# Photoelectric response of Schottky barrier in $La_{0.7}Ca_{0.3}MnO_3$/Nb:$SrTiO_3$ heterojunctions

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Heterojunctions composed of $La_{0.7}Ca_{0.3}MnO_3$ and 0.05 wt % Nb-doped $SrTiO_3$ were fabricated using pulse laser deposition. The current-voltage characteristics of such heterojunctions can be described by tunneling with an effective Schottky barrier. These junctions showed significant response to ultraviolet and visible light. Band-to-band and internal photoemission were characterized by photoelectric experiments. A quantum efficiency of about 86% was observed at an incident energy of ~3.95 eV, which corresponds to the band-to-band excitation of electrons in Nb:$SrTiO_3$. From the internal photoemission, the height of Schottky barrier was determined as 1.64 eV. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2920765]

Manganite-based heterojunctions have recently attracted lots of attention for their special performance. Clear rectifying characteristics, complex magnetoresistance, and photovoltaic effects were observed in various heterojunctions composed of perovskite-type manganese oxides and Nb-doped $SrTiO_3$ (NSTO).[1–8] Although it is still an open question to model the interface between perovskite-type oxides, previous studies revealed that the transport process can be approximated by metal-semiconductor Schottky junction or *p-n* junction.[2,3] Detailed investigations showed that the current-voltage characteristics of $La_{0.7}Sr_{0.3}MnO_3$ (LCMO)/NSTO heterojunction can be well described by tunneling with an effective Schottky barrier.[9,10] This implies that manganite-based heterojunction can work as a probe to detect the shift of Fermi level and the change of density of state near the Fermi level of manganite oxides. However, most of the studies focus on the transport process based on the current-voltage characteristics. During the current-voltage measurement, transport mechanisms such as tunneling and edge leakage may lead to the complexity in extraction of barrier height. Photoelectric measurement, which corresponds to the internal photoemission of excited electrons from metal to semiconductor, is an accurate and direct method for determining the barrier height. In this letter, the spectral responds of LCMO/NSTO were studied. The barrier height was determined by the photoelectric measurement.

The LCMO/NSTO heterojunctions were fabricated by depositing LCMO thin films on 0.05 wt % (NSTO) single crystal substrates with (100) orientation by pulsed laser deposition. Details about the growth of the films were described elsewhere.[11] During the deposition procedure, the substrate temperature was kept at about 650 °C and the oxygen pressure was about 0.1 mbar. The thickness of the LCMO thin film is about 650 Å controlled by the deposition time. After deposition, LCMO thin films were patterned into blocks with an area of 0.12 $cm^2$. Silver electrodes with an area of about 0.005 $cm^2$ were then thermally evaporated on the LCMO films and NSTO substrates. Spectra respond was measured in the range from 200 to 1800 nm in air with three different systems, the light sources of which provide light with different wavelength range. During these measurements, the whole junction was illuminated by light and the photocurrent was recorded. Good quality of the grown films was confirmed by x-ray diffraction and atomic force microscopy. Only $(0l0)$ diffraction peaks of LCMO and $(l00)$ diffraction peaks of NSTO were observed in $\theta$-$2\theta$ x-ray reflections. Four peaks with separation of 90° were detected in $\varphi$ scan. These proved that LCMO films are of single phase and epitaxially grow on the substrates. Atomic force microscopy of LCMO showed three-dimensional islands. The surface of the film has a root-mean-square roughness of $4.92 \times 10^{-1}$ nm.

In thermionic emission theory, the current of a Schottky junction under forward bias can be expressed[12]

$$I = SA^{*}T^2 \exp\left(-\frac{q\Phi_B}{kT}\right)\exp\left(\frac{qV}{kT}\right), \tag{1}$$

where $S$ is the junction area, $A^*$ is the effective Richardson constant, $q$ is electron charge, $q\Phi_B$ is the barrier height, and $k$ is Boltzmann constant. If $\ln I$ is plotted as a function of $V$, a straight line should be obtained, and the barrier height can be calculated from the extrapolated value on the voltage axis. $\ln I$-$V$ curves at various temperatures were showed in the inset in Fig. 1. At high temperatures, the whole curve can be fitted with a straight line, while it deviates from the linear dependence at a lower temperature. According to thermionic emission theory, the slope increases with $q/\mathrm{kT}$ as temperature decreases. However, the change of the observed slope differs from this theoretical prediction. The change in the observed slope is neglectable compared with the value predicted by the theory. Moreover, the lower the temperature is, the larger the deviation is (Fig. 1). Similar behavior has also been observed in other heterojunctions.[9,10] It was attributed to the tunneling of electrons. The depletion region of heterojunctions composed of manganites and NSTO may vary from a few tenths to about 100 Å.[13] It is so small that the tunneling process is dominated. Under this situation, it would be very difficult to obtain the barrier height from current-voltage measurement.

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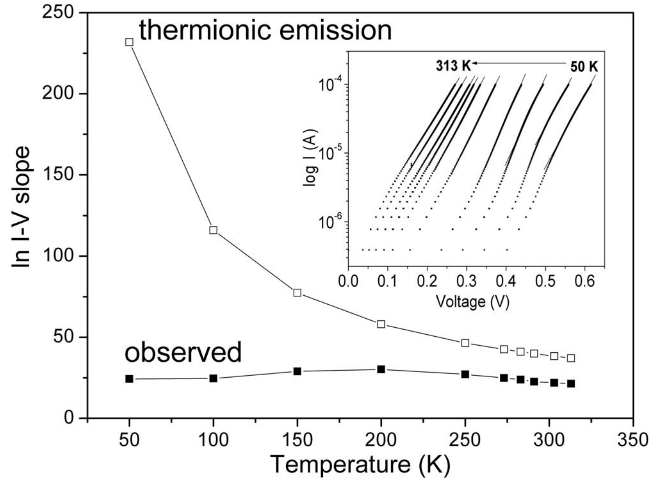


FIG. 1. Slope of $\ln I$ vs $V$ curves at different temperatures. Inset is $\log I$ vs $V$ curves at 50, 100, 150, 200, 250, 273, 283, 291, 303, and 313 K, respectively.

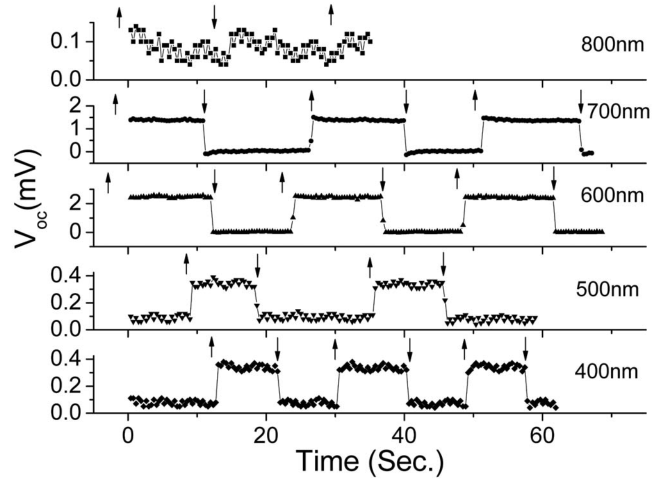


FIG. 3. Respond of open-circuit voltage to the illumination. Up arrows indicated the moments when the shutter of the light source is open and down arrows indicated the moments when the shutter of the light source is closed.

Photoelectric process provides a direct and reliable method to measure the barrier height of Schottky junction. Two kinds of photoelectric processes may occur if a Schottky junction was illuminated with light of different wavelength. When the incident photon energy $h\nu \geqslant E_g$, band-to-band excitation occurs. Electrons in the valance band of NSTO are excited to the conduction of NSTO. Electron-hole pairs are generated. When $q\Phi_{Bn} \leqslant h\nu \leqslant E_g$, the excitation over the barrier occurs (internal photoemission). Electrons near the Fermi level of LCMO get energy from photon, overcome the barrier and collected by NSTO. The quantum efficiency (QE) of the present LCMO/NSTO Schottky junction is very weak (less than 1%) when the incident photon energy is lower than 3.2 eV. QE shows a peak in the range of about 3.2 to 6.2 eV. The highest value of about 86% was achieved at incident photon energy of about 3.95 eV (Fig. 2). This peak corresponds to the band-to-band excitation of electrons in NSTO, as the band gap ($E_g$) of NSTO has a value of about 3.3 eV.[14] In band-to-band excitation mode, QE ($\eta$) is given by[12]

$$\eta = (1 - R)\left[1 - \frac{\exp(-\alpha W_D)}{1 + \alpha L_p}\right], \tag{2}$$

where $R$ is the reflection coefficient, $\alpha$ is the optical absorption coefficient, $W_D$ is the depletion-layer width, and $L_p = \sqrt{D_p \tau_p}$ ($D_p$ is the diffusion coefficient of hole in NSTO and $\tau_p$ is the lifetime of excess carriers). As $\alpha$ is a strong function of wavelength, for photons with energy lower than $E_g$, the small $\alpha$ cannot provide enough absorption. While for photons with energy higher than $E_g$, the $\alpha$ is very large. The incident photons will be absorbed near the surface of LCMO and recombined there. Appreciable value of QE can be achieved only for the photons with energy close to the band gap of NSTO.

Photovoltaic effect has been observed in heterojunctions composed of manganites under the illumination of visible light.[8,15] For the junction in the present study, the open-circuit voltage ($V_{oc}$) immediately jumped to a high value once the shutter of the light source was open and the junction was illuminated by light of 400, 500, 600, and 700 nm and went back to its background value as soon as the shutter is shut down. However, $V_{oc}$ has negligible difference with and without the illumination by the light of 800 nm (Fig. 3). This suggested that the junction really has responded to visible light. Figure 4 showed the light intensity dependence of $V_{oc}$ with the illumination by the light of 650 nm. $V_{oc}$ is nearly linear with the light intensity in log scale and is not saturated up to a light intensity of about 100 mW cm$^{-2}$. For a Schottky junction, $V_{oc} \propto \ln(I_{sc})$ and $I_{sc} \propto \eta * P_{opt}$, so $V_{oc}$ should be lin-

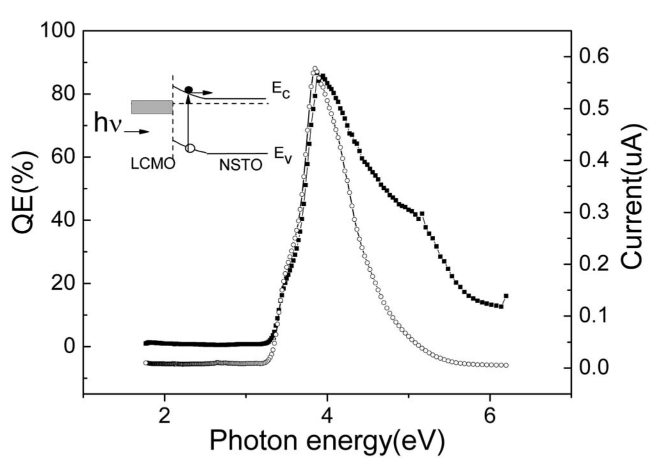


FIG. 2. QE (solid square) and photocurrent (open circle) as a function of incident photon energy. Inset is schematic of band-to-band photoemission.

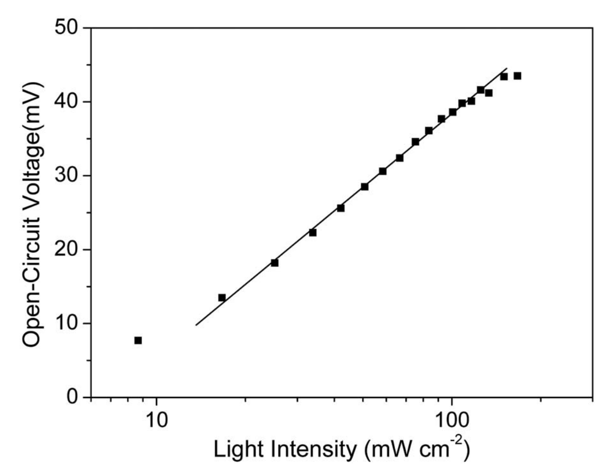


FIG. 4. Open-circuit voltage as a function of light intensity. The wavelength of the incident light is 650 nm.

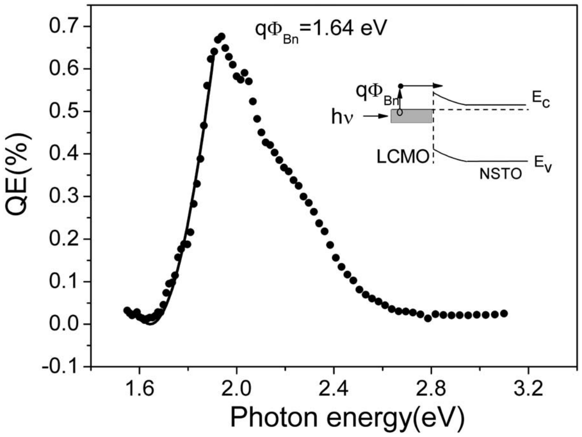


FIG. 5. QE as a function of incident photon energy. Dots are experimental data and the line is the fitting result. Inset is schematic of internal photoemission.

ear to the light intensity if the QE is not a function of light intensity. This demonstrated that the behavior of the present junction follows qualitatively the theory of Schottky junction.

In order to make the underlining physics clear, the QE in the range of 400 to 800 nm (3.10–1.55 eV) was remeasured with a light source of higher power and current meter with higher resolution and the result is shown in Fig. 5. (It was also measured in the range of 800–1800 nm. No response was observed and result is not showed here.) Similar to the behavior near 3.9 eV, there is a peak at about 1.9 eV. However, the QE only has a peak value of 0.66% in this range. This is very small compared to 86% at about 3.95 eV. Considering the band structure of the junction, we contributed the observed phenomenon to internal photoemission. The QE of internal photoemission as a function of the photon energy is given by[12]

$$\eta \propto \frac{(h\nu - q\Phi_B)^2}{h\nu}. \tag{3}$$

Fitting the observed data with Eq. (3), the barrier height ($q\Phi_B$) of 1.64 eV was obtained. One can see that although it is very hard to measure the barrier height of a LCMO/NSTO Schottky junction by current-voltage measurement, it can be determined by internal photoemission.

In conclusion, heterojunctions composed of LCMO and NSTO were fabricated. Current-voltage measurement implied that the transport of the junction is dominated by tunneling process. The junctions have response to ultraviolet and visible light. A QE of about 86% was achieved at incident photon energy of about 3.95 eV. The barrier height of 1.64 eV was determined by the internal photoemission.

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