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Resistive switching properties of TiO_2 film for flexible non-volatile memory applications

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Abstract

Flexible electronics attracts much attention due to its advantages of flexibility and light weight. The resistive switching memory fabricated at low temperature with good performance is possibly used in the flexible electronics. In this work, an $Al/TiO_2/Al$ structural device is successfully fabricated on a flexible substrate at room temperature for the first time. The resistive switching properties of the flexible device are investigated. A possible resistive switching mechanism is proposed. The non-volatility of the flexible device is also demonstrated. Based on the experimental results, the proposed flexible device is possibly used in flexible non-volatile memory.

Keywords: B. Defects; D. TiO_2; Flexible; Resistive switching

1. Introduction

Recently, flexible electronics has attracted intensive study due to its advantages of flexibility, light weight, low temperature process, and low cost [1]. Non-volatile memory with non-volatility is a core element in the flexible electronic devices [2,3]. However, the mainstream of non-volatile memory, flash memory, has degraded dielectric quality in low temperature process [3]. The resistive switching memory processed at low temperature shows good performance, so it can be used in the flexible electronics [4–6].

Most of the resistive switching layers fabricated on flexible substrates in the past are organic materials. However, the fabrication process of organic material is more complicated in controlling external conditions [7]. These limitations require additional efforts to improve memory performance and increase processing cost. On the other hand, inorganic materials, such as binary metal oxides [4–6], are easier to control stoichiometrically. So, inorganic materials are more probable to be used in flexible devices.

In this study, an $Al/TiO_2/Al$ structural device is successfully fabricated on a flexible substrate at room temperature using low cost radio-frequency magnetron sputtering for the first time. Furthermore, resistive switching properties of the flexible devices that are before bending (BB), under bending (UB), and after bending (AB) are investigated. The flexible device AB shows most stable resistive switching behavior, such as most uniform switching voltage and highest switching cycle. A possible resistive switching mechanism of the flexible device is also proposed in this study.

2. Experimental details

First of all, an Al bottom electrode was deposited on a cleaned polyethersulfone flexible substrate. Then, a TiO_2 resistive switching layer of about 60 nm-thick was deposited on the Al bottom electrode. Finally, Al top electrodes with 150 μm in diameter were deposited on the TiO_2 film to complete the $Al/TiO_2/Al$ device structure. All the fabricating processes were carried out by the radio-frequency magnetron sputtering at room temperature. Simultaneously, the TiO_2/Al films were also fabricated on a SiO_2/Si substrate for the analysis of the material properties of TiO_2 film.

The chemical bonding and non-lattice oxygen of the TiO_2 film were determined by an X-ray photoelectron spectroscopy (XPS). The resistive switching properties of the flexible device were recorded by a Keithley 2400 source

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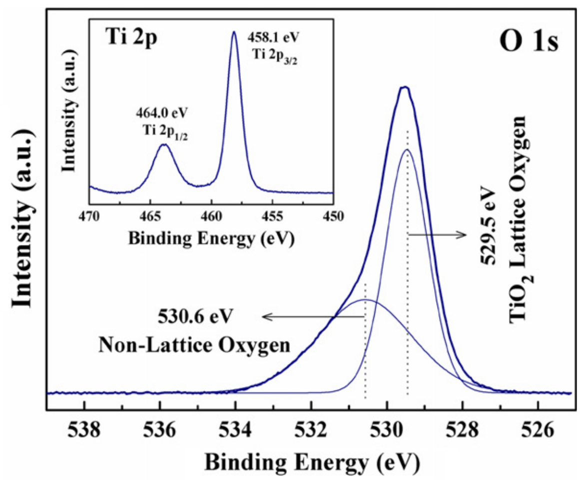

Fig. 1. O 1s XPS spectrum of the TiO_2 film. The inset is the Ti 2p XPS spectrum.

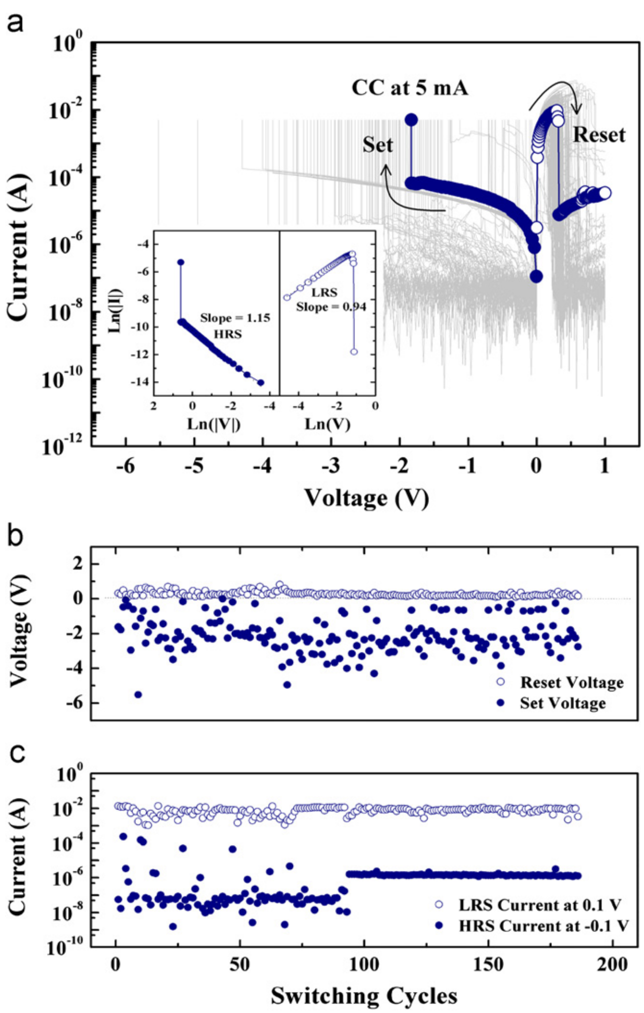

Fig. 2. (a) The resistive switching I–V curves of the $Al/TiO_2/Al$ flexible device that is BB. The inset is the fitting curves of LRS and HRS currents by Ohmic conduction. (b) The reset and set voltages, and (c) the LRS and HRS currents at ± 0.1 V of the flexible device depicted in part (a).

meter. During the electrical measurements, bias voltages were applied on the Al top electrode at room temperature while the Al bottom electrode was grounded.

3. Results and discussion

The Ti 2p XPS spectrum of the TiO_2 film is shown in the inset of Fig. 1. The peaks of Ti $2p_{1/2}$ and Ti $2p_{3/2}$ are near 464.0 and 458.1 eV, respectively, the energy which represents the TiO_2 bonding. On the other hand, the Ti metallic peak at about 453.7 eV is not found. The results show that the film is almost oxidized. The O 1s XPS spectrum of the TiO_2 film is shown in Fig. 1. The film exhibits a TiO_2 lattice oxygen signal at about 529.5 eV, which also indicates the TiO_2 bonding. In addition, the film exhibits a non-lattice oxygen signal at 530.6 eV, which is about 1 eV higher than the lattice oxygen signal [8]. Namely, the TiO_2 film deposited at room temperature possesses a large amount of non-lattice oxygen. Based on our previous research results, the non-lattice oxygen will react with the Al atoms to form an AlO_y interface layer during the sputtering of the Al top electrode [6]. Resistive switching occurring in the interface layer is expected to be more stable than that in the bulk film [4].

Fig. 2(a) depicts the resistive switching I–V curves of the $Al/TiO_2/Al$ flexible device BB. The memory state of the device is initially in a low resistance state (LRS). It can be altered to a high resistance state (HRS) by applying a positive bias voltage, called reset step. In addition, the memory state of the device can be switched back to the LRS by applying a negative bias voltage with a current compliance (CC) at 5 mA, called set step. As the memory states of the device are altered by applying bias voltages with different polarities, the I–V curves are called bipolar resistive switching. The bipolar resistive switching of the flexible device can be reproduced for over 180 times. In addition, the reset and set steps can also be achieved by applying negative and positive bias voltages, respectively, i.e., the reset and set steps are independent of voltage polarities. The inset of Fig. 2(a) is the plots of Ln ($|I|$) versus Ln ($|V|$) of both LRS and HRS currents. The slopes of two curves are close to unity, indicating that the currents are dominated by Ohmic conduction. It fully conforms to the filamentary model [9]. Fig. 2(b) indicates the reset and set voltages of the flexible device BB, depicted in Fig. 2(a). The reset voltages are within 1 V, and the set voltages are less than -6 V. As the resistive switching is performed under bipolar mode, the reset and set voltages are clearly distinguishable. Fig. 2(c) indicates the LRS currents measured at 0.1 V and the HRS currents measured at -0.1 V of the flexible device BB depicted in Fig. 2(a). Two memory states are also distinguishable during the 180 switching cycles.

Fig. 3 describes a possible resistive switching mechanism of the flexible device BB. A large amount of oxygen vacancies exists in the TiO_2 film to form a conductive filament (CF). Carriers can flow through the CF, so the

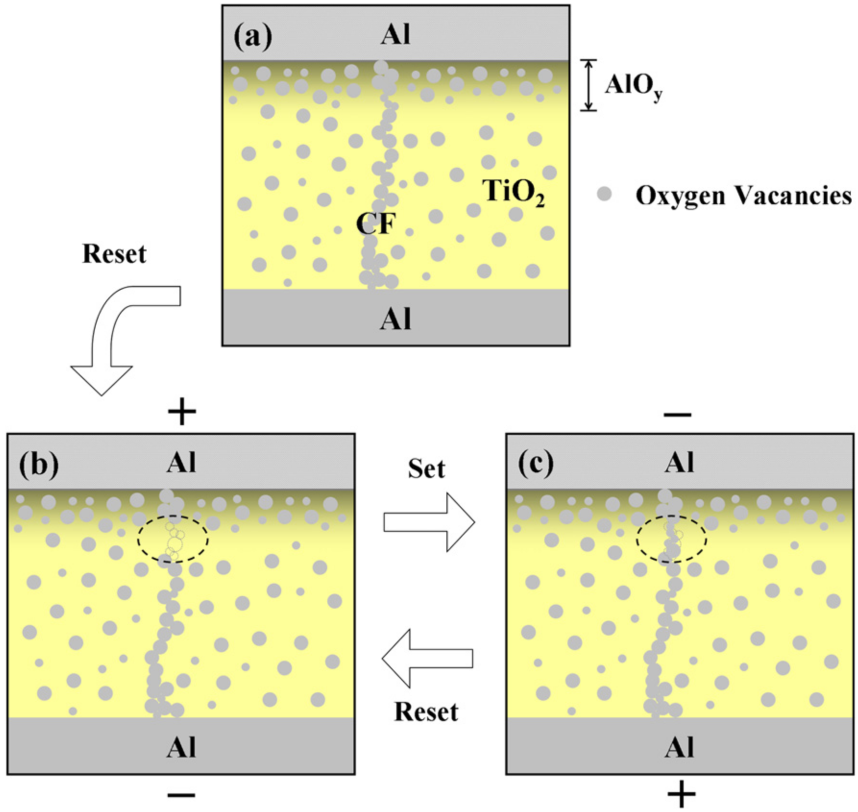

Fig. 3. Possible resistive switching mechanism of the flexible device that is BB. (a) Initially in the LRS, (b) reset to the HRS, and (c) set back to the LRS.

device is initially in the LRS, as shown in Fig. 3(a). While a positive bias voltage is applied on the Al top electrode, as shown in Fig. 3(b), a large current flows through the CF. The reset step happens, i.e., the current suddenly decreases, due to thermal oxidation of the oxygen vacancies near the AlO_y/TiO_2 interface by accumulated local Joule heating, leading to the rupture of CF [6,10]. On the other hand, while a negative bias voltage is applied, oxygen vacancies with positive charges in the TiO_2 film will drift through the interface to connect the Al top electrode again, the connection which leads to re-formation of the CF. Hence, the memory state of the device is set to the LRS. The LRS and HRS currents dominated by Ohmic conduction also demonstrate the filamentary model [9].

Fig. 4(a) depicts the resistive switching I–V curves of the flexible device that is bent to 5 cm in radius of curvature, as shown in the inset of Fig. 4(a). When the flexible device is UB, the resistive switching behavior becomes disordered and unstable. The maximum set voltage increases to about -8 V, and the switching cycles decrease to less than 100 times. On the other hand, while the flexible device is flatted again, i.e., AB, the resistive switching behavior returns to a stable status, as shown in Fig. 4(b). The set voltages decrease to within -6 V, and the HRS currents become more uniform than those of the devices that are BB and UB, and the switching cycles improve to over 300 times. The inset of Fig. 4(b) is a real photo of the flexible device.

Fig. 5(a) is the cumulative probabilities of the LRS currents measured at 0.1 V and the HRS currents measured at -0.1 V of the flexible devices that are BB, UB, and AB. The LRS currents hold on about several milli ampere in three conditions, but the HRS currents of the flexible device AB are higher and more uniform than the others. In addition, the cumulative probabilities of the reset and set voltages of the flexible devices in three conditions are shown in Fig. 5(b). The reset voltages are within 1 V, but the set voltages of the flexible device UB distribute more widely than the others. The effects of bending on resistive switching parameters can be explained as follow.

While the flexible device is UB, we infer that some defects are created in the TiO_2 film and at the AlO_y/TiO_2 interface. However, the defects are tied by the bending stress [11], so they cannot participate in the resistive switching. In addition, a part of oxygen vacancies in the TiO_2 film is also tied by the bending stress, so they cannot drift easily during the set step. Therefore, the set voltages increased, and the switching cycles decreased. On the other hand, while the flexible device is flatted again, the oxygen vacancies and new-created defects participate in the resistive switching, so the resistive switching behavior returns to a stable status, leading to a higher switching cycles. Besides, the HRS currents of the flexible device AB are much higher than the others because there are some new-created defects in the TiO_2 film [11], leading to a higher leakage current.

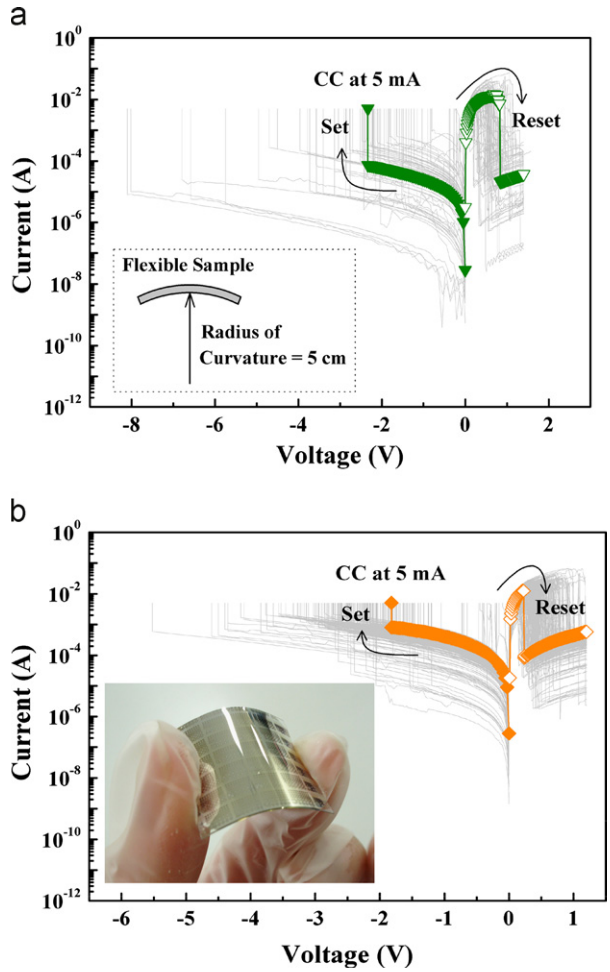

Fig. 4. Resistive switching I–V curves of the flexible devices that are (a) UB and (b) AB. The inset of part (b) is a real photo of the flexible device.

Fig. 6 shows the retention time of the flexible devices that are BB, UB, and AB. The retention time is over 10^5 s while the device is UB, and it is over 10^6 s while the devices are BB and AB. Therefore, the good non-volatility of the flexible device is demonstrated.

4. Conclusions

The Al/TiO_2/Al flexible resistive switching memory fabricated at RT by sputtering with low cost is proposed in this work. The flexible devices that are BB, UB, and AB exhibit good resistive switching properties. The device that is AB shows most stable resistive switching behavior, including most uniform switching voltage and highest

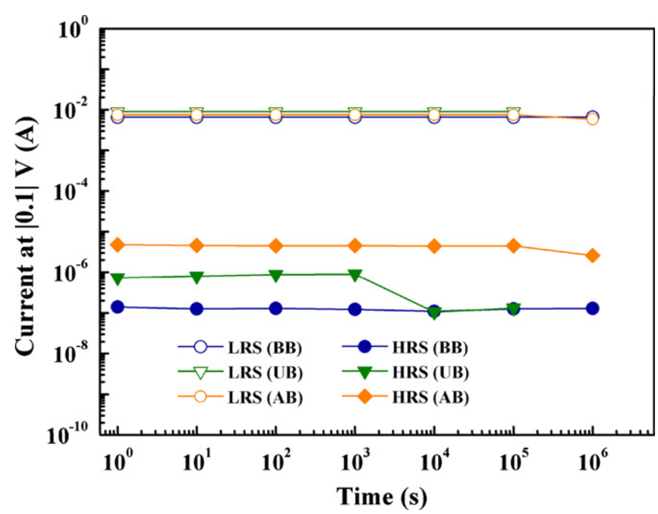

Fig. 6. Retention time of the flexible devices.

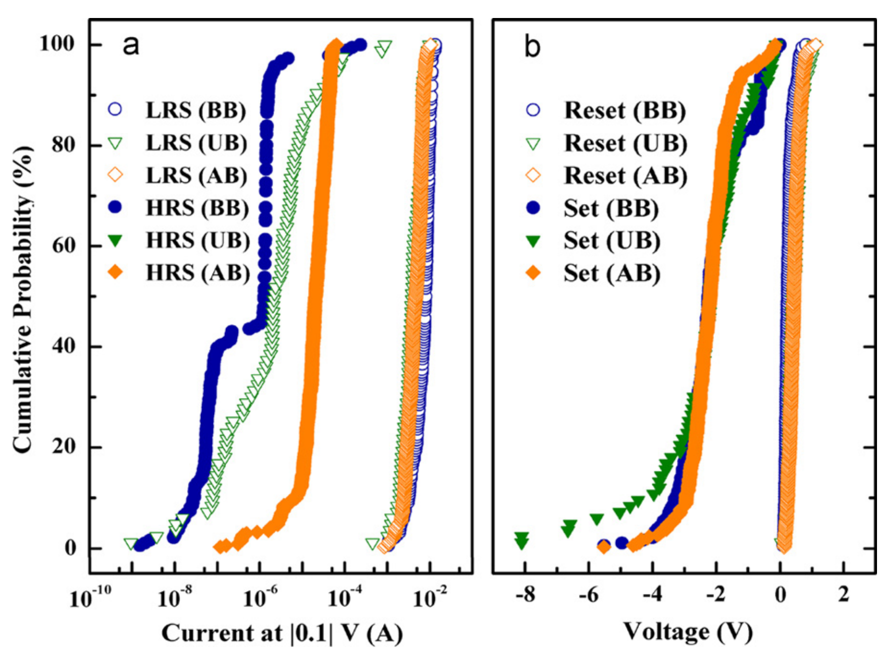

Fig. 5. Cumulative probabilities of (a) the LRS and HRS currents measured at ± 0.1 V, and (b) the reset and set voltages of the flexible devices that are BB, UB, and AB.

switching cycle. A possible resistive switching mechanism of the flexible device is proposed. The non-volatility of the flexible device over 10^6 s is also demonstrated in this work. Based on the experimental results, the proposed flexible device is possibly used in flexible non-volatile memory.

Acknowledgments

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