Enhanced resistance switching stability of transparent ITO/TiO_2/ITO sandwiches*

Meng Yang(孟 洋), Zhang Pei-Jian(张培健), Liu Zi-Yu(刘紫玉), Liao Zhao-Liang(廖昭亮), Pan Xin-Yu(潘新宇), Liang Xue-Jin(梁学锦), Zhao Hong-Wu(赵宏武)†, and Chen Dong-Min(陈东敏)

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, *China*

(Received 9 July 2009; revised manuscript received 17 August 2009)

We report that fully transparent resistive random access memory (TRRAM) devices based on ITO/TiO2/ITO sandwich structure, which are prepared by the method of RF magnetron sputtering, exhibit excellent switching stability. In the visible region (400–800 nm in wavelength) the TRRAM device has a transmittance of more than 80%. The fabricated TRRAM device shows a bipolar resistance switching behaviour at low voltage, while the retention test and rewrite cycles of more than 300,000 indicate the enhancement of switching capability. The mechanism of resistance switching is further explained by the forming and rupture processes of the filament in the TiO_2 layer with the help of more oxygen vacancies which are provided by the transparent ITO electrodes.

Keywords: colossal electroresistance effect, electrical pulse induced resistance switching (EPIR), transparent resistance random access memory (TRRAM)

PACC: 7360, 7290, 7280, 7865P

1. Introduction

In recent years, a large number of resistance switching (RS) phenomena controlled by an external electric field of transition metal oxides have attracted extensive attention for their practical applications of resistance random access memory (RRAM) devices.[1−5] The RS can be classified into unipolar RS (writing and erasing occur with the same voltage polarity) and bipolar RS (with the opposite voltage polarity).[2−4] Bipolar RS is more attractive because it generally has a faster switching speed than unipolar RS. The RRAM devices usually require a large resistance ratio between high resistance state (HRS) and low resistance state (LRS) for obtaining a high signal-to-noise ratio. In addition, the devices need to have features of high-speed and low-voltage operation, low power consumption, high endurance and long retention time, and good switching reliability. While various transition metal oxides were proposed to be used for RS material to achieve these characteristics,[6] there also have been some reports on the use of different electrode materials to improve the switching characteristics.[7,8] For example, In–tin oxide (ITO) films recently have been demonstrated as electrodes to fabricate a novel transparent RRAM (TRRAM) device, which is further suggested to be integrated into a total see-through embedded electronic system.[9]

Note that Seo *et al.*[9] prepared the TRRAM device by means of metal organic chemical vapour deposition (MOCVD) which usually takes more technical complexities and fabrication cost. Naturally, it is proposed to be used to fabricate the TRRAM device with good endurance performance by the conventional magnetron sputtering method. In this study we prepare a fully TRRAM device based on ITO/TiO_2/ITO structure by RF magnetron sputtering. We find that this device is highly transparent in the visible region, and it shows bipolar switching behaviour, manifesting enhanced switching reliability, i.e. writing and erasing cycles can be performed more than 300,000 times.

2. Experimental procedure

The sandwiches of ITO/TiO_2/ITO structure were deposited by RF magnetron sputtering on commercial glass substrates. The oxide targets were used for ITO and TiO_2, separately. The bottom ITO electrode of 240 nm in thickness was prepared at room temper-

*Project supported by the National Basic Research Program of China (Grant No. 2007CB925002), the National High Technology Research and Development Program of China (Grant No. 2008AA031401), and Chinese Academy of Sciences.

†Corresponding author. E-mail: hwzhao@aphy.iphy.ac.cn

© 2010 Chinese Physical Society and IOP Publishing Ltd

ature and an Ar pressure of 0.6 Pa, followed by annealing at 400 °C for 10 min under an O_2 pressure of 0.33 Pa. Without breaking vacuum the TiO_2 film of 90 nm in thickness was grown subsequently at room temperature in an Ar pressure of 0.73 Pa, followed by annealing at 400 °C in O_2 atmosphere of 0.33 Pa for 10 min. Finally, the top ITO electrode of 30 nm was prepared under the same condition as that for the bottom ITO film. For investigating the electrical characteristics, the junctions were patterned with a diameter of 200 μm by a standard photolithography technique.

The sourcemeter Keithley 2400 was used for I–V characterization of the TRRAM device. In addition, electrical pulse induced resistive switching (EPIR) characteristics were measured with the Keithley 2400 and pulse pattern generator Agilent 81110A. The test of continuous writing/erasing cycles was characterised by using an Agilent arbitrary function generator (33220A) and an Agilent digital storage oscilloscope (8104A). For all the above electrical measurements the top electrodes were always biased and the bottom electrodes were grounded. The crystal structure of the oxide films was investigated by x-ray diffraction (XRD, Rigaku, Japan, Cu Kα = 1.5405 Å (1 Å=0.1 nm)). The transmittance of the oxide films was characterised by a spectrometer (SpectraPro-500i, Acton Research Corporation, USA).

3. Results and discussion

The XRD pattern for the ITO/TiO_2/ITO structure is shown in Fig. 1. From these XRD spectra it follows that the TiO_2 thin film of 90 nm thick shows anatase TiO_2 (101) and rutile TiO_2(110) peaks, indicating the polycrystalline structure of the TiO_2 layer. This result is consistent with the previous report.[10]

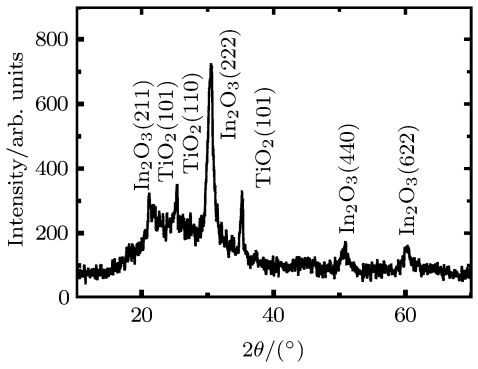


Fig. 1. X-ray diffraction pattern for ITO/TiO_2/ITO sandwich.

Next, we investigate the optical transmittance of the TRRAM device. Since the ITO, TiO_2 layers and the commercial glass substrate are all transparent, the details of the device cannot be distinguished by eye, and the logo (IOP) on the bottom of the TRRAM device is clearly seen through as shown in the inset of Fig. 2. Furthermore, the transparency of the fabricated TRRAM device is characterised by a spectrometer. As shown in Fig. 2, the average transmittance of the TRRAM device (deducting the substrate's contribution) is approximately 87% in the visible region (400–800 nm in wavelength), illustrating the excellent transparency of the TRRAM device.

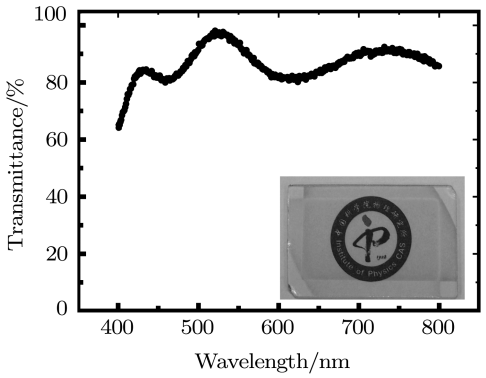


Fig. 2. Transmittance of TRRAM device in the visible wavelength region, where the inset shows the fabricated TRRAM device.

Figure 3 shows the typical current–voltage characteristics of the ITO/TiO_2/ITO sandwich. The TRRAM device structure and electrical measurement setup are shown in the inset. In contrast to the unipolar memory switching as reported by Seo *et al.*,[3] the ITO/TiO_2/ITO sandwich shows bipolar RS behaviour. While a small bias voltage is applied, the initial I–V curve of the TRRAM device in the virgin state reveals a rectifying behaviour at first (not shown here). Thereafter, the voltage was scanned as $0 \rightarrow +\text{Vmax} \rightarrow -\text{Vmax} \rightarrow 0$ in steps of 20 mV and with 1 ms integration time to avoid the thermal effect. As a result, the current increases nonlinearly with voltage increasing from 0 V to +Vmax without forming steps, displaying the HRS. When the bias voltage swept from +Vmax to – Vmax, a higher current is observed, displaying the LRS. The 10-fold continuous scanning of I–V curves in a bias voltage region of ±2.5 V demonstrates the high repeatability of the bipolar switching.

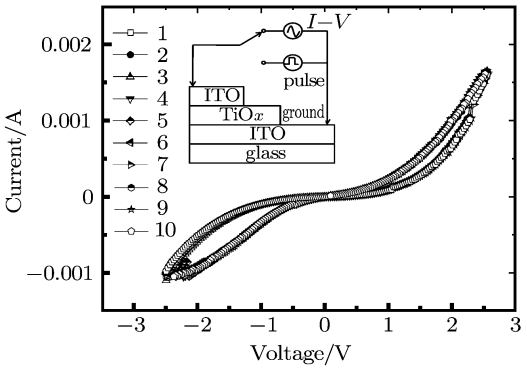


Fig. 3. Typical I–V characteristics of the TRRAM device in bipolar RS mode, where the inset shows the device structure and electrical measurement schematic.

For practical device application, it is necessary to investigate RS characteristics, with electric pulses applied. Accordingly, Fig. 4 shows a typical EPIR behaviour on applying set (–5.2 V/4 μs) and reset (+5 V/4 μs) voltage pulses. The resistance value was measured at 0.5 V after the electric pulse had been applied. The resistance during the read step was about 2×10^5 Ω in the ON state and 1.3×10^6 Ω in the OFF state. So the EPIR switching ratio defined as $(R_{\rm high} - R_{\rm low})/R_{\rm low}$ is about 600%.

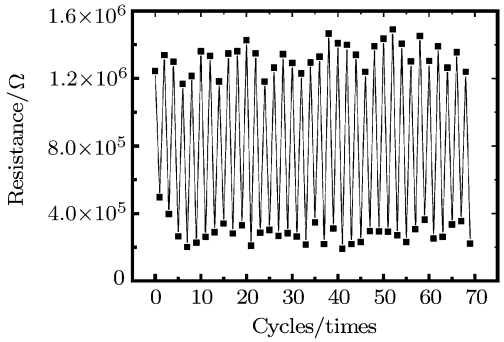


Fig. 4. Typical set and reset cycles (set: –5.2 V/4 μs, reset: +5 V/4 μs, reading: 0.5 V).

The retention characteristics of the device were also investigated in the laboratory environment at room temperature as shown in Fig. 5. At first the LRS is reset by dc sweep (0 V→2.5 V→0 V). Thereafter, a constant voltage of 0.5 V was periodically used to read the LRS in steps of 5 s so as to measure the retention behaviour. Similarly, the retention properties of the HRS were measured after the HRS had been set by dc sweep (0 V→ −2.5 V→0 V). It is noted that the LRS is more stable than HRS.

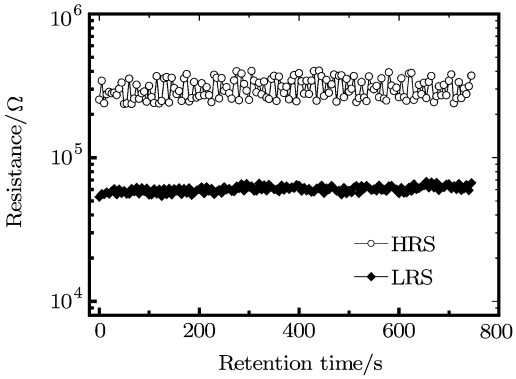


Fig. 5. Retention properties of HRS and LRS at room temperature. The read voltage is 0.5 V.

To further evaluate the endurance performance of the TRRAM device, more than 300000-fold continuous writing and erasing operations were performed on the device. In Fig. 6(a), continuous voltage signals of triangular waveform (dashed line) were applied by an arbitrary function generator. The current signal (solid line) was characterised by an oscilloscope which was connected with the TRRAM device. The maximum applied voltage signal is +/–3 V with a period of 2 ms,

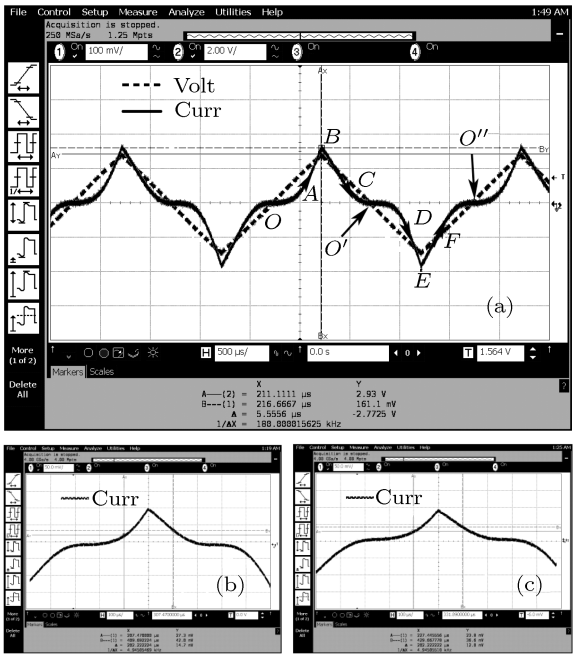


Fig. 6. (a) Voltage of triangular waveform (dashed line) with voltage signal being +/−3 V in amplitude and 2 ms in period, and when it was continuously applied to the device, the current signal (solid line) was measured. Panels (b) and (c) show the original and the final records of the continuous writing and erasing process, respectively.

and the maximum current passing through the TRRAM device is about 4 mA. The voltage sweeping trail of $O \to A \to B \to C \to O' \to D \to E \to O''$ completed a continuous writing and erasing measurement, analogous to the I–V scanning depicted in Fig. 3. For simplicity the original and the final records of the more than 300000-fold continuous measurements are shown in Figs. 6(b) and 6(c), respectively. At a read voltage of 0.5 V, the current ratio $((I_{\rm low} - I_{\rm high})/I_{\rm high})$ is about 51% for the original state, and 53% for the final state after 300000-hold writing and erasing operations, which indicates the excellent device reliability. Based on the hardly changed signal of RS between the original state and the final state after 300000-fold rewrites, it is naturally expected that the TRRAM device will enhance the switching stability in future application.

Now we turn to the discussion of the mechanism of RS. There have been several reports on metal/TiO_2/metal sandwich structures which have been used to investigate the RS property.[10−13] For example, Kim *et al.*[11] reported a unipolar RS behaviour with only 42-fold switching in Pt/TiO_2/Pt prepared by atom layer deposition.[12] They found that the conducting filaments propagated from the cathode interface and that the RS was induced by the rupture and the recovery of the filaments in the localised region near the anode. On the other hand, Tsunoda *et al.*[10] prepared TiO_2 films by the oxidation of Ti films at high temperature, and found bipolar RS after the forming process in Ag/TiO_2/Pt structure. They ascribed the switching phenomenon to the formation and the rupture of a filamentary conductive path of diffused Ag atoms in the TiO_2 matrix. Jeong *et al.*[12] investigated the relation between the electroforming procedure and the resulting bipolar switching behaviour in Pt/TiO_2/ Pt structure fabricated by sputtering, and proposed that both oxygen gas and vacancies in the vicinity of the anode played an important role. Similar results were reported by Yoshida *et al.*[13] in Pt/TiO_2/TiN structure in which the TiO_2 was formed by oxidation of the TiN layer.

In our experiment, we think that conducting filaments which consist of oxygen deficient TiO_2 formed or ruptured during RS, and the extra oxygen within ITO electrodes provides a greater chance to enhance the endurance. Because TiO_2 thin film is deposited by the sputtering method only under Ar atmosphere and at room temperature, a lot of oxygen vacancies nucleate in TiO_2 films, then the conductive chains can be formed even without the initial forming process. The RS of the ITO/TiO_2/ITO device might be described as the formation and the rupture of the filamentary conductive paths via the generation/recovery of oxygen vacancies and oxygen ions. During the reset process oxygen ions in the filament may move toward the anode electrode, thereby disconnecting the filament by anodizing Ti into TiO_2. In the set process as the electric field is applied in the opposite direction, the oxygen ions move toward the cathode electrode while the insulating TiO_2 at the filament edge is reduced and a metallic filament is formed again. Furthermore, the polycrystalline phase of the ITO electrode is suggested to act as the reservoir of defects such as O_2 vacancy sites and simultaneously O_2 ions (O^{2-}). The ITO electrode contains enough vacancy sites near the interface, which can easily provide resting sites for the migrating O^{2-}. This implies that the ITO electrode can be treated as an O_2 ion source. The O_2 ions move into or away from the ITO layer under the electrical field with the opposite polarity, hence take part in the forming and rupture processes of the filament in the TiO_2 layer. Thereafter, the ITO electrode also plays an important role in the RS process with enhanced endurance compared with the metal electrodes. Thus, the improvement of switching stability can be expected based on the above discussion.

4. Conclusion

We fabricate fully TRRAM devices based on an ITO/TiO_2/ITO sandwich by conventional RF sputtering. The TRRAM devices exhibit excellent transmittance of more than 81% in the visible region. Without the initial forming process, the RRAM devices show bipolar RS behaviour. In addition, more than 300000-fold continuous rewrite measurements indicate the reliable retention and the enhanced switching capability. The forming and the rupture processes of the filament in the TiO_2 layer rely on more oxygen vacancies provided by the transparent ITO electrodes.

References

[1] Liu S Q, Wu N J and Ignatiev A 2000 *Appl. Phys. Lett.* **76** 2749

[2] Choi B J, Jeong D S and Kim S K 2005 *J. Appl. Phys.* **98** 033715

[3] Seo S, Lee M J, Seo D H, Jeoung E J, Suh D S, Joung Y S, Yoo I K, Hwang I R, Kim S H, Byun I S, Kim J S and Park B H 2004 *Appl. Phys. Lett.* **85** 23

[4] Wu X, Zhou P, Li J and Chen L Y 2007 *Appl. Phys. Lett.* **90** 183507

[5] Xu N, Liu L F, Liu X Y, Han D D, Wang Y, Han R Q, Kang J F and Yu B 2008 *Appl. Phys. Lett.* **92** 232112

[6] Inoue I H, Yasuda S, Akinaga H and Takagi H 2008 *Phys. Rev.* B **77** 035105

[7] Lee C B, Kang B S, Benayad A, Lee M J, Ahn S E, Kim K H, Stefanovich G, Park Y and Yoo I K 2008 *Appl. Phys. Lett.* **93** 042115

[8] Hasan M, Dong R, Choi H J, Lee D S, Seong D J, Pyun M B and Hwang H 2008 *Appl. Phys. Lett.* **93** 052908

[9] Seo J W, Park J W, Lim K S, Yang J H and Kang S J 2008 *Appl. Phys. Lett.* **93** 223505

[10] Tsunoda K, Fukuzumi Y, Jameson J R, Wang Z, Griffin P B and Nishi Y 2007 *Appl. Phys. Lett.* **90** 113501

[11] Kim K M, Choi B J, Shin Y C, Choi S and Hwang C S 2007 *Appl. Phys. Lett.* **91** 012907

[12] Jeong D S, Schroeder H, Breuer U and Waser R 2007 *J. Appl. Phys.* **104** 123716

[13] Yoshida C, Tsunoda K, Noshiro H and Sugiyama Y 2007 *Appl. Phys. Lett.* **91** 223510