Rectifying and ultraviolet photovoltaic characteristics of La$_{0.9}$Na$_{0.1}$MnO$_3$/SrTiO$_3$-Nb heterostructures

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Rectifying and photovoltaic properties of a La$_{0.9}$Na$_{0.1}$MnO$_3$/SrTiO$_3$-Nb (LNMO/STON) heterostructure have been experimentally studied. The heterostructure exhibited abnormal rectifying behavior, i.e., the threshold voltage increased with the increasing temperature in a wide range of 40 to 300 K. A temperature dependent photovoltaic response was observed when the heterostructure was excited by a 248 nm ultraviolet laser with a duration of 30 ns. The increased photovoltage was found to result from two distinctive carrier accumulation processes (from the edge of the depletion layer to the surface electrodes in LNMO and STON). The two characteristic times $\tau_1$ and $\tau_2$ were determined by the hole and electron mobility in the LNMO and STON. The significant temperature-dependent $\tau_1$ resulted from different transportation mechanisms in the metallic and insulator states of LNMO. The very short $\tau_2$ was related to the high electron mobility in STON. The lifetime of the nonequilibrium carrier was determined to be $\sim$10 ms by the analysis on the decaying process, indicating a relatively longer charge diffusion length as compared with that in other doped manganite p-n junctions. Published by AIP Publishing.

Manganese materials, especially for manganite based heterostructures, have aroused great scientific and application interest since the discovery of the colossal magnetoresistance effect in manganite oxides. Due to the interplay among the freedoms of charge, orbital, spin, and lattice degrees, these manganite based heterostructures exhibit superior physical properties, such as positive magnetoresistance effect, magnetic tuned photovoltage, and efficient ultraviolet photovoltage characteristics. Among these unique properties for manganite based heterostructures, optic tunable properties are more important for their potential applications in photoelectric devices. Until now, the photovoltaic effect in the heterojunction based on La-Sr-Mn-O, La-Ba-Mn-O, La-Pr-Ca-Mn-O, Pr-Ca-Mn-O, and La-Ce-Mn-O has been reported. The complex interplay between photo- and electric properties relies strongly on the doping, which can be tuned by the chemical substitution of constituent elements. So far, single layer film manganite heterostructures doped with univalent ions (such as Li$^+$, Na$^+$, and K$^+$) have shown unique properties compared to the manganite films doped with other valence ions (such as Ca$^{2+}$, Sr$^{2+}$, and Ce$^{4+}$). However, the photo-electric properties of the p-n junction based on univalent ion doped-manganite have not been well studied. On the other hand, the voltage variation versus light wavelength, illumination power, and temperature has been reported as well, whereas the time dependent photoelectric response is still not well understood.

In the present work, a univalent Na-doped LaMnO$_3$/SrTiO$_3$-0.5%Nb heterojunction was built. A good rectifying property was observed in a wide temperature range of 40 to 300 K. Meanwhile, the temperature and time dependent ultraviolet photovoltaic characteristics were investigated in detail. The time response of photovoltage not only is a critical parameter for a p-n junction but also offers key information for generating, transporting, and annihilating processes for the nonequilibrium carriers to analyze the physical nature of the p-n junctions.

The sol-gel method was used to synthesize La$_{0.9}$Na$_{0.1}$MnO$_3$ (LNMO) powders. Briefly, analytically pure La$_2$O$_3$, LiNO$_3$, and Mn(NO$_3$)$_2$ were mixed as the moles ratio 4:5:1:10 in an acid solution. In addition, citric acid and polyethylene glycol with easy operation were used as complexing agents for the synthesis. The collosol was dried to xerogel and burned to remove the organic matter. Finally, La$_{0.9}$Na$_{0.1}$MnO$_3$ powders were obtained after annealing. The powders were sintered at 1200°C for 24 h in air to create a bulk target, which was determined to be single phase by X-ray diffraction (XRD).

The LNMO film was then deposited on a single crystal Nb-0.5 wt. %-doped SrTiO$_3$ (100) substrate by pulse laser deposition (PLD), during which the laser with a wavelength of 248 nm and a pulse energy of 120 mJ was applied. A substrate temperature of 750°C and an oxygen pressure of 8 Pa were maintained throughout the deposition. The as-deposited LNMO/SrTiO$_3$-Nb (STON) heterostructure was annealed at 750°C in an oxygen atmosphere for 30 min. The thickness of the film was evaluated to be 80 nm by using a
SpecEl-2000-VIS ellipsometer. The crystal structure was analyzed by Panalytical X’Pert XRD, and the surface morphology was observed by Asylum MFP-3D atomic force microscopy (AFM). The indium (In) electrodes were placed on the surface of LNMO and STON layers, and the in-plane resistance of LNMO and the voltage current characteristic of the p-n junction were measured by using a Keithley 2400 meter in a Janis CCS-300 closed-cycle refrigerator cryostat system in the temperature range of 40 to 300 K. The carrier mobility in STON and LNMO was measured by the Hall effect in the pure STON substrate and LNMO film grown on the insulated SrTiO3 substrate, respectively. The time response of the ultraviolet photovoltage was measured by using a Tektronix 500 MHz oscilloscope with an input impedance of 1 MΩ in the temperature variable environment of a Janis VPF-475 liquid nitrogen thermostat. The light resource was a 248 nm ultraviolet pulse laser with a pulse width of 30 ns.

Figure 1(a) and the inset show the topography of the upper LNMO layer and the height distribution along the diagonal of the measuring square, respectively. The surface height in the z axis is observed to be in the range of ±0.5 nm, and the root mean roughness is 0.31 nm. The XRD pattern, Fig. 1(b), indicates a good epitaxial growth of the upper LNMO film on the STON (100) substrate. On the reciprocal space mapping (RSM) in (−1 0 3) lattice plane reflection [inset of Fig. 1(b)], the peak positions in qx of the LNMO film and STON substrate are the same, suggesting that the film is fully in-plane strained. These results suggest the fabricated high-quality LNMO/STON heterostructures.

Figure 2(a) shows the current-voltage (I–V) relationship of the LNMO/STON heterostructure in a wide temperature range of 40 to 300 K, which is a typical feature of p-n heterojunction and characterized by the asymmetric I–U dependence against the polarity of bias voltage. The positive bias voltage exhibits a tendency to saturate, whereas the negative voltage results in a low leakage current. This dramatic asymmetry of the I–U relationship indicates a good rectifying behavior.16 Figure 2(b) presents the variation of threshold voltage Ud, which is defined as the voltage at I = 1 mA in the positive direction versus temperature. The Ud increases slightly from 1.27 to 1.42 V with the increasing temperature from 40 to about 200 K, and then it rises up linearly and sharply to 1.75 V as the temperature increases to 280 K. Figure 2(b) also shows the resistance variation with temperature for the upper LNMO layer. Clearly, a metal-insulator transition (MIT) at TMI = 255 K is observed, corresponding to the linear region presented in the Ud versus T curve, Fig. 2(b). This reveals that the variation of Ud with temperature for the heterostructure is related to the MIT of the LNMO layer. In the metal temperature region (T < TMI), the Mn⁢³⁺-O²⁻–Mn⁴⁺ double-exchange effect32 describes the electrical conducting mechanism. Electrons can move from the Mn⁢³⁺ eg orbital to Mn⁴⁺.
through $O^{2-}\cdot2p$ orbital. By contrast, in the insulator region ($T>T_{MI}$), a linear relationship of $\ln(R/T) \sim 1/T$ [inset in Fig. 2(b)] indicates a small-polaron transportation model.\(^{33}\) Besides this, there also exists the transition from the ferromagnetic state to the paramagnetic state around $T_{MI}$. The transitions in the charge transportation and magnetization states in LNMO increase the barrier height of the heterojunction, leading to a great change of the $U_d$ ($\sim 40\%$ enhancement from 40 to 300 K).

Figure 3(a) shows the photoinduced voltage ($U_{OC}$) with a time span of 0–200 $\mu$s in the temperature range of 80 to 300 K. Upon light pulse at each temperature, the $U_{OC}$ first exhibits an abrupt jump to the peak value $U_p$ and then gradually tends to saturate. The maximum photovoltage monotonically decreases from 0.58 to 0.24 V with the increase in temperature, as shown in the inset of Fig. 3(a). This is owing to that the built-in electric field at the interface which separates the photogenerated holes and electrons is weakened when the temperature rises.

Considering the fact that the time duration to reach the saturated voltage is much longer than that of the laser pulse ($\sim 30$ ns) and the production of photoinduced carriers is very fast (shorter than 1 ns),\(^{33}\) here the rising process mainly reflects the migration of the photogenerated carriers from the depletion layer to the surface electrodes, like a charging process. In general, during a basic charging process, the electric quantity $Q$ on the electrode at time $t$ can be expressed as $Q = Q_0[1 - \exp(-t/\tau)]$,\(^{18}\) where $Q_0$ is the maximum electric quantity accumulated on the electrode, and $\tau$ is the characteristic time. Since the voltage $V$ on the electrodes is written as $V = Q/C$ ($C$ is the capacitance of the junction that is invariable with charge distribution), the relationship between photovoltage $U_{OC}$ and time $t$ could be deduced as: $U_{OC} = V_0[1 - \exp(-t/\tau)]$, in which $V_0$ corresponds to the saturated voltage.

However, when the laser irradiates on the heterojunction, the photogenerated holes and electrons are separated by the built-in electric field, leading to high concentrations of holes and electrons at the depletion layer boundaries in LNMO and STON, respectively, and then their individual movement towards the LNMO and STON surface electrodes. Due to the difference in the charge transportation mechanism, the carrier migration speed in LNMO and STON may differ. Thus, a simple exponential function cannot well describe the rising stage of photovoltage. To clarify this, the carrier mobility $\mu$ in LNMO and STON was measured by the Hall effect. The results are presented in Fig. 3(b). As temperature rises, the hole mobility in LNMO decreases from 5.05 cm$^2$/V s at 80 K to a minimum value of 0.53 cm$^2$/V s at 260 K (close to $T_{MI} \sim 255$ K) and then slightly increases to 0.59 cm$^2$/V s at 300 K. On the other hand, the electron mobility in STON exhibits a weak dependence on the temperature.

FIG. 3. Characteristics of photo-induced voltage in the LNMO/STON heterostructure in the rising stage: (a) time response of $U_{OC}$ in 0–200 $\mu$s. The inset is maximum voltage $U_p$ versus temperature; (b) carrier mobility in LNMO and STON; (c) characteristic times $\tau_1$ and $\tau_2$ at different temperatures; (d–f) are the schematics of migration of photogenerated carriers in the p-n junction excited by the pulse laser in different temperature regions. The red arrows inside LNMO represent the $e_g$ orbital, which is highly paralleled when $T < T_{MI}$ (d), and the depth of parallelism is weakened with the increasing temperature (e). Small polarons are presented as green circles for $T > T_{MI}$ in LNMO (f).
and is one or two orders of magnitude higher than that in LNMO.

Based on the above analysis, Eq. (1) below is used to describe the rising process of $U_{\infty}$, which is a combination of the charge accumulation in LNMO and STON electrodes

$$U_{OC} = V_1[1 - \exp(-t/\tau_1)] + V_2[1 - \exp(-t/\tau_2)],$$

where $V_1$ and $V_2$ are the saturated voltages in the LNMO and STON electrodes and are determined by the maximum charge quantities $Q_1$ and $Q_2$ in the two electrodes, and $\tau_1$ and $\tau_2$ are the characteristic times for the transportation of holes and electrons from the depletion layer to the surface electrodes in LNMO and STON, respectively. Note that these characteristic time constants should correlate with the carrier mobility in LNMO and STON. The experimental data of $U_{\infty}$ and $t$ are well regressed by Eq. (1), and the fitted $\tau_1$ and $\tau_2$ versus temperature are presented in Fig. 3(c). As temperature rises, $\tau_1$ sharply increases from 6.62 $\mu$s to a maximum value of 125.2 $\mu$s at 260 K and then decreases to 108.8 $\mu$s. This agrees well with the measured hole mobility in LNMO, which first decreases to the minimum value at 260 K and then undergoes a slight increase. On the other hand, $\tau_2$ is relatively stable and shows little dependence on temperature.

This is again in good agreement with the experimental result that the electron mobility in STON is almost constant even with an increase in temperature. Moreover, $\tau_2$ is less than $\tau_1$ by one or two orders of magnitude, which also coincides with the fact that the electron mobility in STON is higher than that in LNMO by the same orders. Therefore, from a physical view, we can reasonably conclude that the first term $V_1[1 - \exp(-t/\tau_1)]$ in Eq. (1) describes the increase of photovoltage induced by hole accumulation at the LNMO side, and the second term $V_2[1 - \exp(-t/\tau_2)]$ corresponds to the contribution of electrons migration in the STON layer.

The schematics illustrated in Figs. 3(d)–3(f) further explain the effect of temperature dependent phase transition on $\tau_1$. In the metallic region ($T < T_{MI}$) of LNMO, the migration of carriers is controlled by a spin correlated double exchange. At very low temperature ($T \ll T_{MI}$), LNMO has a relatively high degree of parallelism of the eg orbital [the ordered red arrow in Fig. 3(d)], and the carriers can easily transport between adjacent orbitals, resulting in a shorter $\tau_1$. As temperature rises, the ferromagnetism of LNMO becomes weakened and the parallelism of the local spin is reduced [the weak ordered red arrow in Fig. 3(e)], resulting in a longer time requirement for carrier movement. When $T > T_{MI}$, the small-polaron transportation is the dominant mechanism [Fig. 3(f)]. The rise of temperature promotes the delocalization of the carriers and increases the transition probability, and consequently, $\tau_1$ decreases. The rising process of the photovoltage in this work is very close to our prior research on $\text{La}_{0.9}\text{Li}_{0.1}\text{MnO}_3$/STON,$^{34}$ which also has a temperature-dependent slower process and a stable faster process. While, in the $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$/STON heterojunction,$^{18}$ the two time constants are about 30 and 260 $\mu$s, which are longer than those in this work. It reveals the difference of non-equilibrium charge transportation in the manganite heterojunction with different valence ions such as Ce$^{4+}$ and Na$^+$. Figure 4(a) shows the falling stage of the photo-induced voltage, which is also well fitted by a second order exponential function at each temperature as follows:

$$U_{OC} = U_1 \exp(-t/t_1) + U_2 \exp(-t/t_2),$$

where $U_1$ and $U_2$ are the voltage coefficients and $t_1$ and $t_2$ are the time constants which describe the falling speed. Figure 4(b) shows the variation of $t_1$ and $t_2$ versus temperature. The shorter time constant $t_1$ ranges from 1.27 to 5.30 ms, and the longer time constant $t_2$ ranges from 10.73 to 24.14 ms, and both the peak values of these two time constants appear at 260 K. It is known that once the light source is shut down, there are no new photogenerated carriers, and the collected carriers at the two sides of the junction may neutralize through the external circuit. Meanwhile, annihilation between holes and electrons inside the heterojunction also occurs. The capacitance of this heterojunction is measured to be 2.62 nF at 300 K, and the time constant of external RC discharge through the oscilloscope is $t_{RC} = 2.62$ nF $\times 1$ $\Omega = 2.62$ ms, which is very close to the constant $t_1$ (23.3 ms at 300 K). Therefore, $U_1 \exp(-t/t_1)$ is related to the contribution of the external circuit. Based on this, $U_2 \exp(-t/t_2)$ is considered to be correlated with the annihilation inside the heterostructure, and $t_2$ describes the lifetime of the nonequilibrium carrier. The temperature effect on this constant arises from the transportation mechanism transition of LNMO.$^{34}$ Below and above the $T_{MI}$ of LNMO, different electrical phases (metal and insulator) result in different annihilating processes. The value at the order of millisecond for the nonequilibrium carrier lifetime is much longer than that in similar p-n junctions based on doped...
manganites, implying that there may be a relatively long diffusion length.

In summary, the LNMO/STON heterojunction has been fabricated by a PLD method. As compared with other traditional manganite based p-n junctions, this heterostructure exhibits the abnormal rectifying property. The threshold voltage acts as a positive correlation with temperature from 40 to 300 K, exhibiting a linear and sharp rise around MIT temperature of LNMO. Under the excitation of the 248 nm ultraviolet laser pulse with a width of 30 ns, the photovoltage presents a fast rising stage in ~10 μs order and slow falling period at the ~10 ms level. It is found that the rising of the photovoltage results from two distinctive carrier accumulation processes from the edge of depletion layer to the surface electrodes in LNMO and STON. The two characteristic times τ1 and τ2 are determined by the hole and electron mobility in the LNMO and STON. The significant temperature-dependent τ1 results from distinct dominant transportation mechanisms, which are spin correlated Mn^{3+}–O^{2−}–Mn^{4+} double exchange transportation in the low temperature metallic region but are a small-polaron transportation in the high temperature insulator region. For the falling process, the lifetime of the carriers is determined to be in 10 ms order and also reaches its peak polarization around MIT temperature of LNMO. Different transportation mechanisms below and above MIT temperature produce divergent effects on the annihilation rate between holes and electrons in the heterostructure. These results demonstrate that the diode behavior and photovoltaic property of the LNMO/STON can be tuned by temperature induced phase transition in LNMO.

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