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Photovoltaic Characteristic of $La_{0.7}Sr_{0.3}MnO_3$/ZnO p-n Heterojunction *

SUN Zhi-Hui(孙志辉)[1], NING Ting-Yin(宁廷银)[1], ZHOU Yue-Liang(周岳亮)[1**],
ZHAO Song-Qing(赵嵩卿)[1,2], CAO Ling-Zhu(曹玲柱)[1]

[1]*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080*

[2]*Department of Mathematics and Physics, China University of Petroleum, Beijing 102249*

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We report on the photovoltaic properties of $La_{0.7}Sr_{0.3}MnO_3$/ZnO heterojunction fabricated by pulsed laser deposition methods. Nanosecond photovoltaic pulses are observed in this junction in the wavelength range from ultraviolet–visible to infrared. A qualitative explanation is presented, based on an analysis of the photovoltaic signals of p-n heterojunction.

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ZnO has been extensively studied recently for potential applications in UV photo-emitters and photodetectors (PDs), etc., due to its wide direct band gap of 3.37 eV (300 K) and a large exciton binding energy of 60 meV.[1] However, one of the big challenges for device fabrication using the ZnO material is the difficulty of obtaining p-ZnO. Scientists have investigated various other materials for the p-layer such as p-SiC, GaN, AlGaN, $SrCu_2O_2$, NiO, ZnTe, Cu_2O, CdTe, diamond, $ZnRh_2O_4$, and GaAs, etc.[2−4] Perovskite-type manganites have been a focus of intensive studies since the discovery of colossal magnetoresistance (CMR) in this kind of materials, due to their potential applications in high-performance magnetic sensors and memory devices, and the underlying physics. The first manganite tunnel junction with considerable MR appeared in 1996.[5] Since then, reports focused on the CMR effects based on the junction have surged in the past years.[6−9] However, work on the manganite-based oxide junction is still rather limited. There are many fields concerning the junction remain unexplored, such as the effects associated with extra (nonequilibrium) carriers, which are the bases of photodetectors and photodiodes. The optical response of manganite oxides thin films has been observed by Hao *et al.* in the single-crystal (La,Ca)MnO_δ thin films.[10] Due to the slow response time and the weak response, the photoelectric effects did not receive much attention until the large photovoltaic effect (PVE) was observed in the manganite oxide junctions, such as $La_{0.29}Pr_{0.38}Ca_{0.33}MnO_3/SrNb_{0.005}Ti_{0.995}O_3$ and $La_{0.7}Ce_{0.3}MnO_{3-\delta}/SrNb_{0.005}Ti_{0.995}O_3$ p-n junctions,[11] and ultrafast picosecond photoelectric signal in the LSMO/Si p-n heterojunction.[12] Thereafter, the photoelectric properties of the heterojunctions become another topic in perovskite-type manganites.[13−16]

Here, we choose $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) as the p-layer to form a p-n junction with functional properties with the n-type ZnO. The bilayer LSMO/ZnO heterojunction is deposited on the *c*-plane Al_2O_3 substrates using the pulsed laser deposition method. The schematic structure diagram of the LSMO/ZnO junction is shown in Fig. 1. It is worth noting that ZnO is a semiconductor with wide direct band gap of 3.37 eV, and can be used as window material to the LSMO layer when this p-n junction is illuminated from the substrate side (that is backside). In this Letter, we perform a comprehensive study on its PVE when the heterojunction was back-illuminated with the light wavelength of 308 nm, 532 nm, and 1064 nm.

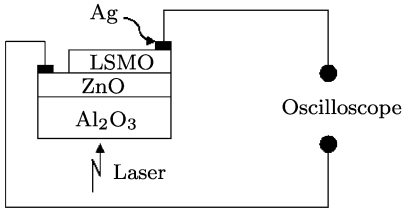

Fig. 1. Illustration of the LSMO/ZnO heterojunction for the measurements of photovoltaic signals.

The LSMO/ZnO heterojunction is fabricated by growing LSMO and ZnO thin films on Al_2O_3 (0001) substrates using pulsed laser deposition. The substrate is kept at about 450°C and the O_2 pressure at about 10^{-3} Pa during the ZnO layer deposition, while the substrate is kept at about 750°C and the O_2 pressure nearly at 10 Pa during the LSMO layer deposition. The thickness of both the LSMO and ZnO layer is about 2000 Å, controlled by the deposition time. Hall measurement reveals that the LSMO is p-type conductive, while ZnO is n-type conductive. The crystalline quality of the films is measured by the x-ray diffraction (XRD) method. Optical properties

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** To whom correspondence should be addressed. Email: ylzhou@aphy.iphy.ac.cn

are investigated at room temperature with a Spectrapro500i spectrophotometer (Acton research Corporation) and PTS-6000 Fourier Transform Infrared spectroscopy (FT-IR). In the measurement of the photovoltaic signals, the Ag electrodes are placed on the corner of the LSMO film surface and ZnO film surface, and the sample is illuminated from backside, as shown in Fig. 1. The photovoltaic signals are measured by a 500 MHz oscilloscope (Tektronix TDS3052B).

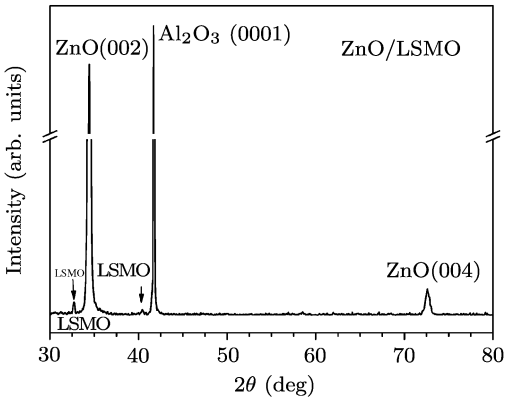

Fig. 2. XRD pattern for the LSMO/ZnO bilayer heterojunction.

The XRD pattern for the LSMO/ZnO bilayer heterojunction on the (0001) Al_2O_3 substrates as shown in Fig. 2 indicates that the ZnO layer is epitaxially grown with the (001) axis orientation, while the LSMO layer is polycrystalline, which is in agreement with the early reports.[17] Figures 3(a) and 3(b) show the transmittance spectra. Figures 3(c) and (d) present the absorption spectra in the wavelength ranges of 330–750 nm and 660–3000 nm, respectively, for the ZnO film and LSMO/ZnO bilayer films, which are deposited on the (0001) Al_2O_3 substrates under the same condition as the samples for PVE measurement. Here, we show αt (t is the thickness of the thin films) rather than absorption coefficient α. As can be clearly seen from Fig. 3, the absorption edge of ZnO is located at around 380 nm, and the transmittance for ZnO is higher than 90% in the visible and IR spectrum, which indicates that the absorption mainly attributes to the LSMO layer in a wide wavelength range. The variation of square of $(\alpha * h\nu)$ with the incident light energy $h\nu$ is shown in Fig. 4. According to the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$, the band gaps for ZnO and LSMO are obtained to be 3.27 eV (about 380 nm), and 1.03 eV (about 1205 nm), respectively, which are similar to those reported in the literature.[1,12] According to the conventional semiconductor p-n junctions, the n-type material with wide bandgap can act as the window material, and most of the incident phonons will be absorbed by the p-type layer. Thus increases the optical response of the p-n junction. Here, we suggest that the ZnO layer will act as a window material when the LSMO/ZnO junction is irradiated from substrate side when the energy of the incident photon is lower than 3.27 eV. According to the above-mentioned absorption spectrum, we expect that the LSMO/ZnO junction could show PVE in the wide wavelength range from UV to IR.

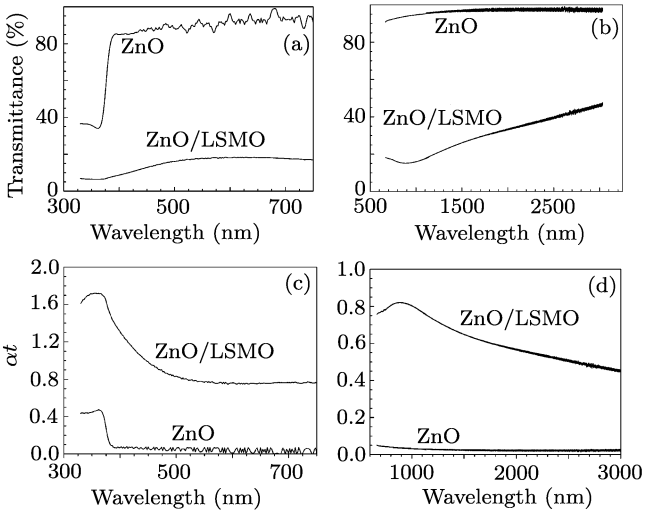

Fig. 3. Transmittance spectra of ZnO and LSMO/ZnO junction in the wavelength range of (a) 330–750 nm and (b) 660–3000 nm. The absorption spectrum of ZnO and LSMO/ZnO junction in the wavelength range of (c) 330–750 nm and (d) 660–3000 nm.

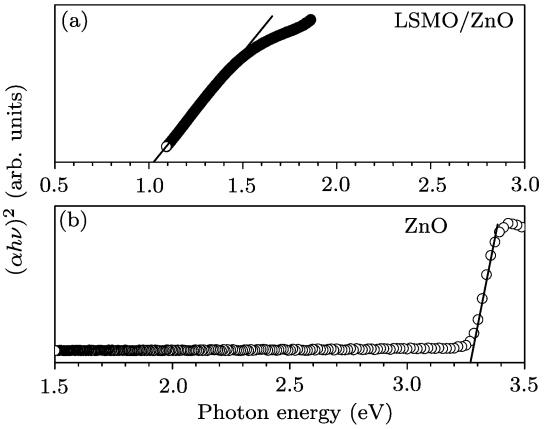

Fig. 4. Behaviour of for (a) ZnO and (b) LSMO/ZnO junction.

Figure 5 exemplifies the open-circuit photovoltaic pulse as a function of time when the LSMO/ZnO junction is irradiated with a laser of 25 ns pulse duration and 308 nm wavelength and an energy density $E_d = 1\,\mathrm{mJ\ mm^{-2}}$ from backside as shown in Fig. 1, and measured by an oscilloscope with 1 MΩ import impedance. The inset in Fig. 5 shows the open-circuit photovoltaic pulse when the junction is irradiated from the front side of the LSMO layer. The

photovoltaic signal when the junction is excited from backside is higher than that when it is irradiated from the front side, that is, the larger photoresponse is obtained when the incident beam irradiates the junction from the substrate side. In addition, it should be noted that the photovoltaic pulses have the same directions, although the signal voltage changes the polarity with time. This is different from that for the $YBa_2Cu_3O_{7-\delta}$ films,[18] in which the signal voltage changes the sign when the direction of the incident laser beam is changed in the same way as stated above. Therefore, this excludes the possibility that the PVE in the LSMO/ZnO junction results from the thermoelectric effects. We suggest that the PVE in the LSMO/ZnO junction results from the photoelectric effect.

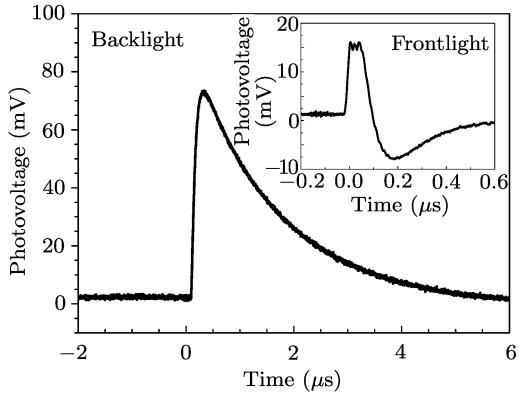

Fig. 5. Open-circuit photovoltaic pulse excited by a 308 nm excimer laser beam on the LSMO/ZnO junction from backside and measured by a oscilloscope with 1 MΩ import impedance. Inset: the open-circuit photovoltaic pulse for the 308 nm excimer laser beam on the LSMO/ZnO junction from the front side.

Figures 6(a) and 6(b) present the PV results of the LSMO/ZnO junction when it is irradiated with the 532 nm and 1064 nm laser light with the Nd:YAG laser (pulse width 25 ps), measured by a 500 MHz oscilloscope with 50 Ω import impedance. The used powers for the laser light with 532 nm and 1064 nm are 4.5 μW and 18.4 μW, respectively. As indicated in Figs. 6(a) and 6(b), the incurred PV has the same values. If the junction is irradiated using the 1064 nm laser with the power of 4.5 μW, no obvious PV signal is obtained by the oscilloscope. That is, the large photoresponse could be obtained in the short-wavelength range. This can be assigned to origin of the PVE. The creation of PVE process can be easily understood as follows.

When LSMO was deposited on the ZnO layer, an energy barrier eV_d can be established at the interface due to the mismatch between the Fermi levels/band structures of the two semiconductors. The established V_d prevents the electron diffusion from ZnO to LSMO. With the radiation of photons, electrons in the valence band absorb photons and transit to the conduction band. When the energy of the incident photons is larger than the band gaps of materials, the nonequilibrium electrons (holes) can be created in the system, and then swept to the ZnO (LSMO) layer. This leads to the accumulation of charge, producing the photovoltage. Thus, the induced PVE signal is closely related with the density of the induced nonequilibrium carriers, which is dependent on the absorption coefficients, the energy of incident photons and the intensity of the incident light. For 532 nm and 1064 nm laser light, the photon energy is nearly 2.33 eV and 1.3 eV, respectively, which are all larger than the band gaps of LSMO (about 1.03 eV), and less than the band gaps of ZnO (about 3.27 eV). The nonequilibrium carriers were mostly created in the LSMO layer, and the ZnO layer just acts as a window material as mentioned above. Due to the ZnO/LSMO junction has larger absorption coefficients and the energy of the incident photons is higher for the 532 nm laser light, more nonequilibrium carriers could be obtained at the same intensity of the incident light than that for the 1064 nm laser light. Therefore, higher PVE is obtained when the junction is irradiated by the 532 nm laser light at the same intensity of the incident light, just as we observe here. In addition, another interesting phenomenon is that the rise times of the PVE all are about 2 ns (the upper limitation of the band pass

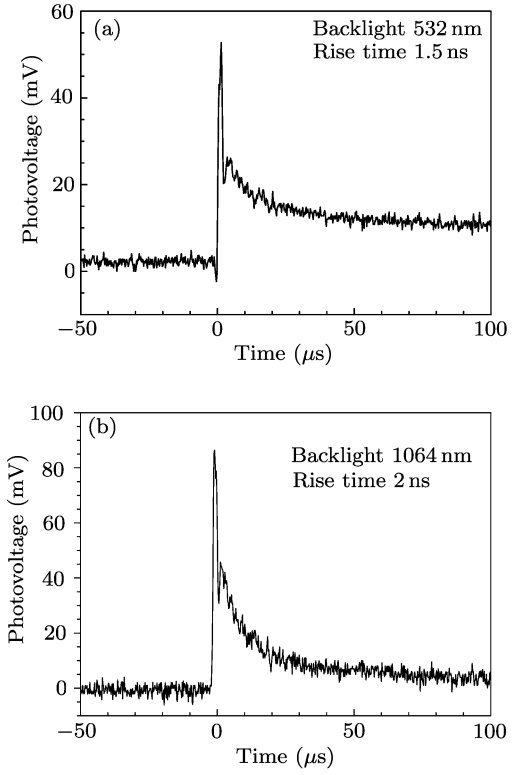

Fig. 6. Open-circuit photovoltaic pulse of LSMO/ZnO junction under the excitation of 532 nm (a) and 1064 nm (b) excimer laser and measured by a oscilloscope with 50 Ω import impedance.

of the used oscilloscope), which demonstrates that the present PVE is an ultrafast photoelectric effect.

Similarly, the PVE signal when the junction is irradiated by the 308 nm laser light can also be interpreted using the same origin. The photon energy of the 308 nm laser light is larger than the band gaps of ZnO and LSMO, and the photon can excite nonequilibrium carriers (electrons or holes) in both the ZnO and LSMO films. Compared the absorption spectra for ZnO and LSMO/ZnO in Fig. 3(c), it is clearly seen that the LSMO has larger absorption coefficient than ZnO. If the laser light incident from the backside, the light can go through the ZnO layer to the LSMO layer and can induce electron-hole pair in both the ZnO and LSMO films. However, if the laser light incident from the front side, most of the light is absorbed in the LSMO layer, so the extra carriers are generated mostly in the LSMO layer. On the other hand, LSMO is an indirect bandgap material, while ZnO is a material with direct bandgap. For an indirect bandgap material, as the emission process must observe both the laws of conservation of energy and momentum, the only way to promote an electron from the top of the valence band to the bottom of the conduction band is to simultaneously emit (or absorb) a phonon that compensates for the missing momentum vector. Such a combined transition has a much lower probability. This means that the quantum efficiency is lower for the indirect bandgap material compared with the direct bandgap material.[19] That is, more nonequilibrium carriers can be induced when the 308 nm light is incident on the LSMO/ZnO junction from the backside. As mentioned above, the signal of the PV is dependant on the density of the nonequilibrium carries induced by the photons. Therefore, the larger PVE signal can be generated in the LSMO/ZnO junction when it is irradiated from the backside, which is in agreement with the result as shown in Fig. 5.

In summary, we have investigated the PVE of the bilayer LSMO/ZnO heterojunctions irradiated by the UV, visible and IR lasers, in combination with the absorption spectra. The band gaps of LSMO and ZnO have been identified to be 1.03 eV (about 1205 nm) and 3.27 eV (about 380 nm), respectively, by optical absorption spectrum measurements. The photovoltaic experimental results for the LSMO/ZnO junction under the back- and front- irradiation by the 308 nm light laser show that the induced photovoltaic signals have the same direction and the larger signal can be obtained when the junction is irradiated from backside. Nanosecond order photoelectric effects have been observed when the junction is irradiated by the 532 nm and 1064 nm laser light. These results can be qualitatively interpreted using the origin of the PV signal based on the p-n junction.

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