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Manganite-based heterojunction and its photovoltaic effects

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A heterojunction is fabricated by growing a $La_{0.29}Pr_{0.38}Ca_{0.33}MnO_3$ (LPCM) film on the 0.5 wt % Nb-doped $SrTiO_3$ (STON) substrate, and its properties have been experimentally studied. In addition to fairly good rectifying behavior, the heterojunction exhibits a significant photovoltaic effect. The photovoltage on the two electrodes LPCM and STON increases almost linearly with the power of the laser beam ($\lambda = 532$ nm) at a rate of ~ 0.19 V/W, and no tendency to saturation is observed up to the light power of 100 mW. The lifetime of the extra carriers is between 7 and 9 ms (slightly pulse laser energy dependent), obtained from the decay of photovoltage after shutting down light illumination. The present work shows a great potential of the manganite-based heterojunction as photoelectric devices. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1702128]

Doped manganese oxides have been a focus of intensive studies since the discovery of colossal magnetoresistance (MR) in this kind of materials.[1] Both the underlying physics and the practical applicability of the colossal MR effects are topics of great interest. After significant efforts, it becomes more and more obvious that the potential of manganites is in the construction of magnetoresistive devices. In addition to the extraordinary MR effects, the perovskite materials own a wide variety of properties such as ferroelectricity, piezoelectricity, and superconductivity, which allow the design and composition of artificial materials with diverse properties. In fact, there have been attempts to prepare new magnetic tunnel junctions from the manganites soon after the discovery of the huge MR effects. The first manganite tunnel junction with considerable MR appeared in 1996.[2] A recently developed trilayer junction $La_{0.67}Sr_{0.33}MnO_3/SrTiO_3/La_{0.67}Sr_{0.33}MnO_3$ even showed a MR as high as $\sim 1800\%$ at low temperatures.[3] Replacing one of the two ferromagnetic (FM) layers in the above junction with an *n*-type semiconductor $La_{0.05}Sr_{0.95}TiO_3$, Sugiura and co-workers obtained a *p-i-n* junction with an excellent rectifying property.[4] Tanaka *et al.* further simplified the fabrication by removing the intermediate insulating layer, constructing a *p-n* junction simply by $La_{0.9}Ba_{0.1}MnO_3$ and Nb-doped $SrTiO_3$.[5]

However, work on the manganite-based oxide junction is still rather limited. Many fields concerning the junction remain to be explored, particularly the effects associated with extra (nonequilibrium) carriers, which are the bases of photodetectors and photodiodes. In this letter, a heterojunction was prepared by combining Nb-doped $SrTiO_3$ (STON) with $La_{0.29}Pr_{0.38}Ca_{0.33}MnO_3$ (LPCM). The former is an *n*-type semiconductor while the latter is *p* type. The current–voltage ($I-V$) dependence of the junction, its relation with the magnetic state of the LPCM film, and the effects of nonequilibrium holes and electrons, created by laser illumination, have been investigated.

The heterojunction was fabricated by growing a LPCM film on the STON crystal using laser ablation. The substrate was kept at $\sim 800\,^{\circ}C$ and the O_2 pressure at 100 Pa during the deposition. The film thickness is ~ 500 Å, controlled by deposition time. As confirmed by x-ray diffraction study, the film is epitaxial, with the (001) axis aligning along the film normal, and high single crystal quality.

Figure 1 shows the resistivity as a function of temperature for the LPCM film measured by four-probe technique. The film is metallic at low temperature ($d\rho/dT > 0$) and semiconductive ($d\rho/dT < 0$) above T_p, where T_p is a temperature corresponding to the maximum of the resistivity. T_p is significantly low (~ 150 K), which is a result of the incorporation of smaller Pr^{3+} ions (compared with La^{3+}).

Figure 2 presents the $I-V$ characteristics of the *p-n* junction measured by tuning bias current. It indicates that the $I-V$ curves are strongly asymmetric with respect to the origin. The voltage exhibits a tendency to saturation at V_D for the positive bias current, but keeps growing rapidly far be-

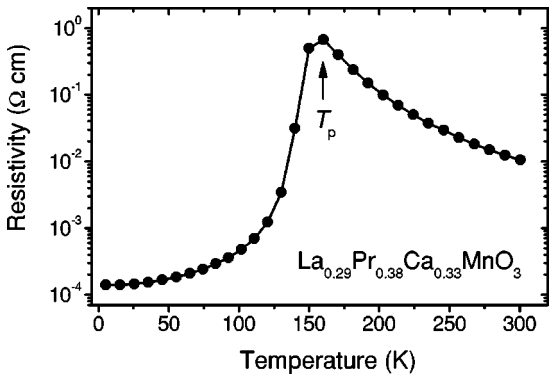

FIG. 1. Resistivity of $La_{0.29}Pr_{0.38}Ca_{0.33}MnO_3$ (LPCM) as a function of temperature. Arrow in the figure marks the temperature for the metal-to-insulator transition.

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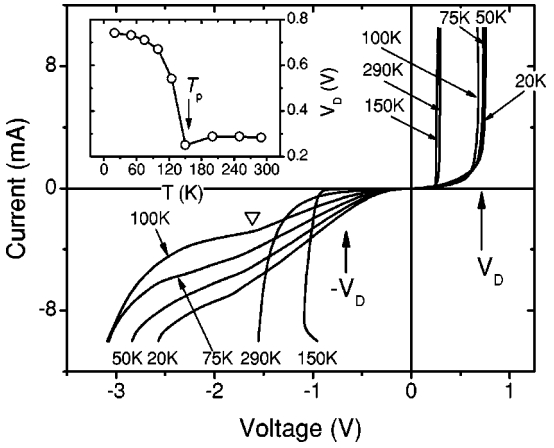

FIG. 2. Current–voltage characteristics of the LPCM/STON junction measured at selected temperatures between 20 and 290 K. The concavity in the $I-V$ curve is marked by a triangle. Inset displays the diffusion voltage as a function of temperature.

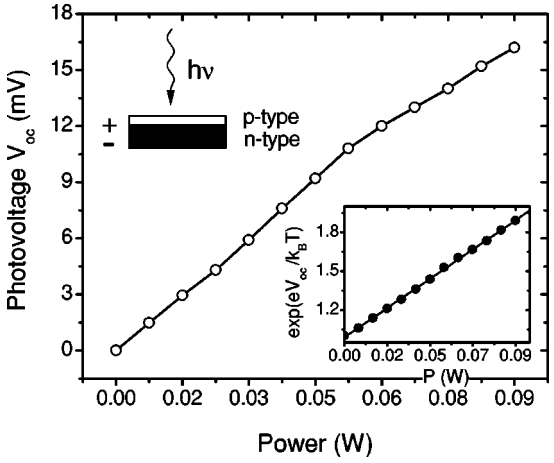

FIG. 3. Photovoltage as a function of light power ($\lambda = 532$ nm) measured at room temperature. Inset is a plot of $\exp(eV_{oc}/k_BT)$ vs P ($T = 295$ K); solid lines are guides for the eye.

yond V_D when the current is applied in the opposite direction. It has been proved that the band diagram description is applicable to the manganites. In this scenario, V_D may be the diffusion voltage between LPCM and STON, which appears when a semiconductor is brought into contact with the other with a different carrier type or band structure. The sudden current increase usually occurs when the applied field exceeds V_D. It is worthy of notice that the current increase at V_D remains steep in our junction as temperature varies, which reveals the high quality of LPCM/STON considering that lattice defects in the junction region usually flattens the $I-V$ curves as occurred in the *p-n* junction of Tanaka *et al.*[4,5] An interesting feature of our junction is that V_D decreases significantly near T_p and remains essentially constant above T_p (inset of Fig. 2). This observation is consistent with the half-metal character of the manganites. In the manganites, spin-up and spin-down e_g bands act as valence and conduction bands, respectively, and the increase in temperature could result in a diminishment of band gap due to the reduction of ferromagnetic order, which may be responsible for the variation of V_D. The gradual slowing down of the voltage growing for the backward bias is a sign of electric breakdown. The complex $I-V$ curves for negative bias (for example, the obvious concavity marked by the triangle) could be a result of inhomogeneity noting the large junction area (3×5 mm^2) measured. Therefore, we observed fairly good rectifying behavior in our heterojunction.

The above studies indicate that the behavior of the equilibrium charge carrier of the heterojunction under electric field can be well understood based on the theory of the conventional *p-n* junction. It is an interesting question as to whether the behavior of extra charge carrier can also be ascribed to the same frame. To get an insight into this problem, we further investigated the photovoltaic effects of our heterojunction. The measurement was undertaken at room temperature. To produce nonequilibrium holes and electrons, the surface of the LPCM film is illuminated by a laser beam of the wavelength of 532 nm, and the voltage on the two electrodes of LPCM and STON is measured as a function of laser power (P). As shown in Fig. 3, these results indicate that light illumination can produce a significant photovoltage (open circuit voltage V_{oc}), and the V_{oc} is ~3 mV for $P = 15$ mW and ~14 mV for $P = 76$ mW, increasing nearly linearly with laser power at a rate of ~0.19 V/W. A careful analysis indicates that the exact V_{oc}-P dependence can be described by $V_{oc} = k_BT/e \ln(1+\alpha P)$ with $\alpha = 7.53$ (inset of Fig. 3), where k_B is the Boltzmann constant, e the electron charge, and $T = 295$ K at room temperature. This is a relation predicted by semiconductor theory for a standard *p-n* junction.

Different from the case at low temperatures, the band splitting of LPCM could be ascribed to the Jahn-Teller effect above T_p, which causes a separation of the two degenerated e_g orbitals. The energy gap between the corresponding valence and conduction bands is ~1.2 eV,[6] which is considerably smaller than the energy gap between the spin-up and spin-down bands below T_p. This is consistent with the observation that V_D is small and nearly independent of temperature above T_p (inset plot of Fig. 2). In contrast, the band gap of STON is ~3.2 eV.[4] Therefore, it is possible for a photon to excite an electron-hole pair in the LPCM film (the photon energy is ~2.33 eV). Meanwhile, a strong built-in electric field is expected in the junction region of LPCM/STON. A simple calculation indicates that the hole density of LPCM is 10^{21}/cm^3 (0.33/Mn), and the electron density of STON is 10^{19}/cm^3. Therefore, the thickness of the depletion layer is rather thin, only a few nanometers for LPCM and ~30 nm for STON. Based on these data, the maximum built-in field can be as large as $\sim 10^5$ V/cm. As a result, extra holes and electrons in the junction region will be driven rapidly to the *p* and *n* regions, respectively, on their appearance by the built-in field, while those carriers outside this region migrate towards the junction region by diffusion. The photovoltage is actually the voltage produced by the charge accumulation on the top and bottom sides of the junction. This analysis implies a photovoltage opposite to the built-in field, i.e., from LPCM to STON, which is also consistent with the experiment results. It is obvious that the more the extra carriers are, the bigger the voltage will be.

Figure 4 displays the spectral response of LPCM/STON, which shows a visible kink at ~2 eV and a gradual decrease below 2 eV of the responsivity. The broad long-wavelength cutoff could be a reflection of the vague band edge of the

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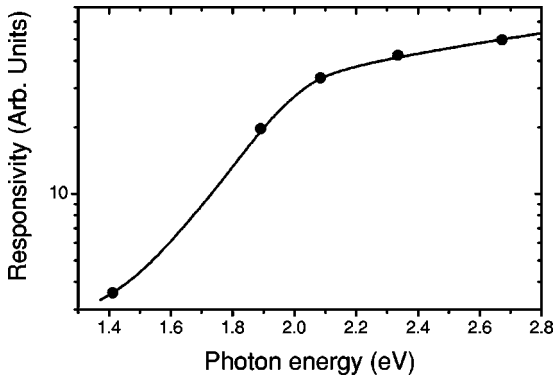

FIG. 4. Spectral response of LPCM/STON; solid line is a guide for the eye.

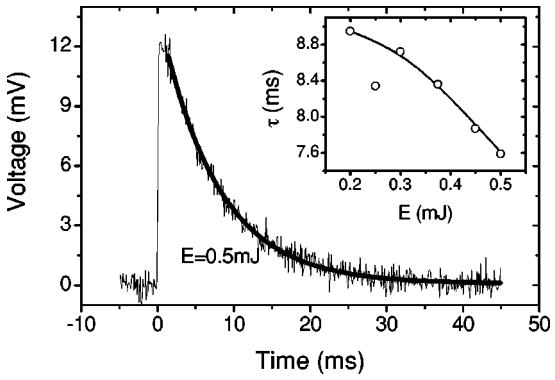

FIG. 5. Variation of photovoltage with time after the light illumination ($\lambda = 532$ nm). Thick line is a fitting to the exponential decay law $V_{oc} \propto \exp(-t/\tau)$. Inset displays pulse energy dependence of lifetime (τ).

manganites.[1] This result indicates that the effective band gap of LPCM/STON is between 1.4 and 2 eV, which is larger than 1.2 eV, the band gap of LPCM, and smaller than 3.2 eV, the band gap of STON. As discussed above, Jahn-Teller effect causes a distortion of the MnO_6 octahedra, resulting in the band gap of LPCM. However, the presence of tensile strain in LPCM due to the LPCM–STON lattice mismatch may enhance the MnO_6 distortion, especially near the LPCM–STON interface, thus the band gap of LPCM. Furthermore, band offset between LPCM and STON could also have an effect on the band structure of LPCM near the depletion layer, making the latter different from that of LPCM alone.

It is obvious that not all the extra carriers contribute to V_{oc}. Part of the holes and electrons annihilate with each other during the diffusion process, which begins accompanying the appearance of hole-electron pairs. This concerns the problem of the diffusion length or lifetime of nonequilibrium carriers. Based on the previous results, V_{oc} is nearly linearly increases with P (proportional to the density of extra carriers) when the latter is not large. Therefore, information on the annihilation process of the nonequilibrium carriers can be extracted from the decay of V_{oc} after shutting down light illumination. Figure 5 shows the photovoltage as a function of time after the radiation of a rectangular laser pulse (pulse width 10 ns). As expected, an exponential decay of V_{oc} is observed, $V_{oc} \propto \exp(-t/\tau)$, and a simple analysis gives the lifetime of 7–9 ms for the nonequilibrium carriers (slightly energy dependent as shown in the inset in Fig. 5). As is well known, the lifetime of the extra carriers is mainly determined by the imperfection of the materials such as impurities and structure defects. The longest lifetime has been obtained in Ge single crystal, and takes the values between 0.1 and 10 ms. The lifetime in LPCM/TON is comparable to that of Ge. Considering a fact that most of the extra charge carriers in LPCM/STON may be contributed by the LPCM film (the band gap of STON is larger than the photon energy of the light of 532 nm), this result, therefore, in addition to confirming the high single crystal quality of LPCM, indicates that LPCM may possess a rather long diffusion length, which is desired by the high efficient photoelectric energy conversion. Therefore, after properly choosing the manganite, carefully calibrating the doping level, and improving the crystal quality, manganite-based heterojunction may be a potential candidate for photodiodes and photosensors.

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[1] For a review, see *Colossal Magnetoresistance, Charge Ordering, and Related Properties of Manganese Oxides*, edited by C. N. R. Rao and B. Raveau (World Scientific, Singapore, 1998); *Colossal Magnetoresistive Oxides*, edited by Y. Tokura (Gordon & Breach, London, 1999).
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