Interfacial potential and photoelectronic properties of manganite heterojunction $La_{0.7}Ce_{0.3}MnO_3/SrTiO_3:Nb$

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The interfacial potential and photoelectronic properties of a heterojunction composed of $La_{0.7}Ce_{0.3}MnO_3$ and $SrTiO_3:Nb$ have been experimentally studied. A two-dimensional spatial distribution of the electrostatic potential across the $La_{0.7}Ce_{0.3}MnO_3/SrTiO_3:Nb$ interface is obtained by the holography technique of the transmission electron microscope, which reveals the presence of a depletion layer of 8 nm in thickness at 120 K and 3 nm at 296 K and a built-in electric field within this layer. Consequently, a complex yet significant photovoltaic effect is observed. It is found that the transient photocurrent is composed of two distinctive processes with the charging-like behavior, and the time constants are surprisingly larger than that expected for a photoelectronic process, ~30 and ~260 μs, respectively. It seems to be an intrinsic property of the manganite junction, and has nothing to do with external circuit and thermolelectric effect arising from light illumination. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2130724]

Sandwiching a $SrTiO_3$ layer of variant thickness between $La_{0.9}Sr_{0.1}MnO_3$ and $La_{0.05}Sr_{0.95}TiO_3$, Sugiura and collaborators fabricated the first manganite *p-n* junction that shows an excellent rectifying property in a wide temperature range.[1] Kawai *et al.* further demonstrated that the intermediate layer was unnecessary, and constructed a heterojunction displaying all the main features of a *p-n* junction by simply using $La_{0.9}Ba_{0.1}MnO_3$ and 0.1 wt % Nb-doped $SrTiO_3$.[2] We also obtained the *p-n* junction exhibiting significant magnetic field effects: the resistance of the junction undergoes a great change under external field.[3] In the scenario of the buildup of interfacial potential due to carrier diffusion and the variation of this potential under magnetic field, these behaviors can be understood qualitatively.

It is obvious that our understanding of the manganite heterojunction is based on the standard semiconductor theory. However, it is a question whether the single-electron band structure can capture all the main features of manganese oxides that exhibit strong electron correlation and other complicacy associated with spin, charge and orbital degrees of freedom. In fact, a possibility of long-range charge transfer between $La_{2/3}Ca_{1/3}MO_3$ and $YBa_2Cu_3O_{7-\delta}$, both are hole doped, has recently been reported in the multilayers composed of these two oxides.[4] A strong coupling between the magnetic moments in adjacent layers was also observed.[5] These behaviors are obviously different from those of the conventional semiconductors. Therefore, a direct measurement of interfacial potential of the junction is of especial importance, though analyses on *I-V* relation and capacitance can also provide a rough profile for this potential. We noticed that most of the previous work focused on the apparent properties of the junction. The only work on band structure, to our knowledge, was given by Sugiura *et al.* based on capacitance measurement.[1] In this letter, we will present a comprehensive study on the interfacial electrostatic potential, particularly its spatial distribution, and the corresponding rectifying and photoelectronic properties of a heterojunction composed of $La_{0.7}Ce_{0.3}MnO_3$ (LCE) and 0.5 wt % Nb-doped $SrTiO_3$ (STON). A spatial distribution of electrostatic potential is obtained by the holography technique of the transmission electron microscope (TEM), which reveals the presence of built-in electric field. Unexpected, the establishment of photovoltage is rather slow.

A LCE/STON heterojunction was fabricated by growing a LCE layer on a STON substrate of (001) orientation using pulsed laser ablation technique. The temperature of the substrate was kept at 750 °C and the oxygen pressure at ~50 Pa during deposition. The film is 3×5 mm^2 in area and ~100 nm in thickness. To improve crystallinity, the film was annealed at 750 °C for 20 min in flowing O_2 after deposition. As revealed by x-ray diffraction study, the resultant film is single-phase and well textured. The high resolution lattice image of the cross section of the junction displays a satisfactory epitaxial growth of the LCE film on STON (not shown).

Hall effect study revealed that LCE is actually hole-doped,[6] regardless of the presence of tetravalent ions Ce^{4+}. The in-plane resistivity of LCE also shows a typical behavior of hole-doped manganites with a metal-to-insulator transition at ~295 K. Therefore, LCE and STON construct a *p-n* junction. This is confirmed by the asymmetric *I-V* relations against the polarity of bias voltage (Fig. 1), which is a typical feature of *p-n* junctions, and generally ascribed to the presence of interfacial potential due to carrier diffusion. The diffusion potential can be measured by the voltage at which a current rush occurs, and its variation with temperature is presented in the inset of Fig. 1.

A Philips CM200/FEG TEM equipped with an electrostatic biprism has been used for the holography study of the interfacial potential.[7] The details for sample preparation, data acquirement, and processing have been described

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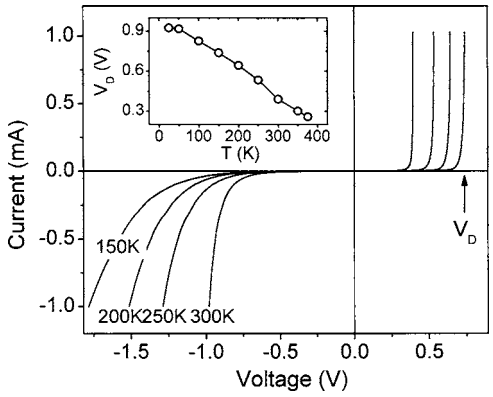

FIG. 1. Selected current-voltage curves measured at different temperatures below 300 K. Inset is a plot of diffusion voltage (marked by the arrow in the main figure) as a function of temperature.

elsewhere.[8] Holograms were acquired from several areas along the LCE-STON interface, and Fig. 2 (top panel) shows a typical reconstructed phase image. The spatial resolution could be better than 0.5 nm, about three times of the average spacing of the interference fringes in the original holograms (~0.16 nm).[8] It has been well established that electrons propagating in an electric field will experience a phase change.[9] There is a simple relation between electron phase and local electrostatic potential $\varphi_{pn}=C_E V_{pn}(L-2L_0)$, where $C_E=7.295\times10^{-3}$ rad/(V nm) for the 200 keV electron, V_{pn} is the electrostatic potential in the junction region of LCE/STON, L and L_0 are, respectively, sample thickness and the thickness of the dead layer due to foil sample preparation. The bottom panel of Fig. 2 is an averaged line scan crossing

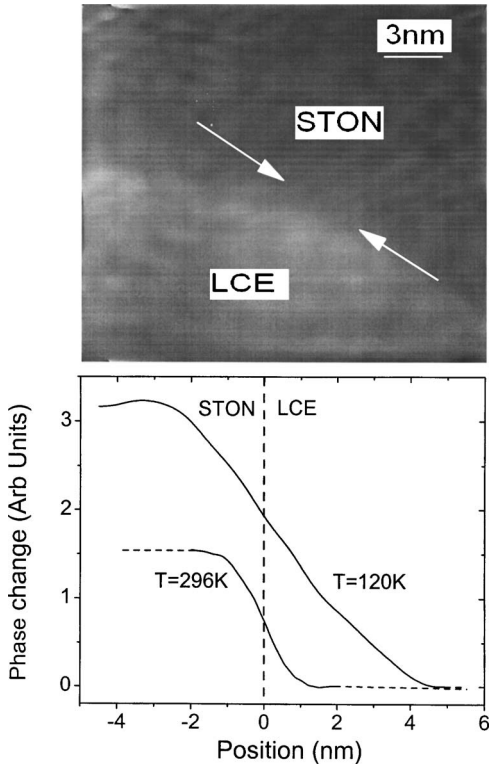

FIG. 2. (Top panel) Reconstructed phase image from the hologram taken at 296 K. (Bottom panel) Phase profiles showing the change of the electrostatic potential across the LCE/STON interface obtained at 120 and 296 K, respectively. Dark and bright areas correspond to high and low electron phase, respectively. Arrows and dashed line mark the LCE/STON interface.

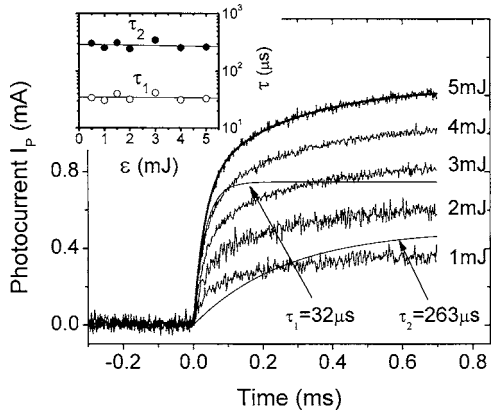

FIG. 3. Photocurrent as a function of time measured under different pulse intensities. Results of curve-fitting based on two exponentials are also provided for $\varepsilon=5$ mJ (thick and smooth curve). Thin curves represent the two distinctive processes for the pulse energy of 5 mJ. Inset plot shows the time constants against pulse intensity.

the junction. It reveals a significant phase change within a narrow layer around the interface, confirming the presence of a depletion layer and built-in electric field therein. Decrease of temperature intensifies interface potential, leading to a thickening of the depletion layer from ~3 nm at 296 K to ~8 nm at 120 K and a doubling of the interfacial energy barrier, the latter is consistent with the result of the *I-V* measurements (inset in Fig. 1).

A rough estimate based on the formula $L=[2\varepsilon\varepsilon_0(N_A+N_D)V_d/eN_AN_D]^{1/2}$ indicates that the depletion layer of LCE/STON is ~6 nm if a hole density of $10^{21}/\text{cm}^3$ for LCE (~0.3 holes/Mn) and an electron density of $10^{20}/\text{cm}^3$ for STON ($\sim2\times10^{-2}$ electrons/Ti) are adopted. Its agreement with the TEM observation is satisfactory considering the fact that the earlier equation is derived for homojunctions and, furthermore, the preparation of the TEM sample may cause some changes of the junction. In the formula ε is the dielectric constant of $SrTiO_3$, N_A and N_D the carrier densities of LCE and STON, respectively.

It is obvious that the rectifying property of LCE/STON is a direct consequence of the presence of built-in electric field. The other effects of built-in electric field may be the occurrence of photocurrent (I_P). The transient photocurrent through the two electrodes LCE and STON was measured by a 500 MHz oscilloscope (TDS 520D, input impedance $R_0=50\ \Omega$) as the LCE film was perpendicularly illuminated by *a laser pulse* of the width of 10 ns ($\lambda=532$ nm) (spot size ~13 mm^2). As shown by Fig. 3, I_P first exhibits an abrupt jump, then a tendency to gradual saturation upon light illumination. It exceeds 1.2 mA for the pulse energy of 5 mJ. This process is reminiscent of the charging of a capacitor. It should be noted that the growth of I_P, though steep, lasts for ~30 μs, i.e., far beyond the width of laser pulse. A close view of the I_P-t curve shows that there is no obvious anomaly at $t=10$ ns, which indicates a continuous growth of I_P after illumination.

The other interesting observation is the complex response of I_P to light illumination. A careful analysis indicates that the I_P-t curve can be well described by $I_P=I_1[1-\exp(-t/\tau_1)]+I_2[1-\exp(-t/\tau_2)]$, where τ_1 is ~30 μs and $\tau_2\sim260$ μs (slightly pulse energy-dependent). This result reveals two distinctive processes. The former corresponds to the rapid increase of I_P while the latter to the slow

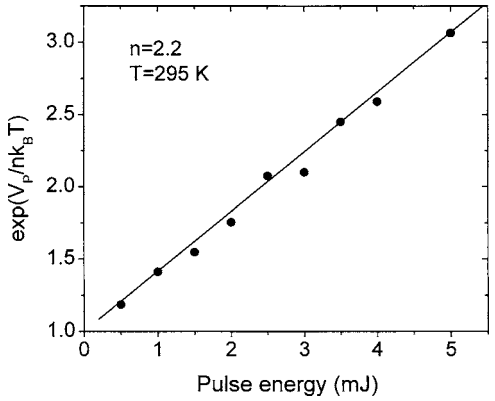

FIG. 4. Photovoltage as a function of pulse intensity measured at ambient temperature. Solid line is a guide for the eye.

saturation of I_P. The saturation current for these two processes is somewhat different, and the former increases linearly with light energy while the latter curves downwards as light intensity increases. The expected photocurrent (I_1+I_2) obeys the relation $V_P=I_PR_0=k_BT/ne\ \ln(1+\beta P)$ quite well though V_P is not the open circuit voltage, where P is the pulse energy, $\beta=0.373(\mathrm{mJ})^{-1}$ and $n=2.2$ (Fig. 4).

Manganites exhibit a complex band structure. The t_{2g} and e_g orbitals of different spin orientation span into different energy bands. It has been supposed that the band gap between the valence and the conduction bands is the order of 0.5–1 eV in magnitude.[10] Therefore, it is possible for a photon to activate an electron-hole pair (photonic energy ≈ 2.4 eV). According to the TEM observation, the width of the depletion layer of the junction is only ~ 3 nm. This implies a strong built-in electric field. As a result, the extra holes and electrons will be swept to the p and n electrodes, respectively, on their appearance, yielding the photovoltaic effects.

It is obvious that the charging of the junction takes place on the appearance of extra charge carriers because of the presence of built-in electric field. Provided that the expected extra charge that can be accommodated by the electrode is Q_0 at the new equilibrium state, the rate for the charge accumulation will be proportional to (Q_0-Q), i.e., $dQ/dt \propto (Q_0-Q)$. This actually means $V=V_0[1-\exp(-t/\tau)]$ noting the relation $V=Q/C$(C=capacitance of the junction). Based on the earlier analysis, we can understand the charging-like behavior of the junction though the occurrence of two exponentials certainly means much more complex processes in reality.

A striking observation of the present work is the significantly slow photoelectronic response. In fact, the separation of the extra holes and electrons in the space-charge region is expected to finish in picoseconds or nanoseconds. The discharging *via* external circuit may affect the transient photocurrent. However, the time constant of the external R-C circuit is at most 5 μs adapting the capacitance of ~ 0.1 μF for the LCE/STON junction (using the capacitance of the $La_{0.9}Sr_{0.1}MnO_3/SrTiO_3/SrTiO_3$:Nb junction as a reference),[1] and the resistance of 50 Ω, the input impedance of the oscilloscope. This indicates that the slow response cannot be simply ascribed to external circuit. From the TEM result we know that the depletion layer in LCE/STON is ~ 3 nm in thickness. This implies that significant contribution to V_P may come from the charge carriers outside the space-charge region. The time required by the outer charge carrier to enter the junction region *via* diffusion is ~ 0.3 μs assuming the diffusion rate of ~ 40 cm/s and the diffusion length of ~ 100 nm for the charge carries in LCE (STON).[11] It is much shorter than 30 μs. The sluggish growth of I_P cannot be a result of local heating due to laser illumination either. As shown in the inset of Fig. 3, the time constants of the transient photocurrent are nearly energy independent when the pulse energy varies between 0.5 and 5 mJ. It is easy to derive that they will be $\tau_1 \approx 35$ and $\tau_2 \approx 293$ μs, respectively, in the limit $\varepsilon \to 0$. In this case no heating effects are expected. It seems to be a distinctive feature of manganite heterojunction. The long-range interfacial charge transfer,[4] magnetic correlation resulted carrier localization,[5] and the special microscopic electronic structure of the interface (Ref. 12) may play a role in determining the photoelectronic process of LCE/STON. Further work in this regard is required.

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