Photovoltaic effect in $La_{0.7}Ce_{0.3}MnO_{3-\delta}$/$SrTiO_3$-Nb heterojunction and its oxygen content dependence

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The photovoltaic effect (PVE) of a heterojunction composed of a $La_{0.7}Ce_{0.3}MnO_3$ (LCE) film and a 0.5 wt. % Nb-doped $SrTiO_3$ crystal has been experimentally studied. A strong PVE was observed, and the maximum photovoltage was ~54.1 mV, when the LCE film was exposed to light with a wavelength (λ) of 460 nm and a power of ~6.5 μW. The PVE remains significant up to $\lambda = 660$ nm, though it decreases gradually with the increase of wavelength. Oxygen release of the LCE film depresses the PVE considerably and modifies the rectifying property of the junction. A logarithmic variation of photovoltage with junction resistance was observed. The weakening of the ferromagnetic order of the LCE film due to the incorporation of oxygen vacancies may be the reason for the depression of the PVE. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1769079]

There were several attempts to fabricate heterojunctions using manganites and other perovskite oxides, and it has been found that *p–n* junctions thus obtained can demonstrate an excellent rectifying property after properly controlling dopant species and the doping level of the oxides.[1–3] A recent study further revealed the magnetically tunable character of the manganite-based junction: the diffusion/breakdown voltage and the junction resistance undergo a great change under external magnetic field.[4] Though the detailed physics is still not clear at present, it is apparent that these phenomena simply reflect the behaviors of equilibrium charge carriers in the junction. It is interesting to note that many important properties of conventional *p–n* junctions are associated with the creation, diffusion, and annihilation of extra carriers. When a junction is illuminated by light, extra holes and electrons are created and their drift under the built-in electric field in the depletion layer of the junction can produce a photovoltaic effect (PVE), and their annihilation gives out light. These are actually the bases of light-emitting diodes (LED), solar cells, and photosensors.

Compared with ordinary semiconductors, the manganites own a wide variety of special features. Among them, the strong electron correlation and the magnetic state dependence of the band structure are most remarkable.[5] Because of these complicated behaviors, the conventional semiconductor theory may be inapplicable to the manganites. With this in mind, it is obviously interesting to ask what behavior can be produced by the extra charge carriers for the manganite-based heterojunction. In this letter, we will perform a comprehensive study on the heterojunction composed of a $La_{0.7}Ca_{0.3}MnO_{3-\delta}$ (LCE) film and a $SrTiO_3$ crystal doped by 0.5 wt. % Nb (STON). Our focus is the relation between the PVE and the *I–V* (current vs voltage) characteristics as the oxygen content of the LCE film varies. A strong PVE was observed, and the maximum photovoltage is ~54.1 mV for the light illumination of ~6.5 μW ($\lambda = 460$ nm). Oxygen loss significantly weakens the PVE, and a close relation between the photovoltage and the junction resistance was observed.

A LCE/STON heterojunction was fabricated by growing a LCE layer on a rectangular STON substrate of (001) orientation, following the procedure reported elsewhere.[4] The film is 3×5 mm^2 in size and ~500 Å in thickness. To improve crystal quality and oxygen stoichiometry, the sample was maintained at 750 °C for 20 min in flowing O_2 gas after preparation (denoted as the as-prepared sample hereafter). The oxygen in the film has been tuned by annealing the sample in high vacuum ($\sim 2 \times 10^{-6}$ Torr): the sample was heated at a rate of 10 °C/min to a predetermined temperature (300 °C for the first annealing), maintained for 5 min, and then cooled to room temperature. After this thermal cycle, the in-plane resistivity, the *I–V* curve, and photovoltage of the LCE/STON junction were measured. This process was repeated to get the data corresponding to different oxygen content (the predetermined temperature was increased by 30 °C after each thermal cycle).

As indicated by an x-ray diffraction study, the film is single phase and epitaxially grown with the (001) axis aligning along the film normal. Resistivity measurement reveals a typical behavior of hole-doped manganites,[5] though LCE is assumed to be electron doped,[6] and the metal-to-insulator transition happens at $T_p \simeq 306$ K (Fig. 1). Vacuum annealing causes an increase of resistivity and a downward shift of T_p. These are signs of oxygen loss, and similar behaviors have been observed in other deoxidized manganites.[7,8]

Figure 2 shows the typical *I–V* characteristics measured at $T = 296$ K by tuning bias voltage. As previously reported,[1–3] the *I–V* curve exhibits an asymmetry for the positive and negative bias. There are two critical voltages, respectively, called diffusion voltage (V_d) and breakdown voltage (V_b), at which the current shows a snowslidelike increase. The small leakage current for the voltage between V_b and V_d indicates a large junction resistance ($R_j = V/I$), and a simple calculation gives $R_j \simeq 310$ kΩ in the zero bias limit

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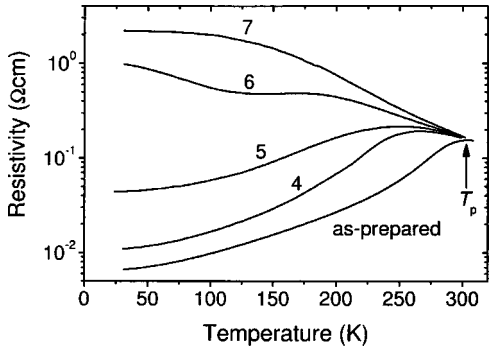

FIG. 1. The resistivity as a function of temperature for the LCE film of different oxygen content. Deoxidization was performed by annealing the sample at temperatures between 300 and 500 °C in a vacuum of $\sim 5 \times 10^{-6}$ Torr. The numbers in the figure mark the thermal cycles.

for the as-prepared sample. The *I-V* curve exhibits a great change after the sample is deoxidized in high vacuum: V_d reduces from ~ 0.49 to ~ 0.075 V and V_b from ~ -1.15 to ~ -0.43 V. The junction resistance also shows a systematic variation with the decrease of V_d (inset in Fig. 2). All these mean that oxygen loss drives the junction through different states.

The PVE of LCE/STON was studied at ambient temperature. The voltage across the junction was measured as the LCE film was perpendicularly illuminated by various dome LEDs (with wavelength $\lambda = 460$, 560, 600, and 660 nm, respectively). The illuminated area is $\sim 3 \times 3$ mm^2, across which the angular spread of the LED beam is below 4°. The average light intensity was measured by a calibrated photometer (Newport model 818) and controlled by adjusting the bias voltage on the LED. One of the most striking observations of the present work is the drastic increase of the photovoltage (V_{oc}) with light illumination. The strongest PVE occurs for $\lambda = 460$ nm, and V_{oc} can be as high as ~ 54.2 mV for the light power of $P = 6.5$ μW. Though the PVE weakens gradually with the increase of wavelength, V_{oc} is still as high as ~ 11.8 mV for $\lambda = 660$ nm under the same illumination (Fig. 3). The responsivity, defined as V_{oc}/P (at $P \to 0$) to describe the response of V_{oc} to light illumination, is $\sim 1.06 \times 10^4$ V/W for $\lambda = 460$ nm and $\sim 2.22 \times 10^3$ V/W for

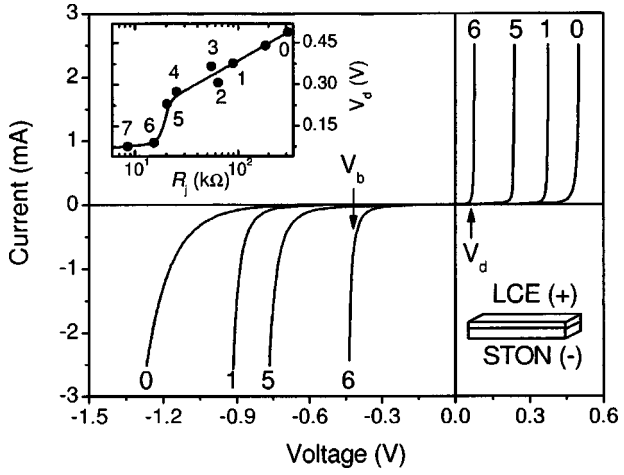

FIG. 2. The current-voltage characteristics measured at 296 K after different thermal cycles. The top inset displays the relation between diffusion voltage and junction resistance in the zero bias limit, and the bottom inset shows the schematic electrode setting for the *I–V* curve and the V_{oc} measurements. The numbers are thermal cycles (0=as-prepared).

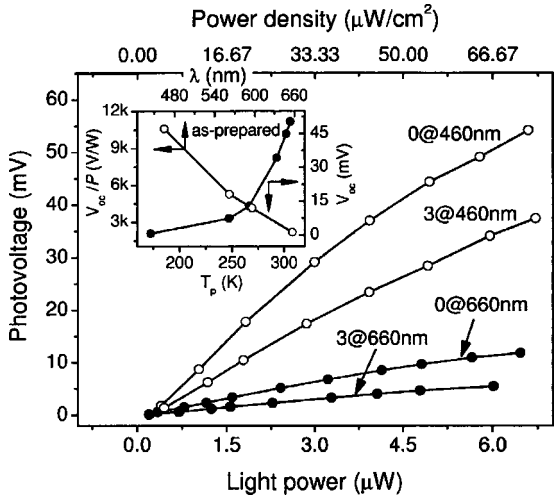

FIG. 3. The photovoltage (V_{oc}) as a function of light power for selected wavelengths of $\lambda = 460$ and 660 nm (illuminated area 3×3 mm^2) Thermal cycle at λ is marked for each curve. The inset displays the $V_{oc}/P - \lambda$ relation (white symbols) for the as-prepared sample and the $V_{oc} - T_p$ dependence (black symbols) for the light of $\lambda = 460$ nm and $P = 6$ μW, where T_p is used to characterize the oxygen effects of LCE.

$\lambda = 660$ nm (as shown in the inset of Fig. 3). It is interesting to note that the responsivity of the bolometer, composed of a carefully chosen $La_{0.7}(Pb_{1-x}Sr_x)_{0.3}MnO_3$, is ~ 100 V/W for the light of $\lambda = 940$ nm and the bias current of 1.2 mA.[9] The response of the bolometer could be even weaker to visible light, regarding that the infrared light is more effective in producing thermal effects. This result shows the obvious advantage of LCE/STON as a photosensor over the manganite bolometer.

The deoxidization of the LCE film causes a rapid decrease of V_{oc}, especially in the beginning of oxygen release. Under the illumination of 460 nm light ($P = 6$ μW), V_{oc} is ~ 50 mV for the as-prepared sample and ~ 0.6 mV after repeated vacuum annealing, reducing by nearly two orders of magnitude. The oxygen effects are reversible, and the original V_{oc} can be recovered by annealing the film in O_2 atmosphere. The inset in Fig. 3 also presents the variation of V_{oc} with T_p, where T_p is used to characterize the oxygen content in LCE, based on the practically linear relation between T_p and oxygen content for the manganites.[7,10]

According to Figs. 1 and 2, oxygen loss greatly modifies the *I-V* dependence of LCE/STON, causing the reduction of V_d, V_b, and R_j. We expect an unambiguous relation between these quantities that characterize the rectifying property of the junction and V_{oc}. Fortunately, this relation is found, and it has a simple form of $V_{oc}/P = \alpha \ln R_j$ for $P \to 0$ (Fig. 4), where α is a λ-dependent parameter. This result reveals the monotonic increase of V_{oc} with R_j, and proposes a possible way leading us to giant PVE, i.e., PVE can be enhanced through increasing junction resistance, which can be realized by, for example, adjusting the carrier concentration of LCE and STON, the band structure of LCE, or depressing the mutual atomic diffusion at the LCE/STON interface.

Significant PVE has also been observed by us in other manganite-based heterojunctions such as $LaMnO_3$/STON, $La_{0.67}Ca_{0.33}MnO_3$/STON, and $CaMnO_3$/STON, though the effect is not as strong as that in LCE/STON, which reveals the generality of this effect. On the analogy of the conventional *p-n* junction, light illumination can create extra charge

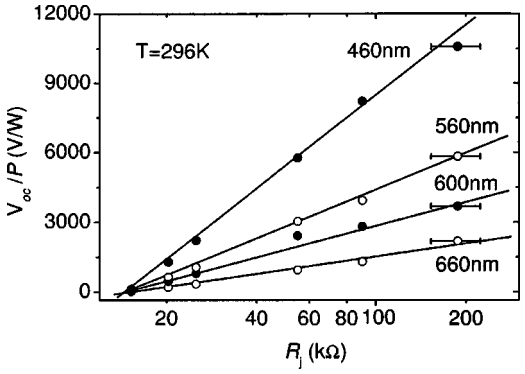

FIG. 4. The responsivity as a function of junction resistance (for $I \rightarrow 0$). The number in the figure denotes light wavelength.

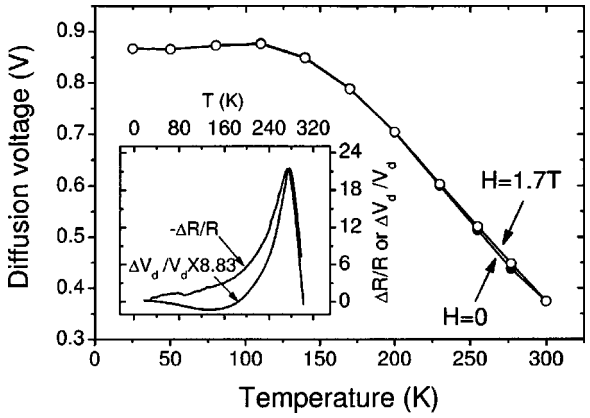

FIG. 5. The diffusion voltage as a function of temperature after first vacuum annealing. The inset plot shows the relative change of junction resistance and diffusion voltage under magnetic field.

carriers noting that the light for illumination has a photon energy (1.9–2.7 eV) of the same order of magnitude as the band gap of LCE or STON (~1 and ~3 eV, respectively).[11] The created charge carriers, electrons and holes, are swept to the bulk STON and LCE regions, respectively, by the built-in field on their appearance if they are located in the space-charge region. This in turn results in a charge accumulation in these two regions, thus producing a photovoltage. In this scenario, we can understand the increase of V_{oc} with R_j: A larger R_j usually corresponds to a thicker depletion layer and a higher built-in field, which implies more extra carriers accommodated by the space-charge region and a larger driving force for these carriers, thus, a higher V_{oc}.

A typical feature of the manganites, including LCE, is the coincidence of Curie temperature with T_p, and the correspondence of reduced magnetization to increased resistivity.[5] Therefore, a direct consequence of oxygen loss is the weakening of the ferromagnetic order of LCE based on the resistivity data in Fig. 1. The change of the magnetic state of LCE could be the main reason for the variation of the *I-V* curves and V_{oc}, though the altered carrier density may also have an effect. In fact, we have observed an exact correspondence between $R_j(H)/R_j(0)-1$, the magnetoresistance of the junction, and $V_d(H)/V_d(0)-1$, the relative change of diffusion voltage under magnetic field (Fig. 5). As is well known, the former arises from the increase of magnetization induced by magnetic field. The correlation between these two quantities manifests the magnetic origin of $V_d(H)/V_d(0)-1$: The enhancement/depression of the magnetization of LCE causes the increase/decrease of V_d. This is further confirmed by the appearance of a rapid increase of V_d below the Curie temperature in other junctions such as $La_{0.32}Pr_{0.35}Ca_{0.33}/O_3/STON$[4] and $La_{0.67}Ca_{0.33}MnO_3/STON$ (not shown). The ferromagnetic transition causes an increase of V_d by splitting the spin-up and spin-down e_g bands. As a result, the thickness of the depletion layer, the strength of the built-in electric field, and, correspondingly, the PVE were enhanced.

In conclusion, the LCE/STON heterojunction exhibits a strong PVE, and the maximum photovoltage is ~54.1 mV, appearing when the LCE film is exposed to the light with a wavelength of $\lambda = 460$ nm and a power of ~6.5 μW. The PVE remains significant up to $\lambda = 660$ nm, though it decreases gradually with the increasing wavelength. Oxygen release of the LCE film depresses the PVE considerably in the meantime modifying the rectifying property of the junction, and a logarithmic variation of photovoltage with junction resistance is observed. The weakening of the ferromagnetic order of the LCE film due to the incorporation of oxygen vacancies may be the reason for the depression of the PVE.

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