Rectifying and photovoltaic properties of the heterojunction composed of $CaMnO_3$ and Nb-doped $SrTiO_3$

J. R. Sun,[a] S. Y. Zhang, and B. G. Shen
State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

H. K. Wong
Department of Physics, The Chinese University of Hong Kong, Hong Kong, China

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A heterojunction composed of $CaMnO_3$ (CMO) and Nb-doped $SrTiO_3$ (STON) was fabricated and its properties were studied and compared with $La_{0.67}Ca_{0.33}MnO_3$/STON and $LaMnO_{3+\delta}$/STON p-n, junctions. This CMO/STON junction exhibits an asymmetric current–voltage relation similar to a *p-n* junction. The most remarkable discovery is that the magnetic state of the manganites has a strong impact on the rectifying behaviors. The diffusion voltage, which is the critical voltage for the current rush, shows a tendency to decrease/increase with the establishment of the antiferromagnetic/ferromagnetic order in the manganites of the junction. Similar to other manganite *p-n* junctions, CMO/STON also exhibits a significant photovoltaic effect, and the maximum photovoltage is ~2.2 mV under the illumination of ~7 mW light ($\lambda = 460$ nm). A qualitative explanation is given based on an analysis on the band diagram of the junctions. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1861112]

Perovskite manganites have been known for their huge magnetoresistance and many other interesting properties associated with the strongly coupled spin-charge-orbital degrees of freedom, and these have stimulated intensive studies on the physics underlying these extraordinary phenomena.[1] With the progress of the research, it becomes more and more apparent that combining manganites with other perovskite oxides could be a promising way both for the exploration of uncovered aspects of the former and for the design of artificial materials which may have practical uses. Based on this consideration, Sugiura and co-workers[2] fabricated the first *p-i-n* junction in 1999 using an *n*-type $La_{0.05}Sr_{0.95}TiO_3$ and a *p*-type manganite $La_{0.7}Sr_{0.3}MnO_3$ sandwiched by an insulating layer, and an excellent rectifying behavior was observed in a wide temperature range. Kawai *et al.*[3] further demonstrated that a p-n junction without the intermediate layer worked equally well. We also obtained a *p-n* junction exhibiting significant magnetic field effects.[4] The resistance of the junction undergoes a great change under external field. In the scenario of the buildup of interfacial potential due to the interlayer diffusion of holes and electrons between manganites and La or Nb-doped $SrTiO_3$ and the variation of this potential under external fields, these behaviors can be understood qualitatively.

Generally, the type of the dominative charge carriers in the manganite is controlled by divalent ion doping. However, it has been demonstrated that the presence of divalent ions influences not only the carrier type but also the band structure of the manganite. Take $La_{1-x}Ca_xMnO_3$ as an example. It is hole doped when x is below 0.5 and electron doped when x is above 0.5. With the increase of the content of Ca^{2+}, the band filling (e_g band) decreases and, finally, vanishes completely in $CaMnO_3$ (CMO). Different from hole-doped manganites, the conduction and valence bands of CMO will be of the e_g and t_{2g} character, respectively, according to the simple band model in Refs. 5 and 6. We noticed that most of the manganite heterojunctions were composed of hole-doped manganites and $SrTiO_3$:Nb(La), and the explanations are based on the consideration that the charge carriers in the two electrodes of the junction are different in type. It is interesting to ask whether the special electronic structure of CMO will affect the properties of the heterojunction. In this letter, we report on a study on a heterojunction composed of CMO and STON (0.5 wt % Nb-doped $SrTiO_3$). There are two interesting observations. The first one is the occurrence of the typical rectifying behavior and photovoltaic effect (PVE) similar to *p-n* junctions and the second one is the diminishment of diffusion voltage with the development of antiferromagnetic (AFM) order in CMO. Based on an analysis on band structure, a qualitative explanation is given.

The heterojunction CMO/STON was fabricated by growing a $CaMnO_3$ film on a Nb-doped $SrTiO_3$ substrate of the (001) orientation following the procedure described 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 deposition. For a comparison study, we also prepared other two heterojunctions composed of $La_{0.67}Ca_{0.33}MnO_3$ and STON (LCMO/STON) and $LaMnO_{3+\delta}$ and STON (LMO/STON), respectively, under the same condition.

As revealed by x-ray diffraction study, the films are single phase and epitaxially grown with the (001) plane parallel to the (001) surface of the substrate. Resistive measurement of the CMO film shows a semiconducting conduction of the form $\rho(T) \propto \exp(\varepsilon / k_B T)$ with $\varepsilon \sim 42$ meV above 130 K and $\varepsilon \sim 50$ meV below 120 K. A visible kink at ~125 K can be identified from the $\ln(\rho)$ vs $1/T$ curve, indicating a PM (paramagnetic) to AFM transition of the CMO film as confirmed by previous neutron diffraction studies.[7]

Figure 1 depicts the representative current–voltage (*I–V*) characteristics of CMO/STON and LCMO/STON measured by tuning current. It is interesting that CMO/STON exhibits a rectifying behavior similar to *p-n* junctions. The current is

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

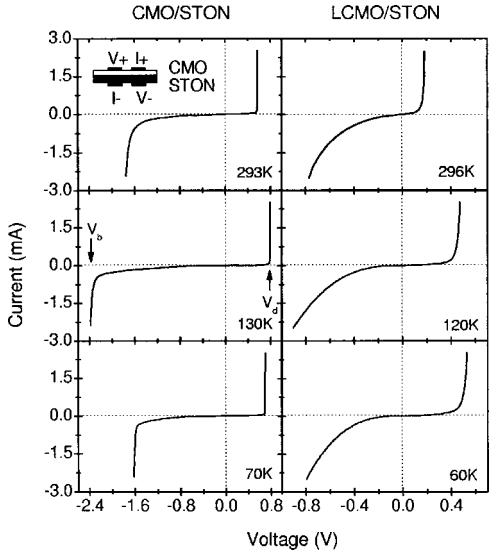

FIG. 1. Current–voltage characteristics of CMO/STON and LCMO/STON measured by tuning bias current. The top inset is a schematic electrode setting for the resistive measurement.

small for small bias voltage and grows steeply at two definite but unequal voltages. These two critical voltages are called diffusion voltage (V_d) and breakdown voltage (V_b), respectively, and their variation with temperature reflects the change of the band structure of CMO with respect to that of STON. In Fig. 2 the diffusion voltage is presented as a function of temperature (top panel). It is clear that V_d first shows a linear increase, at a rate of $\sim$1.5 mV/K, with the decrease of temperature, and gets its maximum value $\sim$0.8 V at T =125 K. Further cooling leads to a diminishment of V_d, and the junction features disappear completely below $\sim$25 K. This result indicates a strong correlation between V_d and the magnetic state of CMO noting the fact that the decrease of V_d begins at the AFM onset of the CMO film. It is possible that the band structure of CMO experiences a great change

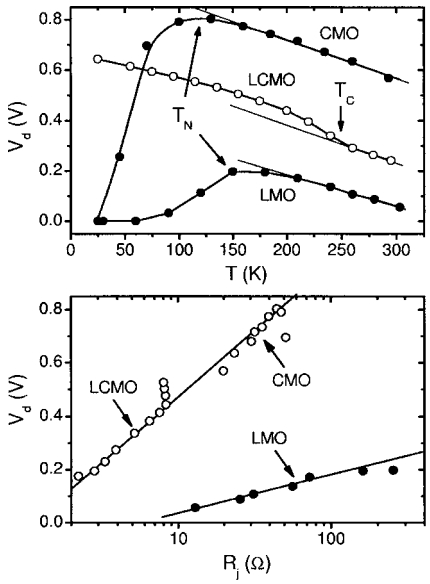

FIG. 2. Top panel: diffusion voltage as functions of temperature for LMO/STON, LCMO/STON, and CMO/STON. Bottom panel: a relation between diffusion voltage and junction resistance in the zero bias limit. Junctions are marked by the corresponding manganites. Straight lines show the similar V_d–T slopes for different junctions well above the magnetic transition temperatures.

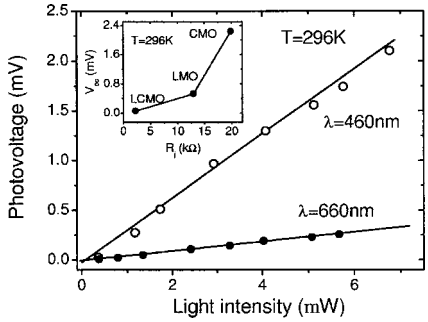

FIG. 3. Photovoltage (V_{oc}) of CMO/STON as a function of light intensity measured for selected wavelengths of λ=460 and 660 nm. The inset shows the V_{oc}–R_j relation for junctions illuminated by 460 nm light (7 mW). Junctions are marked by the corresponding manganites. Solid lines are guides for the eye.

disfavoring interfacial energy barrier when CMO transits into the AFM state. This seems not to be accidental, and a decrease of V_d is also observed in LMO/STON below $\sim$150 K, which is near the Néel temperature of LMO.[7] In contrast, V_d enhances with the establishment of FM order in LCMO/STON. All these clarify a fact that V_d grows in the FM state and reduces in the AFM state of the manganites.

There is a simple relation between the diffusion voltage and the resistance of the junction (R_j), defined by dV/dI of the I–V diode curve in the limit I–0. The bottom panel of Fig. 2 displays an exponential increase of R_j with V_d, and a plot of V_d against $\ln(R_j)$ has a slope $\sim$0.485 V/ln(Ω) for CMO/STON and LCMO/STON. This relation is also observed in LMO/STON but with an obviously small slope ($\sim$0.133), which may be an indication that the leakage current in LMO/STON is small. These results indicate again the presence of common features between CMO/STON and the other two *p-n* junctions. The monotonic increase of R_j with V_d can be understood taking into account the fact that a larger V_d is associated with a higher interfacial energy barrier. Electron tunneling across the energy barrier is unimportant even for LCMO/STON. A rough estimate gives a thickness for the space charge region over $\sim$100 Å adapting the electron density of $\sim 10^{19}/\mathrm{cm}^3$ in STON and hole density of $\sim 10^{21}/\mathrm{cm}^3$ in LCMO. This may be a reason that the typical behavior of a tunnel junction is not observed in our junctions.

The PVE of the junctions was studied at ambient temperature. The voltage across the junction was measured as the manganite films were perpendicularly illuminated by various dome LEDs (with wavelength λ=460 and 660 nm, respectively). The illuminated area is $\sim 3\times 3$ mm^2. The average light intensity was measured by a calibrated photometer (Newport model 818) and controlled by adjusting the bias voltage on the LED.

As shown in Fig. 3, light illumination produces significant photovoltage (V_{oc}). For CMO/STON, the strongest PVE occurs for λ=460 nm, and the V_{oc} is $\sim$2.2 mV for the light intensity of 7 mW. The increase of wavelength causes a decrease of the PVE, specifying a weakening of the efficiency of the long wavelength light in creating extra charge carriers. A considerable PVE is also observed in other two *p-n* junctions, though obviously weaker than CMO/STON. A further analysis shows that a larger R_j favors a higher V_{oc} (inset in Fig. 3). It should be emphasized that CMO behaves as a positive electrode in the V_{oc} measurement, which means a

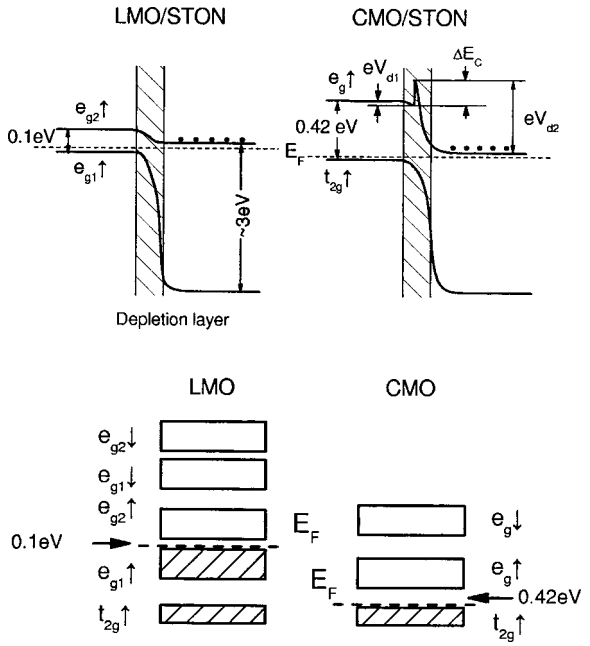

FIG. 4. Schematic diagram of the band structure for LMO/STON and CMO/STON and the Mn-e_g and Mn-t_{2g} energy bands for the corresponding manganites. The band offset in LMO/STON, which could be much smaller than that in CMO/STON, was not considered.

built-in electric field at the junction region from STON to CMO, similar to that occurred in typical *p-n* junctions.

We also prepared a heterojunction using $La_{0.7}Ce_{0.3}MnO_3$ and STON.[8] Though the former is assumed an electron-doped manganite,[9] the presence of cation vacancies or excess oxygen is possible, which makes the carrier type questionable. Different from $La_{0.7}Ce_{0.3}MnO_3$, CMO could be an electron-doped semiconductor when minor oxygen vacancies exist.[10] As, described above, CMO/STON possesses most of the typical features of a *p-n* junction. To get an explanation to these observations, a further analysis on the band structure of the manganite heterojunction is required.

In the hole-doped manganites, three Mn 3*d* electrons form the localized t_{2g} band. The remaining 3*d* electrons occupy two e_g bands ($e_g\uparrow$ and $e_g\downarrow$, classified according to spin orientation) that are energetically higher than the t_{2g} band. Because of the strong cooperative Jahn–Teller distortion of the MnO_6 octahedra, for LMO, each e_g band will further split into two subbands $e_{g1}\uparrow$ and $e_{g1}\uparrow$, each about 1 eV wide, with an indirect gap of the order of ~0.1 eV.[6,11,12] The lower $e_{g1}\uparrow$ band is fully occupied and the others completely empty. In contrast, there are only two e_g subbands of different spin orientation in CMO, and both are unoccupied. As a result, the conduction and valence bands of CMO will be mainly of the $e_g\uparrow$ and $t_{2g}\uparrow$ character, respectively, and the band gap is ~0.42 eV.[6] Theoretical calculations have suggested that the Fermi level is near the top of the lower e_g subband for LMO while of the lower t_{2g} band for CMO as shown in Fig. 4.[6] It is obvious that the introduction of Ca leads to a downward shift of Fermi level.

When a manganite film is deposited on the surface of STON, an energy barrier, that is, eV_d, can be established at the interface due to the mismatch between the Fermi levels/band structures of the two semiconductors. In LMO/STON, a positive V_d is established to prevent the electron diffusion from STON to LMO. The tendency of electron transferring from STON to CMO could be even stronger because of the lower Fermi level of CMO compared with LMO, which causes a larger band bending. As a result, a junction with the typical characters of a conventional *p-n* junction could be formed between CMO and STON despite of the completely different band structure of the former from the hole-doped manganite. Furthermore, the diffusion voltage is expected to be larger in CMO/STON than in LMO/STON because of the enhanced band gap in CMO. These analyses are consistent with the observation that V_d exhibits a monotonic growth with the increase of the Ca content. As shown in Fig. 5, V_d is ~0.06 V for LMO/STON, increases nearly linearly with the content of Ca, and reaches ~0.56 V in CMO/STON (T = 300 K). It is interesting to note that the observed V_d is greater than the expected value ~0.42 V. This could be ascribed to the band offset between CMO and STON, which becomes important due to the significant downward shift of the conduction band of CMO. In this case, the apparent diffusion voltage is jointly determined by V_{d1}, V_{d2}, and ΔE_C, the diffusion voltage of CMO, STON, and the conduction band mismatch of the two semiconductors. It is obvious that band gap plays a dominative role in determining diffusion voltage. Therefore, the schematic diagram in Fig. 4, though simple, provides a reasonable description to the experiment results.

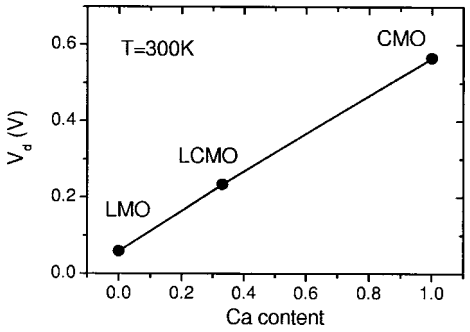

FIG. 5. Diffusion voltage as functions of the content of Ca.

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