Bipolar resistive switching in Cr-doped TiO_x thin films*

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The electric-pulse-induced resistive switching effect is studied for $Ti_{0.85}Cr_{0.15}O_x$ (TCO) films grown on Ir–Si substrates by pulsed laser deposition. Such a TCO device exhibits bipolar switching behaviour with an electric-pulse-induced resistance ratio as large as about 1000% and threshold voltages smaller than 2 V. The resistive switching characteristics may be understood by resistance changes of a Schottky junction composed of a metal and an n-type semiconductor, and its nonvolatility is attributed to the movement of oxygen vacancies near the interface.

Keywords: resistive random-access memory (RRAM), electrical-pulse-induced resistive (EPIR)

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1. Introduction

A giant room-temperature resistance change induced by electric pulses of opposite polarities for $Pr_{07}Ca_{03}MnO_3$ (PCMO) thin films was firstly reported by Liu, Wu, and Ignatiev[1,2] and since then by many research groups. Interestingly, this electric-pulse-induced resistance (EPIR) change is reversible and nonvolatile, exhibiting two stable (higher and lower) resistance states even if the voltage pulse is removed. The EPIR effect is now universally observed in various metal–insulator–metal (MIM) structures with "I" as the transition metal oxide, such as complex perovskite oxides and binary oxides.[1−7] Such a resistive switching effect has received much attention due to its potential applications. The features of EPIR devices, such as fast programming, small device size, low consumption, room-temperature operation and reversibility between the high- and low-resistance states are key factors for future applications in resistive random access memory devices. It is important to look for new materials with better switching properties for memory device applications.

The resistive switching behaviours can be classified into two types: bipolar and unipolar (nonpolar).[8,9] The bipolar resistive switching behaviour often occurs with many semiconducting oxides, such as complex perovskite oxides PCMO,[1] Cr-doped $SrZrO_3$,[3] and Nb-doped $SrTiO_3$;[4] while the unipolar switching has been observed in many highly insulating oxides, such as binary oxides NiO[5] and TiO_2.[6,7] In the bipolar case, the resistive switching depends on the electric pulse polarity; and in the unipolar case, it depends on the pulse amplitude rather than its polarity, being symmetric with positive and negative pulses. Experimental studies have made great progress on both EPIR effects, whereas their underlying physics is not yet well known. The bipolar switching was often related to the Schottky barrier,[4,10] the oxygen ion/vacancy movement near the interface,[11] and a combination of them.[12] The unipolar switching was attributed to formation and rupture of filaments in the bulk.

The TiO_x is a type of semiconducting oxides, having either a tetragonal or rhombohedral structure. It was reported that TiO_2 has unipolar resistive switching with a power-induced mechanism.[6] The doping of TiO_x plays an important role in electric and magnetic properties of the material. For example, Cr-doped Ti_2O_3 films show giant magnetoresistance,[13] changing from about 20% for undoped Ti_2O_3 to −365% for

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0.1 doped film measured at 2 K. In the $SrTiO_3$ oxide, Cr doping may improve the resistive switching performance.[14] In the present study, we investigate the resistive switching behaviour of Cr doped TiO_x. It is found that the Cr doped TiO_x (TCO) exhibits a bipolar switching with a great EPIR ratio and low threshold voltages.

2. Experimental detail

15% Cr-doped TiO_x thin films were grown on Ir–Si (Ir/TiN/SiO_2/Si) wafer substrates by pulsed laser deposition, where Ir is the bottom electrode and TiN/SiO2/Si is the substrate. The target material was prepared by thoroughly mixing high purity TiO_2 powder and chromium oxide powder together, then pressing the mixture into a pellet, and finally sintering it into a $Ti_{0.85}Cr_{0.15}O_2$ ceramic target.[13] The $Ti_{0.85}Cr_{0.15}O_x$ (TCO) thin films were deposited in a forming gas (96% argon blended with 4% hydrogen) ambient of 300 mTorr (1 Torr=133.322 Pa) at 550 °C for 5 min. The laser pulse energy was 380 mJ, and the pulse frequency was 7 Hz. After deposition, the sample was cooled down in 300 mTorr forming gas ambient. We used the reducing ambient for the deposition and cooling down to obtain oxygen deficient[11] TCO thin films, which may have better magnetoresistive and EPIR properties due to the Cr-doping and oxygen deficiency.[11,13] Due to the oxygen deficiency in the film deposition, x is always less than 2 in the present $Ti_{0.85}Cr_{0.15}O_x$ thin films. Finally, the metal (Au) electrodes were deposited on the surface of TCO by a dc-sputtering system. The diameter of the top electrode is about 200 μm, so that its area is much smaller than the area (0.5 cm×0.5 cm) of the bottom electrode. The film thickness is 100 nm for the Au (top) electrode, 300 nm for the TCO film, and 200 nm for the Ir (bottom) layer.

The EPIR device is a metal–insulator–metal (MIM) sandwiched structure with a TCO thin film layer between a top metal (Au) electrode and a conducting bottom layer (Ir). The two-point probe measurement was used for the resistance of this device (shown in Fig. 1). Short positive/negative electric pulses of 100 ns duration were applied across the Au/TCO/Ir systems through the Au electrodes. The resistance between the top and bottom electrodes was measured after each pulse with a very small sensing current of 1 μA.

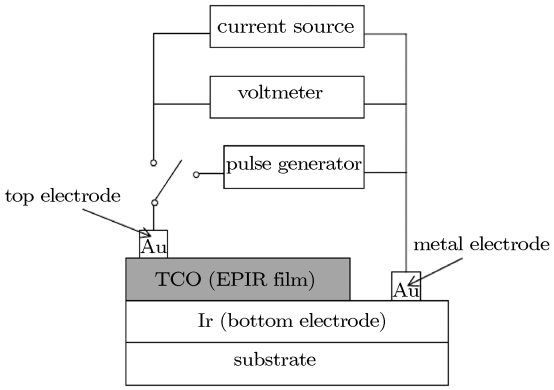


Fig. 1. Schematic diagram of the Au/TCO/Ir structure and the EPIR measurement setup.

3. Results and discussion

Figure 2 shows the nonvolatile resistance changes for the Au/TCO/Ir system at room temperature under alternatively positive and negative pulses of 2.0 V height and 100 ns width. Under the dc measured voltage of 0.001 V, the positive pulse (current into the Au electrode on the TCO film) causes an increase in resistance from the low resistance ($R_L \approx 120\ \Omega$) state to the high resistance ($R_H \approx 1200\ \Omega$) state, whereas a negative pulse causes a decrease in resistance from R_H to R_L, yielding an EPIR ratio of about 1000%. It should be noted that the EPIR ratio can be made much larger by the application of higher pulse voltage and longer pulse width.

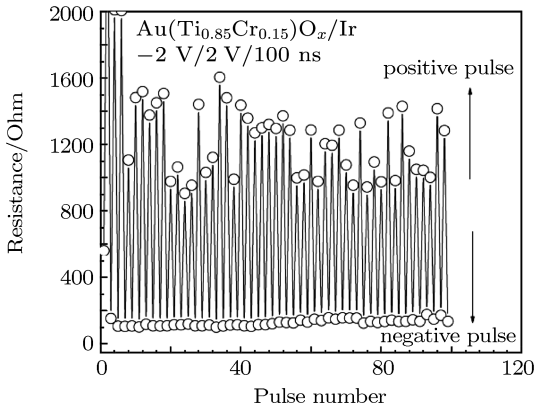


Fig. 2. Two-state switching behaviour of an Au/($Ti_{0.85}Cr_{0.15}$)O_x/Ir device with 2 V, 100 ns electric pulse.

The non-volatile resistance hysteresis loop of the EPIR device is plotted in Fig. 3, from which it follows that the pulse height (threshold voltage) necessary to the resistive switching is about 1.2 V and −1.2 V. The initial state is a R_H state of about 120 Ω. After the negative pulse voltage beyond −0.4 V, the sample resistance decreases gradually; as the pulse voltage approached −1.2 V, the resistance reaches the stable

$R_{\rm L}$ state of about 120 Ω. This $R_{\rm L}$ state remains unchanged (nonvolatile) until a positive pulse with voltage beyond +0.2 V is applied. As the pulse voltage increases from +0.2 V to +1.2 V, the sample resistance returns to the stable $R_{\rm H}$ state, and then remains in that state until the next negative pulse with voltage amplitude greater than 0.4 V. The hysteresis behaviour is not symmetric for applied positive and negative pulse voltages due to the appearance of a "shuttle tail" peak.[11] For PCMO EPIR devices, the "shuttle tail" peak in the hysteresis switching loop appears under negative pulsing, as shown in Fig. 1 of Ref. [11]. However, the present "shuttle tail" peak appears under positive pulsing.

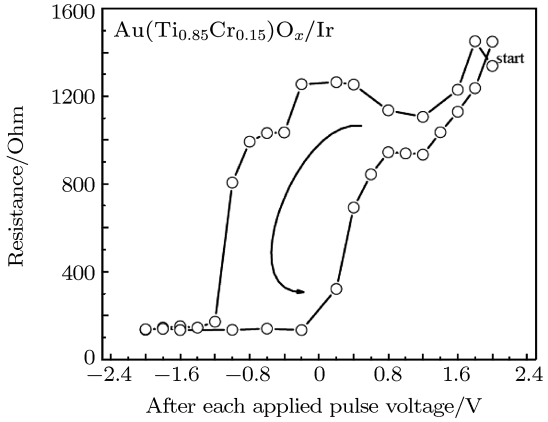


Fig. 3. A resistance switching hysteresis loop of the EPIR device.

Such a difference stems from the fact that PCMO is a p-type semiconductor, whereas Cr-doped TiO_x is an n-type one, as will be discussed below. There is a "shuttle tail" caved in, whose origin is not clear at present. The threshold voltage of TCO is much smaller than that of other materials (for example, the threshold voltage is about 10 V for a PCMO switching device). It is very important for the device industry to have devices working under 5 V.

If the electric pulse is replaced with a direct-current voltage, the threshold voltage of resistance change in TCO becomes smaller. For the voltage swept from 0 → –1 V→1 V→ 0, the I–V curve exhibits hysteresis behaviour, as shown in Fig. 4. Starting from the $R_{\rm H}$ state, the high resistance (lower conductance $\mathrm{d}I/\mathrm{d}V$) state is kept with decreasing V. At about −0.8 V, the current suddenly increases and the TCO device switches to the low resistance (higher $\mathrm{d}I/\mathrm{d}V$) state. With increasing V in paths 2 and 3, the TCO device is always in the $R_{\rm L}$ state. There is a sudden decrease in current at about +1.0 V, and then the $R_{\rm H}$ state is kept in path 4. The I–V curve in Fig. 4 is obtained under a direct-current voltage, whereas the resistance change in Fig. 3 is obtained under electric pulses. They look to be different from each other, but in reality, what they describe is the same switching behaviour as has been discussed in the previous work.[15]

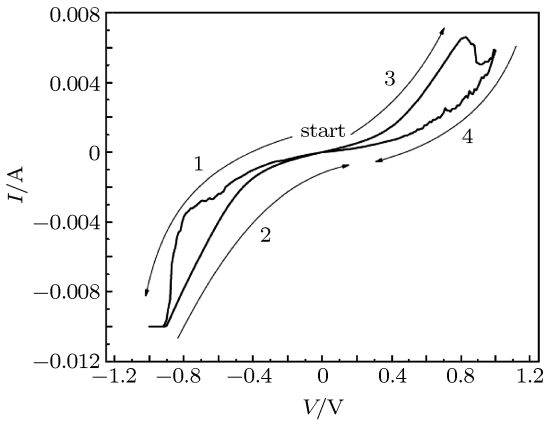


Fig. 4. I–V characteristics of a $(Ti_{0.85}\ Cr_{0.15})O_x$ samples showing resistance hysteresis.

Compared with the switching effect of the PCMO device, we find that the polarity of the electric pulse that makes the resistance of TCO become the $R_{\rm H}(R_{\rm L})$ state is the opposite. From the viewpoint of the Schottky barrier model, it then follows that the TCO is an n-type semiconductor, as the PCMO is a p-type one. While the Hall measurements[13] showed that the carriers are p type for both undoped and Cr-doped Ti_2O_3, recent thermoelectric power measurements[16] indicated that electrons are the majority carriers for Ti_2O_3 over the investigated range of temperature. The present switching effect seems to support the latter. In an n-type semiconductor of the $Ti_{0.85}Cr_{0.15}O_x$ sample with $x < 2$, the electrons in the conduction band play a dominant role in carrier transport. For an Au/TCO contact, since the work function of Au is smaller than that of the n-type TCO, electrons will flow from the conduction band of the TCO into the Au until the Fermi level is aligned. This flow of electrons causes the TCO to become positively charged, forming a depletion region with upward bending of the conduction bands inside the TCO near the interface. Such an upward bending of the bands near the interface forms a Schottky barrier for electrons in the conduction band. For a positive pulse with the electric field directing from the Au to the TCO, electrons are further extracted from the depletion region of the TCO, leading to an enlargement of the depletion region and

an increase of the barrier resistance. On the other hand, a negative pulse will make part of the electrons go back to the depletion region from Au, resulting in a narrowing of the depletion region and a decrease of the barrier resistance. The barrier resistance at the interface plays a dominant role in the total resistance. As a result, the positive and negative pulses can lead to high- and low-resistance states, respectively, which is exactly opposite to the switching behaviour in the PCMO case.

The electric-pulse-induced change of the band bending or carrier depletion region may explain the reversibility between the high- and low-resistance states as well as the reverse polarizations. However, it cannot explain why the EPIR state is nonvolatile. This EPIR effect seems to vanish after the electric pulse is removed. A possible explanation is that the movement of the oxygen ions inside the TCO film near the interface makes electric-pulse-induced changes in the depletion region nonvolatile. For the oxygen-deficient TCO, there are quite a few oxygen vacancies distributed uniformly in the sample, where the movement of the oxygen ions with negative charges is equivalent to that of the oxygen vacancies with positive charges. A negative pulse can move oxygen vacancies in the TCO film toward the Au/TCO interface. Even if the electric pulse is removed, the oxygen vacancies with positive charge still stay there, so that the Coulomb interactions between the oxygen vacancies and electrons near the interface can keep the narrowed depletion region from being volatile. For a similar reason, it is also easily understood that the positive-pulse-induced enlargement of the depletion region is nonvolatile. As a result, the pileup (reduction) of oxygen vacancies at the interface may cause the depletion layer in TCO to become narrow (broad), resulting in a nonvolatile decrease (increase) in the contact resistance.

4. Conclusions

In summary, the bipolar EPIR effect is observed in Cr-doped TiO_x thin films grown on Ir–Si wafer substrates by pulsed laser deposition. The TCO device exhibits a large EPIR ratio ($\sim 1000\%$) and has a low threshold voltage (< 2 V). It can be stably switched with short (nano second) electrical pulses and has good potential in high density, high speed memory device applications. The EPIR switching effect is attributed to the pulse-induced resistance change of the depletion region inside the TCO, and the movement of oxygen vacancies near the interface plays an important role. The pulse polarity that creates the resistance switching indicates that the present TCO is an n-type semiconductor.

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