature dependence of the 'accumulation process' of minority carriers. It is well known that the band gap of silicon is insensitive to the temperature. Therefore, it is reasonable for us to attribute the large dependence of the accumulation process of minority carriers to the manganite films. Actually, the large temperature dependence of the light induced extra carriers in manganites has been proved by many experiments [8, 9]. For our work, we only give a possible explanation for the observed photoinduced effect on the reverse electrical transport of the Pr$_{0.7}$Ca$_{0.3}$MnO$_{3-\delta}$/SiO$_2$/Si heterojunction. A comprehensive understanding of the present observation requires a full knowledge of the band structure of the manganite-based heterojunctions.

In summary, we fabricated a Pr$_{0.7}$Ca$_{0.3}$MnO$_{3-\delta}$/SiO$_2$/Si heterojunction and the junction has good rectifying characteristic within the whole measured temperature range. Moreover, it is found that the electrical transport under forward bias is insensitive to light illumination, while that under reverse bias is sensitive. Similar results have been found in La$_{0.67}$Sr$_{0.33}$MnO$_{3-\delta}$/SiO$_2$/Si heterojunctions. The PR ratio can even reach ~93.8% with reverse current bias $I = 0.04\,\mu$A and is always over 75% within the whole measured current range as the light power density $P = 0.3$ mW cm^{-2} and $T = 200$ K. The observed phenomenon is discussed according to the effect of photocarrier injection to the SIS junction under different direction bias voltages. Clearly, this work reveals the possibility of controlling the electrical transport of manganite-based SIS junctions by light illumination, which is important for the practical application of manganite heterojunctions.

Acknowledgments

The authors would like to thank Dr Liqiang Zhu and Dr Jinping Zhang for technical assistance in measurement in spectroscopic ellipsometry. This work is supported by the National Natural Science Foundation of China under Contract No 10774146 and the Fund of Chinese Academy of Sciences for Excellent Graduates.

References

[1] Tanaka H, Zhang J and Kawai T 2002 *Phys. Rev. Lett.* **88** 027204
[2] Mitra C, Raychaudhun P, Dorr K, Muller K H, Schultz L, Oppeneer P M and Wirth S 2003 *Phys. Rev. Lett.* **90** 017202
[3] Sheng Z G, Sun Y P, Dai J M and Song W H 2006 *Appl. Phys. Lett.* **89** 082503
[4] Pradhan A K, Mohanty S, Zhang K, Dadson J B, Jackson E M, Hunter D, Rakhimov R R, Loutts G B, Zhang J and Sellmyer D J 2005 *Appl. Phys. Lett.* **86** 012503
[5] Lang P L, Zhao Y G, Yang B, Zhang X L, Li J, Wang P and Zheng D N 2005 *Appl. Phys. Lett.* **87** 053502
[6] Zhang P X, Lee W K and Zhang G Y 2002 *Appl. Phys. Lett.* **81** 4026
[7] Sun J R, Xiong C M, Shen B G, Wang P Y and Weng Y X 2004 *Appl. Phys. Lett.* **84** 2611
[8] Sun J R, Shen B G, Sheng Z G and Sun Y P 2004 *Appl. Phys. Lett.* **85** 3375
[9] Sheng Z G, Zhao B C, Song W H, Sun Y P, Sun J R and Shen B G 2005 *Appl. Phys. Lett.* **87** 242501
[10] Hunter D, Lord K, Williams T M, Zhang K, Pradhan A K, Sahu D R and Huang J L 2006 *Appl. Phys. Lett.* **89** 092102
[11] Lord K, Hunter D, Williams T M and Pradhan A K 2006 *Appl. Phys. Lett.* **89** 052116

[12] Hu F X, Gao J, Sun J R and Shen B G 2003 *Appl. Phys. Lett.* **83** 1869

[13] Sheng Z G, Sun Y P, Zhu X B, Dai J M, Song W H, Yang Z R, Hu L and Zhang R R 2008 *J. Phys. D: Appl. Phys.* **41** 135008

[14] Sze S M 1981 *Physics of Semiconductor Devices* 2nd edn (New York: Wiley)

[15] Saitoh T, Bocquet A E, Mizokawa T, Namatame H, Fujimori A, Abbate M, Takeda Y and Takano M 1995 *Phys. Rev.* B **51** 13942