

# Rectifying characteristics, magnetic tunability, and photovoltaic response in $\text{La}_{0.8}\text{Hf}_{0.2}\text{MnO}_3/0.7 \text{ wt}\% \text{ Nb-SrTiO}_3$ heteroepitaxial junctions

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Heterojunctions composed of tetravalent cation-doped  $\text{La}_{0.8}\text{Hf}_{0.2}\text{MnO}_3$  (LHMO) and 0.7 wt% Nb-doped  $\text{SrTiO}_3$  were fabricated using pulsed laser deposition method and investigated under different fields (electric, magnetic, and optic). The heterojunctions exhibited excellent rectifying behavior in a wide temperature range and significant magnetic field modulated properties. Prominent photovoltaic effect was also observed in the formed junctions. Special attention has been paid to the temperature dependence of the diffusion voltage ( $V_d$ ) and photovoltage ( $V_{oc}$ ). When temperature increased from 40 K to 300 K,  $V_d$  decreased from 1.13 V to 0.16 V. It is notable that, under illumination of a light with  $\lambda = 532 \text{ nm}$ ,  $V_{oc}$  dropped from 650 to 80 mV. No sudden change of  $V_d$  and  $V_{oc}$  was observed at the metal-insulator transition temperature, which is probably caused by the band structure of the LHMO. © 2012 American Institute of Physics. [doi:10.1063/1.3678491]

## I. INTRODUCTION

Manganite-based heterojunctions have received wide interest in recent years.<sup>1,2</sup> Superior to traditional semiconductor  $p$ - $n$  junctions, they are expected to exhibit extraordinary behaviors, such as electric, magnetic, and optic tunable properties.<sup>3-7</sup> However, the investigations on these heteroepitaxial junctions are still in their initial stages. Many phenomena exhibited in these structures cannot be perfectly explained by the theory of semiconductor. The underlying physics is still unclear.<sup>8</sup> So far, the works were mainly focused on hole-doped manganites.<sup>5-7</sup> The electron-doped manganite-based heterojunctions were rarely reported. Tetravalent-doped manganite, as a controversial electron-doped manganese oxide that may have different carrier type from those in hole-doped manganites, is of important sense for the development of spin-dependent electronics (spintronics). Among them,  $\text{La}_{0.8}\text{Hf}_{0.2}\text{MnO}_3$  (LHMO) is a tetravalent cation-doped manganite in which the  $\text{La}^{3+}$  ions are substituted by  $\text{Hf}^{4+}$  ions.<sup>9</sup> Unlike other tetravalent cations, Hf does not have multivalent states (e.g., Ce with a mixed valence state of  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ ),<sup>10,11</sup> thus avoiding the complex and unreliable factors in the research.<sup>12</sup> Therefore, fabrication and studies of LHMO-based heterojunctions could improve our understanding of these complicated systems and promote the application of such heterojunctions. In this work, LHMO/0.7 wt% Nb-doped  $\text{SrTiO}_3$  (NSTO) heterojunctions were fabricated. Excellent rectifying characteristic was found in the whole temperature range from 40 K to 300 K. Magnetic and photoelectric effects on their current-voltage ( $I$ - $V$ ) characteristic were studied systematically.

## II. EXPERIMENTAL

LHMO films were grown on NSTO (001) single-crystal substrates by pulsed laser deposition using a KrF excimer

laser ( $\lambda = 248 \text{ nm}$ ).<sup>13,14</sup> The laser repetition rate and energy density were 1 Hz and  $3 \text{ J/cm}^2$ , respectively. The temperature of substrate was maintained at  $750^\circ\text{C}$  in a 0.5 mbar oxygen atmosphere. The thickness of the LHMO film is about 100 nm measured by surface step profiler. To reduce the oxygen deficiency and improve the crystallinity, the as-grown film was *in situ* annealed at  $800^\circ\text{C}$  in an ambient of high oxygen pressure (1 atm) for 1 h before cooling down to room temperature. X-ray diffraction confirmed that the prepared films were formed in single phase with a (001) orientation. In order to measure  $I$ - $V$  curves and photovoltaic response of LHMO/NSTO heterojunctions, the LHMO films were patterned into small blocks ( $0.2 \times 0.2 \text{ mm}^2$ ) by the standard photolithography method. Silver electrodes were evaporated on the LHMO layer and NSTO substrate thermally. Previous research confirmed that the silver electrodes exhibit an ohmic contact with the films and substrates.<sup>4</sup> Semiconductor laser diodes with wavelengths of 532 and 650 nm were used as light sources in the photovoltaic measurements.

## III. RESULTS AND DISCUSSIONS

LHMO films were also prepared on  $\text{SrTiO}_3$  single crystal substrates using the same conditions for the measurement of LHMO film resistance. Figure 1 shows the resistivity-temperature relation for the LHMO film under various magnetic fields (0 T, 1 T, 3 T, and 5 T). In the absence of magnetic fields, LHMO thin film exhibits a metal-insulator (MI) transition at peak temperature  $T_P = 240 \text{ K}$ . When a magnetic field is applied, the resistance decreases in the whole temperature range and  $T_P$  shifts to higher temperature. A magnetic field of 5 T results in a magnetoresistance (defined as  $|MR| = |[R_H - R_0]/R_0 \times 100\%|$ ) of 86% near 233 K. The changes of magnetic and electronic properties in the LHMO film under a magnetic field are similar to those observed in hole-doped manganites.<sup>5</sup>

Figure 2(a) presents  $I$ - $V$  characteristics of the LHMO/NSTO heterojunctions measured in a wide temperature range

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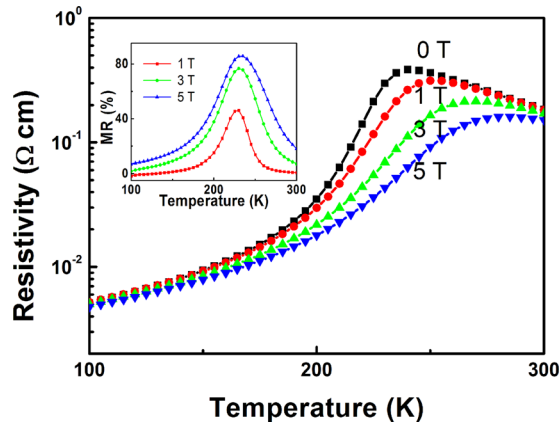


FIG. 1. (Color online) Temperature dependence of resistivity of a LHM thin film under different magnetic fields ( $H=0, 1, 3,$  and  $5$  T). The inset shows the magnetoresistance of the film.

from 40 K to 300 K. The schematic view of the structure is shown in the bottom inset of Fig. 2(a). The asymmetric ratio,  $\beta = I(1V)/I(-1V)$ , is over  $10^3$  at room temperature. Compared with most other reports on manganite-based heterojunctions,<sup>4,5,10</sup> the asymmetry of  $I$ - $V$  relations is more obvious in LHM/NSTO heterojunctions, indicating an excellent rectifying property. The diffusion voltage  $V_d$  reaches 1.13 V at 40 K (the top inset of Fig. 2(a)). It decreases almost linearly as temperature increases. This phenomenon can be understood by considering the energy band structure of the LHM/NSTO heterojunctions. LHM is proved to be an electron-doped

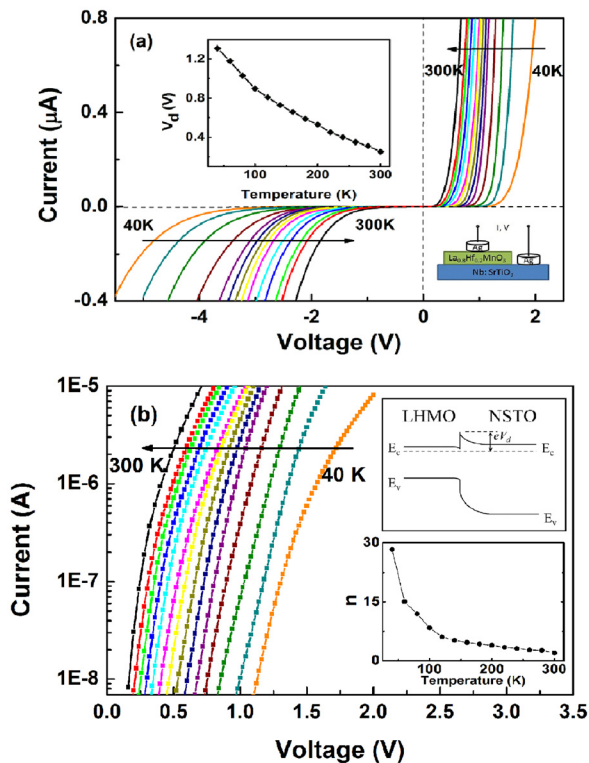


FIG. 2. (Color online) (a) The  $I$ - $V$  curves of LHM/NSTO junction in a wide temperature range from 40 K to 300 K. The top inset presents  $V_d$  as a function of temperature. The bottom inset is a schematic electrode setting for  $I$ - $V$  measurement. (b)  $\log I$ - $V$  curves of LHM/NSTO heterojunctions in forward bias at different temperatures. The inset: Temperature dependences of ideality factor  $n$ .

manganite by XPS and Hall measurements.<sup>9</sup> A heterojunction composed of  $n$ -LHM and  $n$ -NSTO should be treated as an  $n$ - $n$  heterojunction, which is also classified as isotype heterojunction. The schematic diagram for the band structure of the LHM/NSTO junction is illustrated in the inset of Fig. 2(b). When the heterojunction is fabricated, an energy barrier is formed at the interface of the LHM/NSTO junction. Under forward bias, the energy barrier is decreased, so electrons in the conduction band of NSTO can travel to the conduction band of LHM when the forward bias is larger than the energy barrier, which leads to the rapid increase of current. While under the reverse bias, the energy barrier is enhanced. The electron transition between the conduction band of NSTO and that of LHM is forbidden. When the reverse bias is large enough, the electrons in the valence band of LHM can tunnel into the conduction band of NSTO, which leads to the breakdown of the heterojunction.

Although a detailed transport mechanism of manganite-based heterojunctions is still unclear, previous studies indicated that the  $I$ - $V$  relations of these junctions could be interpreted with a model of  $p$ - $n$  junction or Schottky junction.<sup>8,15</sup> It is well known that in an ideal Schottky junction or a  $p$ - $n$  heterojunction, the main transport mechanism is thermionic emission (TE). The  $I$ - $V$  relation can be written in empirical form as  $I = I_0 \exp(qV/nk_B T)$  where  $q$  is unit electronic charge,  $V$  is the bias voltage across the junction,  $n$  is the ideality factor,  $k_B$  is Boltzmann constant,  $T$  is temperature in Kelvin, and  $I_0$  is saturation current.  $I$ - $V$  relations in forward bias (Fig. 2(a)) are re-plotted in the logarithm-linear scale (Fig. 2(b)) to obtain information on the transport mechanism of the junction. The ideality factor  $n$  increases more significantly as the temperature decreases, which is similar to the thermionic emission theory (bottom inset of Fig. 2(b)).<sup>16</sup> Besides, if the electron tunneling mechanism dominates in these heterojunctions, the  $\log I$ - $V$  relations should not be parallel<sup>17</sup> and the reversed  $V_b$ - $T$  behavior all suggest that the thermionic emission mechanism dominates in this LHM/NSTO heterojunction.

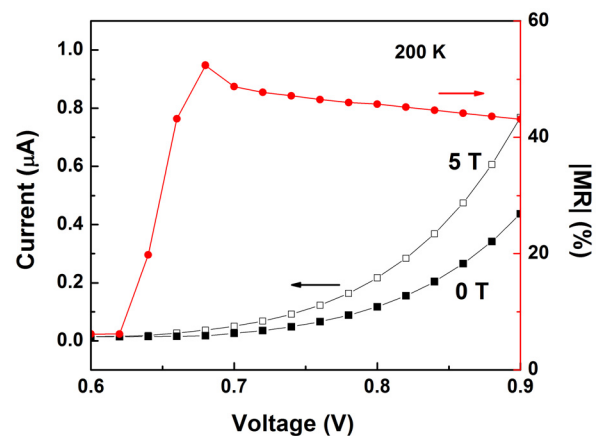


FIG. 3. (Color online)  $I$ - $V$  curves in the forward direction at 200 K under magnetic fields of 0 T (solid square) and 5 T (open square).  $MR$  (solid circle) was also shown in the figure.

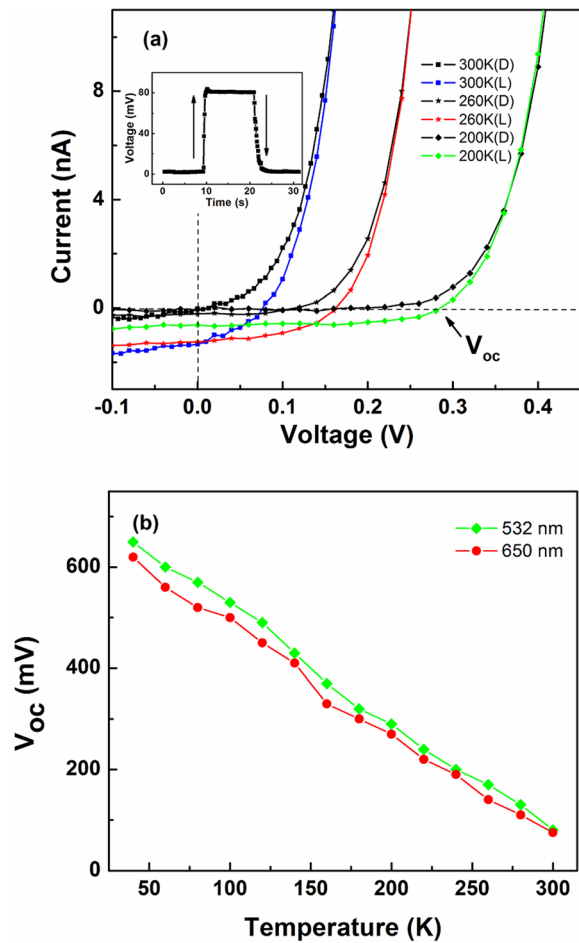


FIG. 4. (Color online) (a)  $I$ - $V$  curves of the LHMO/NSTO heterostructure measured in the dark and under light irradiation ( $\lambda = 532$  nm) at different temperatures (200, 260, and 300 K). The inset shows the response of the open circuit voltage to the illumination in 300 K. Up arrow indicates the shutter opening of the light source and down arrow indicates the shutter closing. (b) Temperature dependences of  $V_{oc}$  ( $\lambda = 532$  and 650 nm).

$I$ - $V$  curves imply the equilibrium charge carriers' behavior. The behaviors of the extra charge carriers, which determine the performance of many practical devices, are essential too. In order to investigate the magnetic field dependence of rectifying behavior,  $I$ - $V$  relations of LHMO/NSTO heterojunctions were measured at 200 K (lower than  $T_C$ ), under fields of  $H = 0$  T and 5 T (see Fig. 3). The magnetic field was applied perpendicularly to the interface of the heterojunction.  $I$ - $V$  curves were shifted to a lower bias voltage under external magnetic fields. A maximum MR of 52% was found, indicating a remarkable magnetic field modulation on the heterojunction.

Figure 4(a) shows the  $I$ - $V$  curves of the LHMO/NSTO heterostructure measured with and without light irradiation ( $\lambda = 532$  nm) at different temperatures (40, 100, 160, and 220 K). Under the illumination of light, holes, and electrons are excited by the incident photons in the valence and conduction band. Only the electrons can transfer to the NSTO across the interface, while the large barrier will block the photon-excited holes. This leads to the accumulation of charges and appearance of the photovoltage, which is normally characterized by the open circuit voltage ( $V_{oc}$ ). Under

light irradiation, the  $I$ - $V$  curve shifts downward along the current axis with an open-circuit voltage  $V_{oc}$  of 0.28 V at 200 K and 0.08 V at 300 K. A thicker depletion layer or a higher diffusion voltage results in a larger photovoltage. The junction also has a quick response to the light. As seen from the inset in Fig. 4(a),  $V_{oc}$  jumps to 0.08 V immediately when the shutter of the light source is opened and goes back to its background value as soon as the shutter is shut down. The temperature dependences of  $V_{oc}$  are presented in Fig. 4(b). Both  $V_d$  and  $V_{oc}$  decrease almost linearly as temperature increases without any sudden changes. This is similar to some previous works.<sup>4</sup> In junctions of  $\text{La}_{0.1}\text{Sr}_{0.9}\text{MnO}_3$  (LSMO)/NSTO,  $V_d$  and  $V_{oc}$  also show no connection with the magnetic state of LSMO layer. The band structure of manganites was determined by both Jahn-Teller (JT) distortion and Hund's coupling. For low-doped LHMO thin film, the JT distortion is stronger than the Hund's coupling, so the bandgap is mainly determined by the JT distortion. This might be the reason why no sudden changes were observed in  $V_d$ - $T$  and  $V_{oc}$ - $T$  for our LHMO/NSTO heterojunctions.

#### IV. CONCLUSION

LHMO/NSTO heterojunctions were fabricated using pulsed laser deposition. These junctions show excellent rectifying properties, remarkable bias tunable magnetoresistance and pronounced photoelectric effects. In a wide temperature range, the asymmetric ratios in  $I$ - $V$  curves are over  $10^3$ . The maximum MR at 200 K is around 52% in a magnetic field of 5 T. The open circuit voltage is  $\sim 0.08$  V at 300 K and increases almost linearly to  $\sim 0.65$  V when temperature is down to 40 K.

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