Effect of oxygen content and superconductivity on the nonvolatile resistive switching in $YBa_2Cu_3O_{6+x}$/Nb-doped $SrTiO_3$ heterojunctions

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The authors report on the resistive switching effect in $YBa_2Cu_3O_{6+x}$/Nb-doped $SrTiO_3$ heterojunctions. The current-voltage curves of these heterojunctions show hysteresis, which increases with decreasing temperature and oxygen content. Multiresistance states are realized by voltage pulses with different amplitudes. The relaxation of the junction current after switching follows the Curie–Von Schweidler law. More interestingly, the resistance of the low resistance state for the heterojunction shows a metallic behavior with a remarkable drop at T_c. The results were discussed in terms of the trapping-detrapping process via oxygen vacancies near the interface of the heterojunction and the conducting filaments through the junction barrier. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3095493]

Recently, the resistive switching effect in transition metal oxides has attracted much attention due to its importance in both basic research and potential applications in resistance random access memory (RRAM).[1] RRAM combines the advantages of flash and dynamic random access memories while avoiding their drawbacks and has been proposed as the basis for the future nonvolatile memories.[1] So far, most of the reports on resistive switching effect are related to the heterostructures composed of metal and transition-metal oxide. Very recently, a few reports demonstrated that heterostructures composed of two oxides can also show the resistive switching effect.[2,3] This is significant because there are a lot of oxides with various properties, which can result in many combinations of different oxides. Another point is that the interface of oxides can be better controlled and epitaxy can be realized, which is helpful for uncovering the mechanisms of the resistive switching effect since it has been proposed that the interface plays an important role in this effect.[4] Therefore, it is essential to study the resistive switching effect in heterostructures composed of two oxides.

The origin of the resistive switching effect in the transition metal oxides is still an open question.[1] One of the interesting scenarios attributes the origin of the switching effect to the migration of oxygen vacancies,[5] which has been regarded as one of the key issues in understanding the switching effect.[1,6] Thus, it is interesting to explore this scenario in heterostructures composed of two oxides by selecting oxide with well characterized oxygen vacancies. In this regard, $YBa_2Cu_3O_{6+x}$ (YBCO) is a good candidate since it has been well established that x can be tuned between 0 and 1, resulting in dramatic change of property.[7] Moreover, there were some reports on the electromigration of oxygen in YBCO (Ref. 8) and oxygen ordering process at room temperature (RT),[9,10] suggesting the mobile nature of oxygen in YBCO. Oxygen vacancies also introduce defects in the structure so the influence of oxygen vacancies on the switching effect can be explored. Furthermore, the effect of superconductivity on the resistive switching effect is also an interesting topic, which has not been reported up to now. In this letter, we report the resistive switching effect in heterostructures composed of YBCO with different oxygen contents and Nb-doped $SrTiO_3$. It was found that oxygen deficiency favors the resistive switching effect, which becomes more remarkable at low temperatures. The effect of superconducting transition on the resistive states was also observed.

YBCO thin films was deposited on (100) oriented, 0.7 wt % Nb-doped $SrTiO_3$ (NSTO) substrates using the pulsed laser deposition, and the details have been described elsewhere.[11] The thickness of the films is about 150 nm. In order to get the oxygen deficient samples, some films were annealed in vacuum at 300 °C for 1 h. The films are single phase with (001) alignment. According to the correlation between the lattice parameter c and oxygen content for YBCO,[12] the oxygen contents of the as-prepared samples and the oxygen deficient samples are 6.9 and 6.4, respectively. Hereafter, the two samples are denoted as $YBCO_{6.9}$ and $YBCO_{6.4}$. For the electrical measurement, Au pad was deposited on YBCO film as the top positive electrode by magnetron sputtering using a shadow mask. Indium was pressed on the back of NSTO substrate as the bottom negative electrode. The *I-V* curves of the junction were measured using a two-probe method with a Keithley 2400 source meter with a compliance current of 10 mA. A pulsed dc voltage with a width of 2 ms and an interval of 2 s was applied in the *I-V* measurements. In order to estimate the contributions from the Au/YBCO interface and YBCO films, same measurement was done for the YBCO film grown on the insulating $SrTiO_3$ substrates with two Au pads on the surface of YBCO film and its *I-V* curve shows linear behavior without hysteresis. The contact between indium and NSTO substrate is Ohmic.

Figure 1(a) is the *I-V* curves of $YBCO_{6.9}$/NSTO at different temperatures. The rectifying behavior is consistent with our previous work,[11] indicating that *p-n* junction has been formed between $YBCO_{6.9}$ and NSTO. Interestingly, *I-V* curves show minor hysteresis at RT and remarkable hysteresis at low temperatures, manifesting the resistive switching effect. This result suggests that the resistive switching effect in $YBCO_{6.9}$/NSTO is related to some electronic process rather than atom movement, e.g., oxygen, because oxygen

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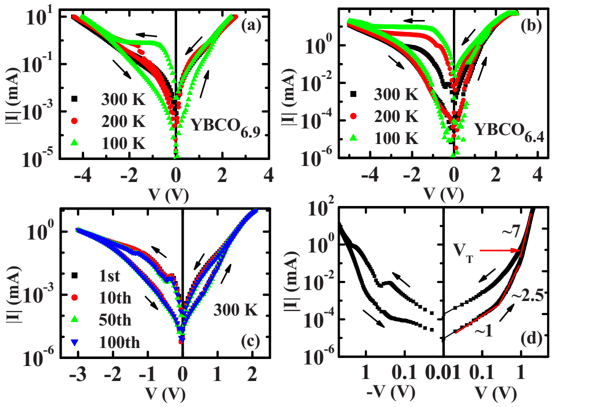

FIG. 1. (Color online) (a) The *I-V* characteristics of $YBCO_{6.9}$/NSTO at different temperatures. (b) The *I-V* characteristics of $YBCO_{6.4}$/NSTO at different temperatures with a voltage sweep $0 \rightarrow 3 \rightarrow 0 \rightarrow -5 \rightarrow 0$ V. (c) Endurance performance of $YBCO_{6.4}$/NSTO with 100 set/reset cycles. (d) log-log plot for the *I-V* curve of $YBCO_{6.4}$/NSTO at 300 K.

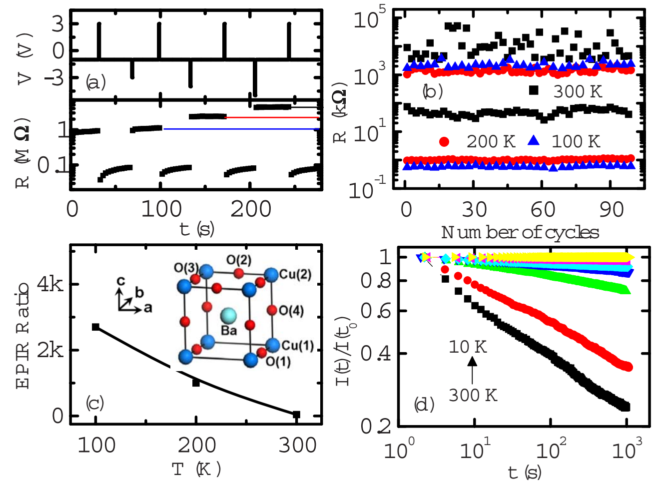

FIG. 2. (Color online) (a) Switching of junction resistance of $YBCO_{6.4}$/NSTO with a train of voltage pulses. The trigger voltages are +3, −3, −4, and −5 V and the reading voltage is −0.5 V. (b) Switching between the HRS and LRS at different temperatures with 100 set/reset cycles for $YBCO_{6.4}$/NSTO. (c) Temperature dependence of the EPIR ratio of $YBCO_{6.4}$/NSTO. The inset is the relevant structure of YBCO with the Cu–O chain and CuO_2 plane. (d) Relaxation of the junction current for the LRS of $YBCO_{6.4}$/NSTO at 300, 250, 200, 150, 100, 50, and 10 K, respectively.

atoms in YBCO are more mobile at RT than that at low temperatures.[9,13]

In order to check the effect of oxygen content or oxygen vacancy on the resistive switching effect, we also measured the *I-V* curves of $YBCO_{6.4}$/NSTO at different temperatures, and the result is shown in Fig. 1(b). The *I-V* curves show remarkable hysteresis even at RT, and the hysteresis also increases with decreasing temperature, consistent with the temperature dependence in $YBCO_{6.9}$/NSTO. Figure 1(c) gives the *I-V* curves measured for 100 times, demonstrating the endurance of the resistive switching in $YBCO_{6.4}$/NSTO. The dependence of hysteresis on temperature and oxygen content suggests that oxygen vacancies in YBCO favor the resistive switching effect and some electronic process plays the dominant role.

To study the junction resistance change and its temporal variation with voltage pulse, the variation of the junction resistance for $YBCO_{6.4}$/NSTO with a train of voltage pulses of given polarity and amplitude was measured at RT, and the result is shown in Fig. 2. The upper panel of Fig. 2(a) shows the train of voltage pulses and the lower panel of Fig. 2(a) is the response of the junction resistance. It can be seen that the train of voltage pulses can switch the heterojunction between different resistive states with the positive voltage pulses decreasing the resistance (increasing current) and the negative voltage pulses increasing the resistance (decreasing current). The junction resistance also changes with the amplitude of the pulse voltage, resulting in multiresistance states. Figure 2(b) shows the resistance switching between a high resistive state (HRS) and a low resistive state (LRS) in the cycling test for $YBCO_{6.4}$/NSTO at different temperatures with the train voltage pulses of +3 and −3 V, respectively, and a reading voltage of −0.5 V. The ratio of the electrical pulse induced resistance change (EPIR), defined by R_{HRS}/R_{LRS}, is about 42 at RT and increases with decreasing temperature, reaching about 2700 at 100 K, as shown in Fig. 2(c). It should also be mentioned that the resistance switching of the junction is very stable after 100 switching cycles. In our previous work,[3] we found in $SrTiO_{3-x}$/NSTO heterojunction that the variation of the junction current with time after switching follows the Curie–Von Schweidler law for the LRS. So it is interesting to check whether this law is also satisfied in $YBCO_{6.4}$/NSTO heterojunction. Figure 2(d) is the relaxation of $YBCO_{6.4}$/NSTO heterojunction current with time after switching to the LRS at different temperatures. It can be seen that the Curie–Von Schweidler law $J \propto t^{-n}$ is also satisfied with $n=0.216$ at RT and $n=0.003$ at 10 K. In contrast, the heterojunction current after switching to the HRS remains unchanged within the experimental error (not shown here).

The behavior of YBCO/NSTO can be understood by considering the trapping-detrapping process of carriers due to oxygen vacancies near the interface of YBCO and NSTO. Figure 1(d) shows the log-log plot for the *I-V* curve of $YBCO_{6.4}$/NSTO. For the positive bias voltage, the *I-V* curve shows a linear behavior for $V<0.2$ V, followed by a slope of 2–3 for $V<1.1$ V, and then a sharp current rise with a slope of 7 for $V>1.1$ V (V_T). This behavior can be described by the trap-controlled space charge limited (SCL) conduction mechanism,[14] with V_T as the transition voltage from the trap-unfilled to trap-filled SCL regimes. Upon decreasing the voltage, the current retains the higher value indicating that the trapped carriers are not released from the trap centers, which result in the hysteresis behavior. For the reverse bias voltage, it aids the release of the carriers from the traps, leading to switch to HRS when the trapped carriers are released. The mean time t spent by a carrier in a trap with depth E_t is proportional to $\exp(E_t/kT)$,[15] where k is Boltzmann's constant. So the mean time that a carrier spends in a trap increases with decreasing temperature. This can account for the experimental observation that the resistive switching effect becomes more remarkable at low temperatures and the resultant increase of EPIR ratio, as well as the slower relaxation at low temperatures with smaller n value. It was also shown that space charge trapping can lead to the Curie–Von Schweidler behavior.[16] For the Curie–Von Schweidler law, n is positive and smaller than 1 (Ref. 17). The small value of n for $YBCO_{6.4}$/NSTO may be related to the deep traps since they can lead to slow relaxation. As mentioned earlier, x can be tuned between 0 and 1 for $YBCO_{6+x}$ (Ref. 7). The relevant features of the crystal structure of $YBCO_{6+x}$ are copper-oxygen chains sandwiched between copper-oxygen planes,

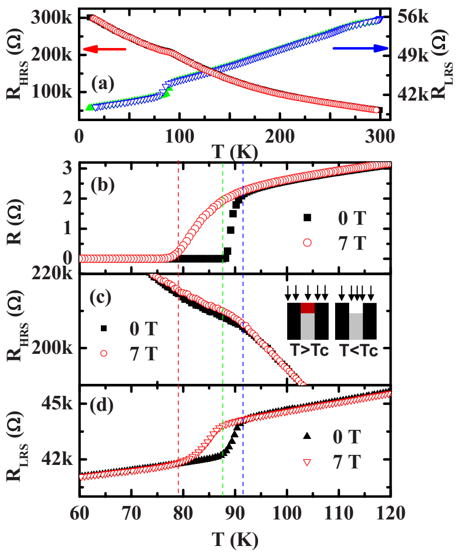

FIG. 3. (Color online) (a) *R-T* curves for the LRS and HRS of $YBCO_{6.9}$/NSTO. (b) *R-T* curves of $YBCO_{6.9}$ film. (c) and (d) Resistance change around T_c for the HRS and LRS. The inset is a scheme showing the variation of the depletion layer thickness along the interface of the junction.

as shown in the inset of Fig. 2(c). The chains run along the crystallographic *b* direction and their oxygen atoms [O(1)] are removed from the chains with decreasing *x*. These oxygen vacancies are expected to play the role of trapping centers, which lead to the resistive switching effect in $YBCO_{6+x}$/NSTO.

We also studied the effect of superconductivity on the resistive states of YBCO/NSTO. Figure 3(a) shows the temperature dependence of resistances for the HRS (−3 V switching) and LRS (+2.5 V switching) of $YBCO_{6.9}$/NSTO. The LRS shows a metallic behavior, while the HRS shows a semiconducting behavior. The metallic behavior of the LRS is significant, suggesting the existence of conducting filaments through the junction barrier. Figures 3(b)–3(d) show the resistance changes at around T_c for $YBCO_{6.9}$ film, LRS and HRS of $YBCO_{6.9}$/NSTO with and without a magnetic field. It can be seen that superconducting transition has remarkable influence on the resistance of the LRS with strong correlation. In contrast, the influence of superconducting transition on the HRS is minor. It has been shown in our previous paper that $YBCO_{6.9}$/NSTO is an inhomogeneous junction.[11] The inhomogeneity of the barrier height distribution leads to the inhomogeneous distribution of the thickness of depletion layer, as shown in the inset of Fig. 3(c). For the HRS, the resistance is mainly determined by the junction resistance, which gives a semiconductinglike behavior. Redistribution of current through the interface occurs at around T_c because the red region adjacent to the thinner depletion layer becomes superconducting [inset of Fig. 3(c)] and more carriers flow via low barrier regions, leading to the minor effect of superconducting transition on the junction resistance.[11] For the LRS, the traps are filled by carriers and higher voltages result in the conducting filaments due to possible soft breakdown of the regions with low barrier height [gray region in the inset of Fig. 3(c)]. The conducting filaments are composed of $YBCO_{6.9}$ and NSTO in series and go through the barrier layer. So the resistance of $YBCO_{6.9}$/NSTO shows a metallic conducting behavior and remarkable drop (much larger than the resistance of $YBCO_{6.9}$) at around T_c of $YBCO_{6.9}$. Interestingly, it has also been shown in Au/$SrTiO_3$:Nb Schottky junction that in the LRS some filaments formed through the junction barrier.[18]

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