Photoelectric Characteristic of $La_{0.9}Sr_{0.1}MnO_3/SrNb_{0.01}Ti_{0.99}O_3$ p–n Heterojunctions *

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(Received 28 December 2005)

Good rectifying current–voltage characteristics and nanosecond photoelectric effects are observed in the p–n heterojunctions of $La_{0.9}Sr_{0.1}MnO_3/SrNb_{0.01}Ti_{0.99}O_3$ fabricated by laser molecular beam epitaxy. The rise time is about 26 ns and the full width at half maximum is about 125 ns for the open-circuit photovoltaic pulses when the $La_{0.9}Sr_{0.1}MnO_3$ film in the heterojunction is irradiated by a laser operated at wavelength 308 nm with pulse duration of about 25 ns. A qualitative explanation is presented, based on an analysis of the photoelectric effect of p–n heterojunction.

PACS: 75. 47. Lx, 85. 30. Kk, 72. 40. +w

Great effort has been devoted to investigation of perovskite oxides because of their interesting properties including ferromagnetism, antiferromagnetis, metal-insulator transition, high-T_c superconductivity, colossal magnetoresistance, nonlinear optics and so on, depending on the carrier concentration due to strong coupling among the spin, charge, and orbital degrees of freedom.[1−4] Perovskite oxides can be changed from insulator to semiconductor then to conductor by reducing or doping impurity ion. In particular, in Mn perovskite oxides, complex interplay between magnetic and electronic properties depending on the behaviour of equilibrium charge carriers has attracted a great deal of attention.[5,6] However, there have been only a few studies on dynamics of nonequilibrium carriers of manganese oxides, excited by short laser pulses. In the previous reports, Zhang *et al.*[7] found laser-induced thermoelectric voltages in $La_{1-x}Ca_xMnO_3$ films with a photovoltaic pulse of about 2 μs full width at half maximum (FWHM) when the film was irradiated by a 1064-nm laser pulse with duration 15 ns. Sun *et al.*[8] reported the photovoltaic effect in $La_{0.29}Pr_{0.38}Ca_{0.33}MnO_3/SrNb_{0.005}Ti_{0.995}O_3$ p–n heterojunction with a photovoltaic pulse of about 8 ms FWHM when the junction was irradiated by a 532-nm laser pulse with pulse duration 10 ns.

In this Letter, we report a nanosecond-order photoelectric effect in $La_{0.9}Sr_{0.1}MnO_3/SrNb_{0.01}Ti_{0.99}O_3$ (LSMO/SNTO) p–n heterojunctions, and the photovoltaic pulse appears with a rise time of 26 ns and with FWHM of about 125 ns when the LSMO film in the heterojunction is irradiated by a laser of 25-ns pulse duration and 308-nm wavelength. Based on the semiconductor theory, we discuss the mechanism of movements of photo-created carriers for LSMO/SNTO p–n heterojunctions irradiated by the pulsed laser.

To fabricate the oxide p–n heterojunctions, we chose Sr-doped manganites, i.e. $La_{0.9}Sr_{0.1}MnO_3$ (LSMO), as the p-type semiconductor, and Nb-doped strontium titanate, i.e. $SrNb_{0.01}Ti_{0.99}O_3$ (SNTO), as the n-type substrates. To obtain the best p–n interface, a computer-controlled laser molecular-beam epitaxy (MBE) was used to fabricate the p–n heterojunctions.[9] The LSMO films were layer-by-layer epitaxially grown on the SNTO substrates by the laser MBE.[10,11]

The thicknesses of the LSMO film and the SNTO substrates are 800 nm and 0.5 mm, respectively. The size of the samples for the measurements of optical properities is $5 \times 6\,mm^2$, which is assumed to be an active area. The indium electrodes were placed on a corner of the LSMO film surface and SNTO surface as shown in the insets of Figs. 2 and 3. The photovoltaic signals were measured by a 500-MHz oscilloscope (Tektronix TDS3052B).

Figure 1(a) shows a typical cross-sectional high-resolution transmission electron microscopic (HRTEM) image of an LSMO/SNTO interface. The HRTEM image shows that the interface is perfectly oriented, and the measured orientation relation is SNTO (001)//LSMO (001), and SNTO [100]//LSMO [100].

* Project Supported by the National Natural Science Foundation of China (Grant No 10334070) and by the National Key Basic Research & Development Programme of China (Grant No 2004CB619004).

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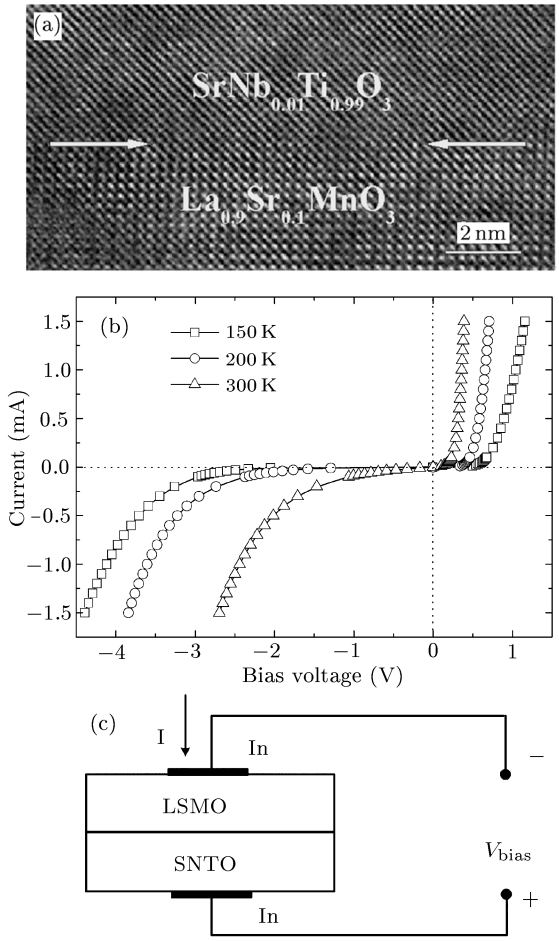

Fig. 1. (a) Cross-sectional HRTEM structural image of the interface in an LSMO/SNTO p–n junction; (b) the I–V curves of the p–n junction at various temperatures; (c) the illustration of the p–n junction for electrical measurement.

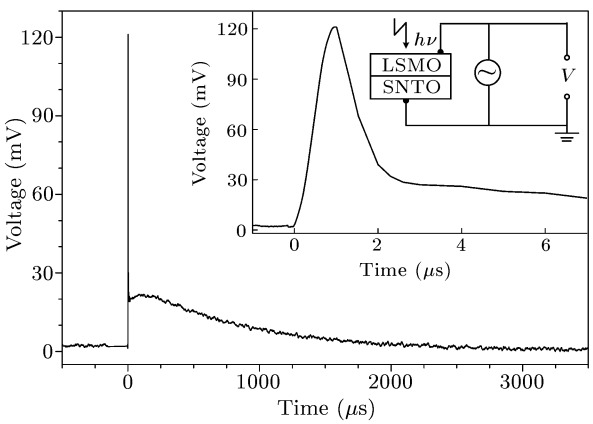

Fig. 2. Variation of the open-circuit photovoltage with time excited by a 308-nm excimer laser beam on the LSMO film of the p–n junction. The zoom of the sharp rise and the schematic circuit of the sample measurement are shown in the inset.

The current–voltage (I–V) characteristic of the LSMO/SNTO p–n heterojunction was measured with a pulse-modulated current source. To avoid Joule heating, the measurement current was kept below 1.5 mA. Figure 1(b) shows the I–V curves of an LSMO/SNTO p–n junction at various temperatures, and a schematic illustration for the measurement is also shown in Fig. 1(c). The heterojunction exhibits good nonlinear and rectifying I–V characteristics. If the current through the p–n heterojunction is 0.1 mA, the positive bias voltages $V_{\rm bias}$ are 0.25 V, 0.45 V and 0.65 V at the temperature of 300 K, 200 K and 150 K, respectively. These values can be taken as the switch voltages of the diode at the above temperatures.

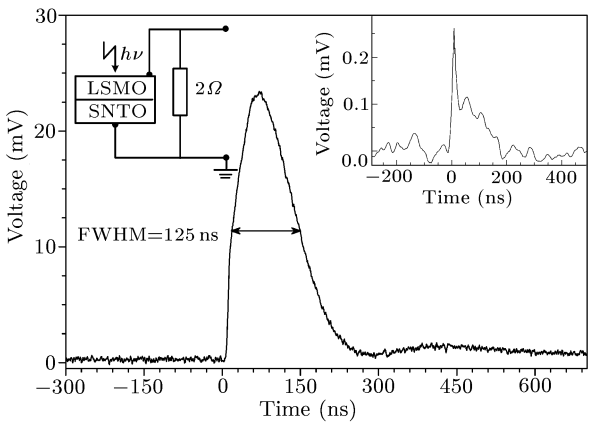

Fig. 3. Transient response of the photovoltage under the same condition as Fig. 2, except a 2-Ω resistance connected in parallel across the p–n junction. Inset displays a schematic circuit of the sample measurement and the transient response of the photovoltage illuminated on the surface of the SNTO substrate of the p–n junction by a 308-nm laser pulse.

The optical characteristics of LSMO/SNTO p–n heterojunctions were investigated using a 308-nm excimer laser (pulse width ∼ 25 ns). An open-circuit photovoltage pulse to the p–n heterojunction was observed between the two electrodes when the surface of the LSMO film was irradiated by a 0.5-mJ·mm^{-2} laser pulse. Figure 2 shows the photovoltaic pulse as a function of time. The photovoltaic sensitivity is 80 mV·mJ^{-1}. It should be noted that there is a sharp rise of the photovoltaic pulse at the beginning and then the signal gradually decreases, corresponding to a ∼2 ms decay process. The inset in Fig. 2 displays the zoom of the sharp rise and the FWHM is about 1.2 μs, accordingly. Generally, there is a junction capacitance in the LSMO/SNTO p–n heterojunction as well as the impedance of the measurement system. In this system, the junction capacitance is about 1.2 nF at 500 MHz for the sample, and the input impedance of the oscilloscope is 1 MΩ. Thus the discharge time constant coming from the RC circuit of the measurement system is of the order of about ms, which is comparable with the ∼2 ms photovoltaic pulse in Fig. 2. In order to reduce the effect of the measurement system, a 2 Ω resistance was connected in parallel with the p–n junction as shown in the inset of Fig. 3. Under

the same experimental conditions as shown in Fig. 2, the rise time dramatically reduces to 26 ns and the FWHM also reduces to 125 ns for the photovoltaic pulse as shown in Fig. 3. The lifetime of nonequilibrium carriers was estimated to be about 65 ns by fitting the exponential decay time, photovoltaic signal $V_{oc} \propto \exp(-t/\tau)$, as shown in Fig. 3. It seems that there is a more realistic process of laser-induced voltage in the p–n heterojunction.

It is known that $SrTiO_3$ is a very stable compound with a band gap of 3.2 eV, which absorbs photons with a wavelength less than 390 nm, insensitive to visible lights.[12,13] The absorption coefficient is as large as $\sim 10^5\,\mathrm{cm}^{-1}$, because of the nearly direct band gap.[13] For better understanding the photovoltaic effects of the heterojunctions, the absorption spectra of the LSMO/SNTO p–n junction and the SNTO substrate were measured, as shown in Fig. 4. It exhibits spectra from 270 nm (4.6 eV) to 620 nm (2 eV). From the measurement of SNTO in Fig. 4, we can conclude that the band gap of the SNTO substrate is much narrower than that of $SrTiO_3$ due to Nb doping, which is consistent with the previous reports.[14–16] The coincidence of the absorption spectra in the range around 308 nm for the LSMO/SNTO p–n heterojunction and the SNTO substrate shows that photons are mostly absorbed by the LSMO film and partially pass through the LSMO layer to the SNTO substrate. In other words, photon absorption occurs not only in the LSMO layer but also in the SNTO material.

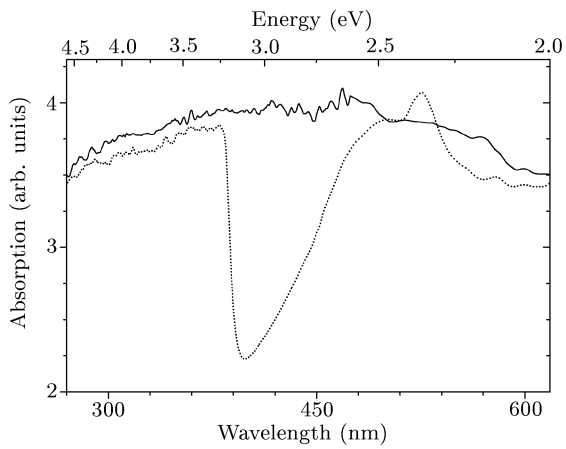

Fig. 4. Absorption spectrum of the SNTO substrate (dotted line) and the LSMO/SNTO p–n junction (solid line).

The schematic energy diagram of the p–n heterojunction to explain the observed photovoltaic effect is shown in Fig. 5. The SNTO exhibits metal-like behaviour with a band gap much smaller than the band gap of $SrTiO_3$ (3.2 eV). While LSMO has a band gap of about 1.0 eV, which shows semiconductor behaviour. The hole concentration of the LSMO film is $1.19 \times 10^{18}\,\mathrm{cm}^{-3}$, and the electron concentration of the SNTO is $1.63 \times 10^{20}\,\mathrm{cm}^{-3}$ at room temperature by Hall measurement. When LSMO is connected with SNTO, electrons from n-type SNTO diffuse into the adjacent p-type LSMO, and holes in LSMO move into SNTO due to the carrier diffusion. Then an electric potential barrier V_D in the depletion layer with the thickness d around the interface is built up to stop the further diffusion of carriers in the system. The 308-nm photon energy is larger than the band gap of LSMO and SNTO, so the UV photons are absorbed to create electron-hole pairs in the LSMO film layer and the SNTO substrate. Here we discuss the photovoltaic mechanism quantitatively. The thickness of the depletion layer, d, is calculated in the Schottky model:

$$d = -x_P + x_N = \left(\frac{2\varepsilon_1\varepsilon_2(V_D - V)}{e}\frac{N_A + N_D}{N_A N_D}\right)^{1/2}$$
$$= \left(\frac{2\varepsilon_1\varepsilon_2}{eN_A}(V_d - V)\right)^{1/2}, \quad N_D \gg N_A,$$

where x_P and x_N are the thickness of the depletion layer of the LSMO and SNTO, respectively; N_A and N_D are the acceptor (LSMO) concentration and the donor (SNTO) concentration; e_1 and e_2 are the dielectric constants of the LSMO and SNTO, respectively; V_D is the diffusion voltage, which is determined from the I–V curve in Fig. 1 at the room temperature. When $N_D \gg N_A$, the thickness of the depletion layer is divided by the low concentration of N_A. For LSMO, $\varepsilon_1 = 30$; for SNTO, $\varepsilon_2 = 330$ with an electric field parallel to the c axis.[17,18] Therefore, the thickness of the depletion layer is rather thin, only $\sim$7 nm for LSMO and $\sim$30 nm for SNTO at $V = 0$. Based on these data, the maximum built-in electric field gradient can be as large as $\sim 10^5\,\mathrm{V{\cdot}cm}^{-1}$, so this drift process in the heterojunction region must proceed rapidly. The nonequilibrium carriers near the interface of the heterojunction are separated by the built-in electric field: holes in the valence band of SNTO are drifted into that of LSMO. Meanwhile, electrons in the conduction band of LSMO are drifted into SNTO. Consequently, the Fermi level in the SNTO is raised and that of the LSMO is lowered, causing the prompt occurrence

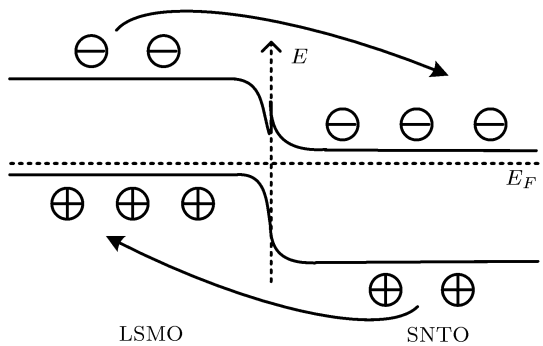

Fig. 5. Schematic band diagram of the LSMO/SNTO p–n junction and the carrier movement induced by laser.

of the photovoltage in the heterojunction. Furthermore, the photovoltaic pulse smaller than 0.3 mV can be observed when the SNTO surface in the heterojunction is irradiated by the laser pulse (inset of Fig. 3). The phenomenon is attributed to the fact that few carriers can reach the interface due to the thickness of SNTO (0.5 mm) much larger than the drift length (only nm order), so that the photovoltaic signals are much smaller than those illuminated on the LSMO film surface in the p–n heterojunction.

In summary, the good rectifying I–V characteristics and nanosecond order photoelectric effects irradiated by a UV laser of ∼25 ns pulse duration have been observed in the LSMO/SNTO p–n heterojunctions. However, no photovoltaic effect was observed under irradiation by the laser with a wavelength of 1.34 μm for which photon energy is smaller than the band gap of either LSMO or SNTO. The experimental results of absorption spectrum measurements and the photoelectric effects for different irradiation from both the surfaces of LSMO and SNTO as well as different laser wavelengths demonstrate that the photovoltage is a photoelectric effect and produced at the interface of the heterostructure. We have also reported the positive magnetoresistance effects for LSMO/SNTO p–n junctions in our earlier work.[19] Therefore, the LSMO/SNTO p–n heterojunctions are possessed of multifunctional properties of electricity, optics and magnetics. Further investigations on device development and applications for such systems are in progress.

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