TiO₂ thin film based transparent flexible resistive switching random access memory

Kim Ngoc Pham¹, Van Dung Hoang², Cao Vinh Tran² and Bach Thang Phan¹,²

¹Faculty of Materials Science, University of Science, Vietnam National University in Ho Chi Minh City, 227 Nguyen Van Cu, District 5, Ho Chi Minh City Vietnam
²Laboratory of Advanced Materials, University of Science, Vietnam National University in Ho Chi Minh City, 227 Nguyen Van Cu, District 5, Ho Chi Minh City Vietnam

E-mail: phamngoc@hcmus.edu.vn

Received 20 October 2015
Accepted for publication 22 January 2016
Published 18 March 2016

Abstract
In our work we have fabricated TiO₂ based resistive switching devices both on transparent substrates (ITO, IGZO/glass) and transparent flexible substrate (ITO/PET). All devices demonstrate the reproducibility of forming free bipolar resistive switching with high transparency in the visible light range (~80% at the wavelength of 550 nm). Particularly, transparent and flexible device exhibits stable resistive switching performance at the initial state (flat) and even after bending state up to 500 times with curvature radius of 10% compared to flat state. The achieved characteristics of resistive switching of TiO₂ thin films seem to be promising for transparent flexible random access memory.

Keywords: transparent, flexible, RRAM, TiO₂, thin film
Classification numbers: 4.00, 4.10

1. Introduction
Recently, resistive random-access memory (RRAM) has attracted great attention due to potential advantages such as simple capacitor structure, excellent scalability, low power consumption and non-destructive readout [1]. RRAM is based on the reversible dielectric (soft) breakdown of an insulator layer to distinctively change the resistance between high resistance state (HRS) and low resistance state (LRS) under bias stress. Among the various oxide materials demonstrating resistive switching, including ZnO, HfO₂, Ta₂O₅, WO₃ and CuOₓ, TiO₂ appears to be one of the most promising switching materials because of its non-toxic behavior, low cost and, especially, its relatively well-known operation mechanism [2–6]. Therefore, RRAM devices based on TiO₂ thin films for transparent and/or flexible applications such as displays, sensors, solar cells, and organic light emitting diodes have recently been developed [7, 8]. However, the electrical reliability characteristics of the devices still had some limitations.

In earlier work [7, 8], plasma enhanced atomic layer deposition and solution process were used to deposit TiO₂ thin films. In this study, we use DC sputtering technique to investigate TiO₂ based resistive switching devices on transparent/flexible substrates. The structural simplicity and high uniformity of transparent conductive oxide (TCO) bottom electrodes result in good performance of RRAM devices. In addition, durable and flexible properties have also been investigated in detail.

2. Experimental
A 100 nm-thick TiO₂ thin film was deposited by reactive sputtering from the titanium metal target (99.99% purity) in a mixture of Ar and O₂ (6%) gases at a working pressure of 7 × 10⁻² torr. We use a transparent substrate including indium gallium zinc oxide (IGZO), indium tin oxide (ITO)/glass substrates and flexible indium tin oxide/polyethylene terephthalate (ITO/PET) substrate. The resistance of IGZO and ITO layers is approximately 15 Ω and 20 Ω, respectively.
TCO layers were used as the bottom electrode (BE) and Ag layer was used as the top electrode (TE). During deposition of top Ag layer, a mask was used for top electrode patterning. The sourcemeter Keithley 4200 SCS was used for I–V characterization of the RRAM device. For all electrical measurements the BE were always biased and TE were grounded. For the flexible test, bending cycles of RRAM devices were applied in the bending system by mechanical stress with a unique curvature radius for 4 cycling times/min.

3. Results and discussion

3.1. Transparent RRAM devices

Figure 1 shows the current-voltage (I–V) characteristics of RRAM devices on glass substrates. During all the electrical measurements, an external bias was applied to the bottom electrode (IGZO, ITO) and Ag top electrode was electrically grounded. All devices exhibit stable bipolar switching behavior without forming process in the sweeping range of $-2 \text{ V} \rightarrow +2 \text{ V}$.

On the Ag/TiO$_2$/IGZO device, when the negative bias voltage was applied from 0 to $-2 \text{ V}$, the current of the device increases gradually, which represents the transition from HRS to LRS. In this case, set voltage ($V_s$) was unclear and relative hard to readout. Sequentially, by sweeping positive bias, the switching from LRS to HRS occurs at around $1.25 \text{ V}$ ($V_{rs}$) exhibiting the reset process. For further analysis, memory reliability was evaluated. The result is presented in the insert data at the right corner of figure 1. Although slight fluctuation was observed, both the resistance states reading at 0.2 V are stable after 100 cycles, maintaining resistance difference around one order of magnitude. In addition, the insert image at the lower left corner also shows that device is high transparent in the visible range.

Similarly, typical I–V curve of Ag/TiO$_2$/ITO device exhibits the bipolar resistive switching in the range of $-1.5 \text{ V} \rightarrow 2 \text{ V}$. However, the switching from HRS to LRS and reversibility is more sharp than that of Ag/TiO$_2$/IGZO device. It is easier to examine the operation voltages in this device. The set and reset voltages are around $-0.75 \text{ V}$ and $1 \text{ V}$, respectively. Compared to the Ag/TiO$_2$/IGZO device, the resistance states of Ag/TiO$_2$/IGZO device are rather stable and more than one order of magnitude. Additionally, transparent property of device have been demonstrated in the inserted image at the lower left corner of figure 1.

All these electrical and transmission characteristics indicate that TiO$_2$ thin film is really suitable for transparent RRAM devices.

3.2. Transparent flexible RRAM devices

Next, transparent and flexible RRAM device has been developed on polyethylene terephthalate (PET). Figure 2
exhibits the I–V characteristics of Ag/TiO₂/ITO device formed on flexible PET substrate. Device image is inserted at the left corner of figure 2. It is obviously similar to the Ag/TiO₂/ITO device on the glass substrate. However, the resistance of LRS maintains stable state while the resistance of HRS has large fluctuation. Some reports about transparent flexible devices also provided that there was a little instability of resistance states. This may be one of disadvantages of device on flexible PET substrate compared to device on glass substrate. The second difference is that the switch from LRS to HRS on positive bias is completely abrupted at 1.5 V.

To figure out further detail analysis for flexible properties, figure 3 shows the I–V characteristics of Ag/TiO₂/ITO/PET after bending. The level of mechanical endurance was evaluated by bending the system with cycling compress stress, and the curvature radius measurement scheme is inserted in figure 3. A vibrator was used to induce substrate bending 4 times/min for a total of 500 bends. After bending process, I–V behavior of device was measured carefully again. Encouragingly, the resistive switching behavior displays no significant change to that of the device before bending. It is demonstrated that the Ag/TiO₂/ITO/PET device has been bendable.

One of the key requirements for flexible memory application device is the robustness to withstand repetitive bending cycles. To verify this characteristic, two resistance states were measured as a function of bending cycles. The results are presented in figure 4. It should be noted that the resistive switching behavior of device is still available even after bending up to 500 times. The resistance state of LRS is completely stable. On the other hand, the resistance state of HRS showed a slight reduction, leading to the decrease of resistance ratio with increasing bending cycles. However, the difference of resistance states still ensures operation of an RRAM device. These results indicate that the switching characteristics of flexible RRAM are dependent on bending radius and bending cycle.

4. Conclusion

In conclusion, we successfully fabricated transparent RRAM devices on glass substrates and transparent flexible RRAM device on PET substrate of TiO₂ thin film. Through the current–voltage measurements, our devices exhibited high stable bipolar switching behavior and good endurance before/after the bending process. These results suggest that TiO₂ thin film based memristors are promising for use in the fabrication of nonvolatile random access memories.

Acknowledgment

This research is funded by Vietnam National University HoChiMinh City (VNU-HCM) under grant number C2015-18-17.

References

[1] Waser R and Aono M 2007 Nature Mater. 6 833
[2] Yang Y, Pan F, Zeng F and Liu M 2009 J. Appl. Phys. 106 123705
[3] Kim W and Rhee S 2009 Microelectron. Eng. 86 2153
[4] Dao T T T, Pham K N, Cheng Y L, Kim S S and Phan B T 2014 Curr. Appl. Phys. 14 1707
[5] Mao Q, Ji Z, and Xi J 2010 J. Phys. D: Appl. Phys. 43 395104
[6] Pham K N, Nguyen D T, Dao B T T, Ta K H T, Tran V C, Nguyen V H, Kim S S, Maenosono S and Phan N T 2014 J. Electron. Mater. 43 2737
[7] Jung S, Kong J, Song S and Lee K 2010 J. Electrochem. Soc. 157 H11042
[8] Kim S, Yarimaga O, Choi S and Choi Y 2010 Solid State Electron. 54 392