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Temperature-dependent photovoltaic effects in the manganite-based heterojunction

J. R. Sun[a] and B. G. Shen
State Key Laboratory for Magnetism, Institute of Physics and Centre for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, China

Z. G. Sheng and Y. P. Sun
Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230036, China

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Strong temperature-dependent photovoltaic effects have been observed in the heterojunction composed of a $La_{0.32}Pr_{0.35}Ca_{0.33}MnO_3$ (LPCM) film and a 0.5 wt % Nb-doped $SrTiO_3$ substrate. The photovoltage shows a monotonic increase with the decrease of temperature, and its relative change can be as large as ~7000% for a modest light intensity of 20 mW (wavelength=632 nm) when cooled from room temperature down to 17 K. The synchronous variation of photovoltage and the magnetization of LPCM indicates the magnetic origin of the temperature dependence of the photovoltaic effect. It is suggested that the temperature affects the photovoltaic effect by modifying the magnetic order, then the band structure of LPCM. An enhancement of the photovoltaic effect under strong light illumination is also observed, which is probably a result of illumination-induced change of the band structure of LPCM. © *2004 American Institute of Physics*.

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The electronic structure of the perovskite-type manganese oxides exhibits a strong dependence on the magnetic state. It has been well established that when the manganites undergo a paramagnetic (PM) to ferromagnetic (FM) transition, the two degenerated e_g subbands, associated with the spin-up and spin-down states, respectively, will experience a band splitting.[1] This assigns the manganites a magnetic tunable semiconductor character that is particularly valuable in the design of artificial materials and devices with various interesting temperature–magnetic field-amendable behaviors. A typical example of the manganite-based artificial material is the *p*–*n* heterojunctions composed of properly divalent ion-doped $LaMnO_3$ and La/Nb-doped $SrTiO_3$.[2–5] In addition to the excellent rectifying property,[2–4] it has been found that the diffusion potential (breakdown voltage) and the resistance of these kinds of junctions experience a dramatic increase at the temperature corresponding to the magnetic transition of the manganites. A great modification of magnetic field to the rectifying behavior of the junction was also observed.[5]

Although the underlying physics remains to be explored, 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 features of the *p*–*n* junctions are associated with extra charge carriers, which reflect a completely different aspect of the *p*–*n* junction. The electronic processes associated with these charge carriers and the accompanied effects are not only fundamentally but also technologically interesting, especially when the manganite exhibits a magnetic order-dependent feature, considering the fact that they are the basis of light-emitting diodes, photosensors, and many other optoelectronic devices.[6] Based on these considerations, in this letter, we will present a comprehensive study on the photovoltaic effect (PVE) of manganite *p*–*n* heterojunctions, which directly relates to the creation, diffusion, and annihilation of extra charge carriers. Special attention has been paid to the temperature dependence of the PVE, especially the relation between the PVE and the magnetic and rectifying properties of the junction.

A bilayer heterojunction has been prepared by depositing a $La_{0.32}Pr_{0.35}Ca_{0.33}MnO_3$ (LPCM) film of 500 Å on a 0.5 wt % Nb-doped $SrTiO_3$ (STON) crystal using the laser ablation technique following the procedure described elsewhere,[5] and the total area of the junction is 3×4 mm^2. X-ray diffraction indicates an epitaxial growth of the LPCM film on STON with the (001) axis aligning along the normal of the film plane.

The transport and rectifying behavior of this *p*–*n* junction have been reported in a prior paper.[5] In this letter we will focus on its PVE when LPCM undergoes a magnetic transition. The temperature of the sample was controlled by a cryogenic refrigerator, and a He-Ne laser, which can provide a laser beam of the wavelength of 632 nm and the intensity (P) up to 25 mW, was used as light source. The voltage on the two electrodes of LPCM and STON was recorded as the top electrode (LPCM) was perpendicularly illuminated (the illuminated area is ~0.12 cm^2).

Figure 1 exemplifies the response of photovoltage (V_{oc}) to light illumination measured at a selected temperature $T=50$ K ($P=20$ mW). A sizeable PVE is observed, and the photovoltage shows a quick switch between ~0 and ~14.6 mV corresponding to the “light on” and “light off.” V_{oc} is stable for a constant illumination, unaffected by the repeated light on and off. Measurements performed at other temperatures between 17 and 296 K yield similar results. These data confirm unambiguously that light illumination does produce a significant and stable voltage.

Figure 2 shows the temperature-dependent photovoltage measured for different light illuminations. A monotonic increase of V_{oc} with a decrease of temperature is observed,

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[a] Electronic mail: jrsun@g203.iphy.ac.cn

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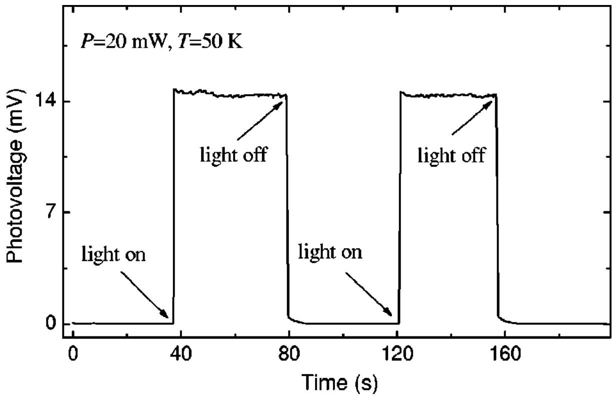

FIG. 1. Response of photovoltage to light illumination measured at a constant temperature of 50 K under the light intensity of 20 mW ($\lambda = 632$ nm).

although the detailed V_{oc}–T relation slightly depends on light intensity. For the light intensity below 8 mW, with the decrease of temperature, V_{oc} first displays a slow and smooth increase (I), then grows rapidly in the temperature region between 150 and 200 K (II), and, finally, saturates at a constant value below 100 K (III). This is reminiscent of the PM-to-FM transition of the LPCM film. A simple calculation reveals that, from $T = 296$ down to 17 K, V_{oc} increases from 0.047 to 2.57 mV for $P = 4$ mW and 0.24 to 17.44 mV for $P = 20$ mW; the maximum relative change is ~7100%. The main feature of the V_{oc}–T relation remains when P exceeds 8 mW except for that the V_{oc} saturation is replaced by an accelerated increase towards low temperatures. The increase of V_{oc} with the decrease of temperature could be a general feature of the PVE of the manganite junction because similar behaviors have also been observed in $La_{0.67}Ca_{0.33}MnO_3$/STON (not shown).

It has been known that the manganite is a semiconductor with a narrow band gap of ~1 eV.[1] Therefore, photocarriers can be created in the junction by light illumination through exciting electrons across the band gap (photon energy ≈2 eV). To counteract the current thus produced, a voltage has to be established between the two electrodes of the junction. This is the origin of the photovoltage.[6] At low temperatures, a large bias voltage is required to establish a current that counterbalances the photocurrent due to the reduction of the concentration of thermal charge carriers. This actually implies an increase of photovoltage. This analysis seems to be consistent with the experiment observation that the PVE enhances at low temperatures. However, the presence of three different processes for the variation of V_{oc} with temperature in Fig. 2 indicates that the actual situations in the LPCM/STON junction may not be so simple.

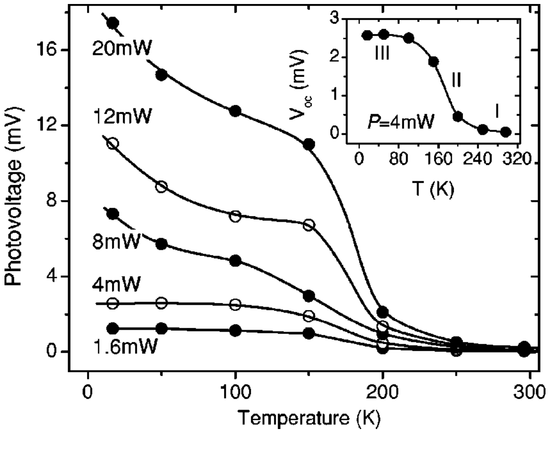

FIG. 2. Photovoltage as a function of temperature measured under different light intensity. Inset is a close view of the V_{oc}–T dependence for a weaker light illumination ($P = 4$ mW). Solid lines are guides for the eye.

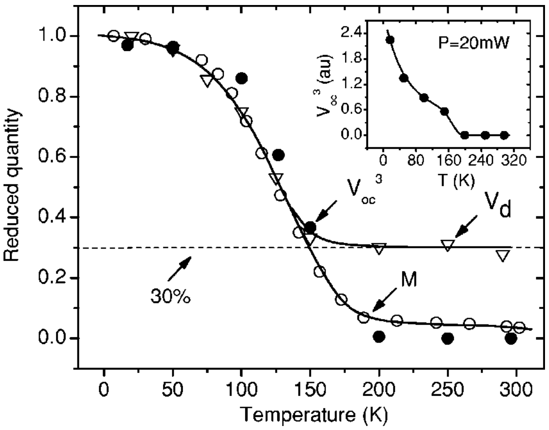

FIG. 3. Comparison of the normalized $V_d(T)$, $M(T)$, and $V_{oc}^3(T)$ relations. The $M(T)$ curve was measured under a field of 0.1 T in the field-cooling mode, and the $V_{oc}^3(T)$ curve was obtained under the light intensity of 4 mW. The inset plot shows the photovoltage corresponding to the light intensity of 20 mW. Solid lines are guides for the eye, and the dashed line marks the expected threshold for magnetic percolation.

As proved by various experiments, the manganites undergo a change in band structure with a decrease in temperature: the spin-up and spin-down subbands split in the FM state. This process produces two possible consequences. The first one is the variation of the concentration of photocarriers, which depends strongly on the energy band of the junction, and the second one is the change of the thickness of the depletion layer, which bears a close relation to the diffusion potential that is determined by the relative difference of the band structures of LPCM and STON.[6] All of these show a corresponding change of photovoltage with the development of the FM order of LPCM, and could be the reason for the complex V_{oc}–T relation observed, noting the fact that only the photocarriers that locate at or can reach, by diffusion, the depletion region directly contribute to photovoltage.

These analyses actually imply a strong interplay between the magnetic and rectifying properties and the PVE of the LPCM/STON junction. This correlation is indeed observed in Fig. 3, in which the normalized diffusion potential of LPCM/STON, $V_d(T)$, magnetization of LPCM, $M(T)$, and $V_{oc}^3(T)$ are presented. An interesting observation is that the three sets of data collapse into a common curve below $T = 150$ K, exhibiting a synchronous variation of M, V_d and V_{oc}^3. This result unambiguously proves that the change of magnetic order does induce a change in the band structure of LPCM or in the diffusion potential of the LPCM/STON junction, and these are the main factors affecting the PVE, although temperature itself may also have an effect. The decoupling of the M and V_d correlation above 150 K may be a result that the FM order does not prevail when the reduced magnetization is below ~30%, a value near the percolation threshold for a three-dimensional system with a cubic structure.[7] As a result, changes in the band structure are not obvious, and thus V_d remains constant.

It has been theoretically predicted that at a constant temperature V_{oc} will vary with light intensity as[6]

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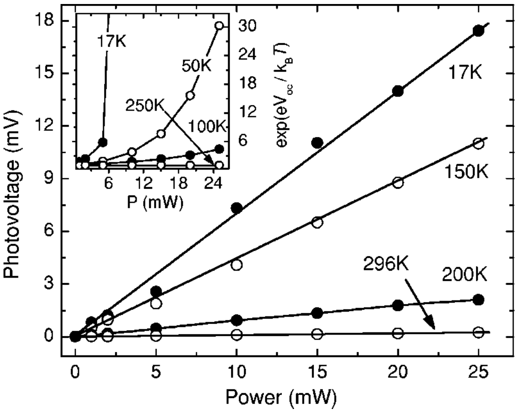

FIG. 4. Photovoltage as a function of light intensity measured at fixed temperatures. Inset shows an exponential plot of photovoltage against light intensity. Solid lines are guides for the eye.

$$V_{oc} = (k_B T/e)\ln(1 + \beta P), \tag{1}$$

where k_B is the Boltzmann's constant, e the electron charge, $\beta \propto \exp(E_g/k_B T)$ (E_g is the band gap). Although this equation has been derived for the idealized p–n diode, and the effects due to the creation/annihilation of extra carriers in the depletion region and the presence of significant electrical leakage[5] have not been considered, we hope that the underlying physics may not change too much for LPCM/STON. Noting the fact that the band splitting with the decrease of temperature in LPCM can cause an exponential increase of β, the strong V_{oc}–M correlation in Fig. 3 can be understood qualitatively.

Deviations from the systematic in Fig. 3 appear when the light intensity exceeds 8 mW due to the accelerated increase of V_{oc} below 100 K (inset in Fig. 3). The strong illumination-induced anomaly can also be seen from the V_{oc}–P relation obtained at fixed temperatures. Figure 4 depicts an essentially linear dependence of V_{oc} on P regardless of light intensity and temperature. According to Eq. (1), however, V_{oc} would increase linearly with P, when the latter is small, and logarithmically, when $\beta P \gg 1$. This implies that a much faster growth of the experimental V_{oc} with P occurs than theoretically expected (inset in Fig. 4), indicating the presence of extra effects in our heterojunction.

Based on Eq. (1), in the case of a constant temperature, the only parameter affecting V_{oc} is β. It has been revealed that light illumination can affect the magnetic structure of the manganite, and a collapse of charge-ordered state, characterized by a significant magnetization increase or resistivity decrease, due to the illumination of visible light or x rays, has been reported in the Pr-doped manganites.[8,9] Noting the close relation between the magnetic order and the band structure in the manganese oxides, it could be a reasonable postulation that light illumination, when strong enough, induces a considerable change of the energy band of LPCM, thus the V_{oc} anomaly for $P > 8$ mW. (We have not measured the magnetization of LPCM under light illumination to check this effect because of the limitation of experiment condition.)

In summary, the PVE of the heterojunction composed of a $La_{0.32}Pr_{0.35}Ca_{0.33}MnO_3$ (LPCM) film and an Nb-doped $SrTiO_3$ (STON) crystal has been experimentally studied, and a dramatic increase of photovoltage with the decrease of temperature has been observed. A comparison of photovoltage, diffusion potential, and magnetization, which characterizes the magnetic order of the LPCM film, shows a synchronous variation of these quantities, which is indicative of the magnetic origin of the PVE in LPCM/STON. It is suggested that the development of ferromagnetic order on cooling affects the PVE by modifying the band structure of the LPCM film. An enhancement of the PVE produced by strong illumination has been observed, which is probably a result of illumination-induced change of the band structure of LPCM.

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