Effect of temperature on the $La_{1-x}Ca_xMnO_3/SrTiO_3:Nb$ ($x=0-0.75$) heterojunctions

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Influence of temperature on the $La_{1-x}Ca_xMnO_3/SrTiO_3:Nb$ heterojunctions with the Ca content ranging from 0 to 0.75 has been experimentally studied. Obvious temperature effect occurs in the junction with a Ca content of 0.1. As experimentally shown, the interfacial barrier is insensitive to temperature below 340 K, and experiences a decrease from ~1.24 to 0.85 eV as temperature grows from 340 to 375 K. However, the temperature effect in other junctions is weak, and the energy barrier change is typically ~0.03–0.08 eV. In the scenario of temperature-driven orbital order-disorder transition in the $La_{0.9}Ca_{0.1}MnO_3$ film, the temperature effect can be qualitatively understood. © *2010 American Institute of Physics*. [doi:10.1063/1.3462322]

The interfacial effect of the Mott insulator has been a topic of intensive study in recent years. Different from the bulk, the interface usually exhibits unexpected behavior. The most typical examples are the enhancement of superconductivity[1] and ionic conductivity at the interface.[2] Dramatic magnetic and resistive changes accompanying the interfacial orbital-and-charge ordering were also observed in manganite films.[3]

$La_{1-x}Ca_xMnO_3$ (LCMO) is a typical system that shows an well orbital ordering below a critical temperature between 300 and 780 K, varying with Ca content.[4,5] The LMCO-based heterojunction could be a suitable sample for interface study based on the following reasons: First, the interfacial barrier (Φ_B) in the junction provides a feasible measure to interface state, through which the evolution of the electronic structure can be traced. Second, manganite junction may exhibit abundant effects due to the presence of the spin, charge, and orbital degrees of freedom and the order-disorder transition associated with either degree of freedom.[6]

There are intensive studies on the LCMO junctions with the hole content of 0.33 or above,[7] and diverse behaviors associated with special magnetic and transport processes have been observed. As well established, however, the robust orbital ordering occurs only when the Ca content is low. It is, therefore, worthwhile to explore the effect of phase transition of the LCMO film with a low Ca content on the corresponding junctions. Based on this consideration, in this paper, we performed a systematic study on the $LCMO/SrTiO_3:Nb(0.05wt\,\%Nb)$ (STON) junction with a Ca content between 0 and 0.75, with a focus on the influence of temperature on interfacial barrier. Strong temperature effect is observed in the junction of $x=0.1$, as demonstrated by the rapid decrease in the Φ_B from ~1.25 to 0.85 eV as temperature grows from 295 to 375 K. In contrast, the barrier change in other junctions is relatively small, and $\Delta\Phi_B$ ~0.03–0.08 eV. In the scenario of temperature-driven orbital order-disorder transition in LCMO of $x=0.1$, the temperature effect can be qualitatively understood.

LCMO/STON junctions were fabricated by growing, via the pulsed laser ablation technique, LCMO films with the Ca content of 0, 0.1, 0.2, 0.33, 0.67, and 0.75, respectively, on (001)-STON. During the deposition, the temperature of the substrate was kept at 720 °C, and the oxygen pressure at 10 Pa, for $x=0$, 30 Pa, for $x=0.1$, 50 Pa, for $x=0.2$, or 80 Pa, for $x\geq 0.33$. The film thickness is ~150 nm, controlled by deposition time.

The lateral size of the junction is $1\times 1\ mm^2$, fabricated by the photolithographic technique. As electrodes, two copper pads were deposited on LCMO and STON, respectively, and the contact resistance is ~15 Ω for the Cu-STON contact and ~150 Ω for the Cu-LCMO contact. Laser with a wavelength between 532 and 980 nm was used in the present experiment. The spot size of the laser is ~1 mm in diameter. Photocurrent, I_P, yielded by laser illumination was acquired by a Keithley 2611 SourceMeter.

Figure 1 presents the temperature dependence of the photocurrent for two selected junctions of $x=0.1$ and 0.33. For clarity, only the data acquired at the temperatures of 295 and 355 K are shown. As expected, I_P exhibits a strong dependence on photon energy, and the typical value for the

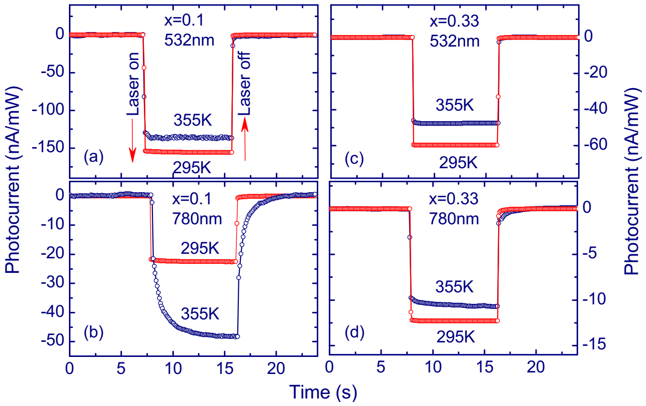

FIG. 1. (Color online) Photocurrent of the LCMO/STON junctions measured at two typical temperatures of 295 and 355 K and under the incident lasers of 532 nm and 780 nm. [(a) and (b)] $x=0.1$. [(c) and (d)] $x=0.33$. The sluggish growth of photocurrent in (b) for $T=355$ K could be attributed to the trapping of nonequilibrium carriers by defects.

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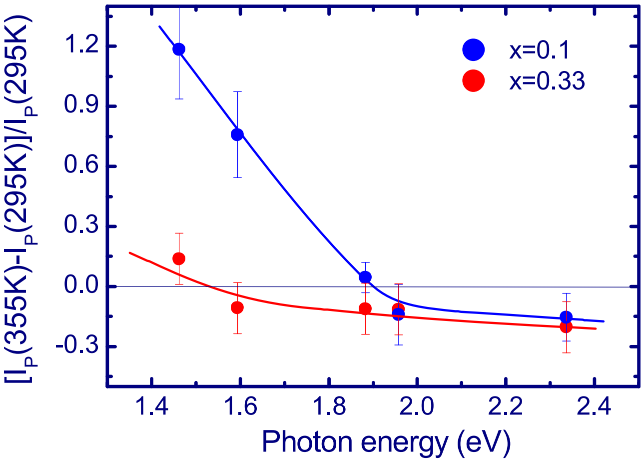

FIG. 2. (Color online) Relative change in photocurrent as temperature varies from 295 to 355 K for two LCMO/STON junctions with $x=0.1$ and 0.33, respectively. Solid lines are guides for the eye.

junction of $x=0.1$ is, at the ambient temperature, ~156 nA/mW for a laser of 532 nm and ~22 nA/mW for a laser of 780 nm. Probably due to the variation of the diffusion length of the non-equilibrium charge carriers, the photocurrent for a fixed wavelength shows a remarkable dependence on Ca content.

The most remarkable observation of the present work is the strong temperature dependence of the photocurrent. This feature is particularly obvious in the junction of $x=0.1$. When the temperature changes from 295 to 355 K, as shown in Figs. 1(a) and 1(b), I_P displays either a reduction by ~15% or a growth by ~110%, depending on the wavelength. Similar phenomena are observed in other junctions except that the photocurrent usually displays a reduction upon warming, even under the light with a long wavelength. As an example, Figs. 1(c) and 1(d) present the photocurrent for the junction of $x=0.33$, measured at different temperatures and wavelengths. Figure 2 shows the temperature-driven photocurrent change, as a function of photon energy.

The I_P reduction upon warming for high photon energy can be ascribed to the enhancement of the thermal scattering of charge carriers. However, the significant photocurrent growth for low photon energy, which is as high as ~118% for the junction of $x=0.1$ (Fig. 2), may indicate a temperature-induced reduction of interfacial barrier. As well established, the information on Φ_B can be extracted from the internal photoemission data. According to Fowler,[8] there is a simple relation between the quantum efficiency R of the photoemission process, defined as the photocurrent yielded by each photon, and photon energy $R \propto (h\nu - \Phi_B)^2$ if $E_F \gg |h\nu - \Phi_B| \geq 3\ k_B T$, where $h\nu$ is the photon energy. LCMO/STON can be approximated by a Schottky junction since the depletion layer mainly develops in STON, and the Fowler equation should be applicable.

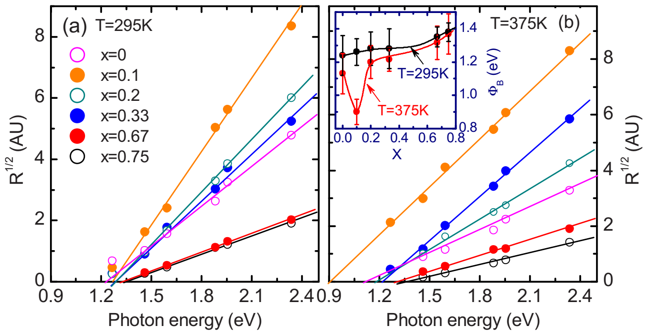

FIG. 3. (Color online) Square-root quantum efficiency as a function of photon energy for the LCMO/STON junctions with different Ca contents. (a) $T=295$ K and (b) $T=375$ K. The inset plot in (b) shows the variation in the interfacial barrier with the Ca content. Solid lines are guides for the eye.

Figure 3 exemplifies the square root of the quantum efficiency as a function of photon energy for the $La_{1-x}Ca_xMnO_3$/STON junctions, measured at two typical temperatures of 295 and 375 K. Satisfactory linear $R^{1/2}$-$h\nu$ relations are obtained for all of the samples, indicating the presence of a definite interfacial barrier in the junction. With the increase in the Ca content, the $R^{1/2}$-$h\nu$ slope decreases and the x-axis intercept of the $R^{1/2}$-$h\nu$ curve shifts to high energy, a signature of the Φ_B variation. The deduced energy barrier is presented in the inset plot of Fig. 3(b). Two distinctive features can be identified from these data. The first one is the monotonic increase of the barrier height with Ca content, which is consistent with the results deduced from the current-voltage analysis in our previous work,[9] and the second one is the great reduction of the interfacial barrier at high temperatures for the junction $x=0.1$ ($\Delta\Phi_B \approx 0.36$ eV). The latter is a feature that appears only for $x=0.1$, and the energy barrier in other junctions, which can have a Ca content either larger or smaller than 0.1, is nearly invariant against temperature ($\Delta\Phi_B \sim 0.03-0.08$ eV).

To get a clear picture about the temperature effect, in Fig. 4 we present the interfacial barrier as a function of temperature for junction $x=0.1$. The influence of temperature is weak below 340 K, and only a slight change in interfacial potential, $\Delta\Phi_B \sim 0.02$ eV, is observed from 295 to 340 K. Considerable temperature effect, characterized by a rapid decrease in Φ_B, emerges and develops when the temperature exceeds ~340 K, and the interfacial barrier reduces from ~1.25 to 0.85 eV when the temperature increases from 340 to 375 K. The tendency to decreasing for Φ_B does not stop up to 375 K, the maximal temperature of the present experiment. We repeated the experiments several times with different electrode settings, and obtained essentially the same results.

As well known, both the $SrTiO_3$ and the $La_{1-x}Ca_xMnO_3$ are typical thermoelectric materials.[10,11] We found that the maximal thermopower of LCMO/STON is ~10 mV, obtained by optimizing the position of the lead lines on the Cu

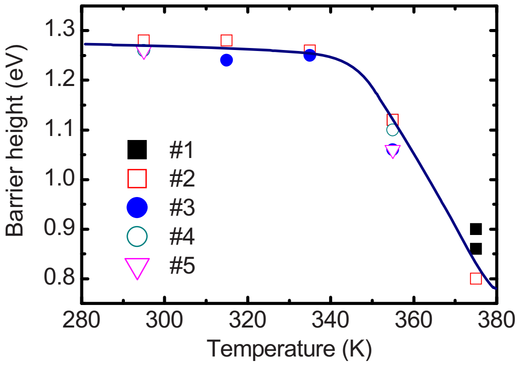

FIG. 4. (Color online) Interfacial barrier as a function of temperature for the LCMO/STON junction with $x=0.1$. Different symbols represent the data of different experiments. Numbers in the figure indicate the sequence of the experiments. Solid line is a guide for the eye.

electrode. This is a value much lower than $\Delta\Phi_B/e \sim 0.4$ V. This result indicates that the variation in Φ_B cannot be ascribed to thermoelectric effect.

Considering the close relation of the built-in potential with the electronic structures of the junction, the obvious change in Φ_B of LCMO/STON may suggest a variation of the band structure of either LCMO or STON. In general, the change of the electronic structure of the materials with temperature is rather small and smooth. The presence of a critical temperature for the temperature effect in LCMO $(x=0.1)$/STON reminds us of phase transition. As well documented, STON is insensitive to temperature in the temperature range investigated here. However, LCMO can experience an orbital order-disorder transition upon warming. The most typical orbital ordering occurs in $LaMnO_3$ below the temperature of ~780 K, yielding a sudden increase in resistivity.[4,5] The transition temperature varies strongly with Ca content, reducing from ~780 to 180 K for $x=0$ to 0.17.[5] Correspondingly, the resistive anomaly becomes weak, and no signature of phase transition can be identified as x approaches ~0.17. The transition temperature is very high for LMO, beyond the scope of our experiment. This may be the reason for the absence of significant temperature effect in the corresponding junction. In contrast, the transition temperature is ~400 K in the case of $x=0.1$, which is close to the threshold temperature for the significant Φ_B decrease. As well established, the orbital disordering can produce a structure change due to the disappearance of cooperative Jahn–Teller distortions. This will in turn affect both the interfacial states and the Fermi level. This may be the reason for the Φ_B drop upon warming. Indeed, it has been found that, for the $La_{1/8}Sr_{7/8}MnO_3$/STON junction, a transition from the orbital ordered to disordered state can occur accompanying a considerable reduction in Φ_B.[12] We noted that the Φ_B-x dependence observed here is much smoother than that expected from the μ-x relation of the LCMO film,[13] which may indicate a pinning of the Fermi level by interfacial states, where μ is the chemical potential of LCMO. It is possible that the phase transition in LCMO $(x=0.1)$ modifies Φ_B via affecting the Fermi level pinning.

We have measured the in-plane resistance of LCMO $(x=0.1)$ to identify the signature of phase transition. Activated resistance, with an activation energy of ~0.14 eV, is observed in the whole temperature range from 295 to 375 K, without obvious resistive anomalies (not shown). It is possible that the lattice clapping of the LCMO film by STON has smeared the phase transition. This explains the widening of the phase transition from 340 up to 375 K. In fact, a charge and orbital ordering without a definite transition temperature has been observed in the $Pr_{0.5}Ca_{0.5}MnO_3$ film grown on a $SrTiO_3$ substrate.[14] The present work suggests a possible approach monitoring the electronic transition at the interface.

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