

Effects of electrodes on resistance switching characteristics of TiO₂ for flexible memory*

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Flexible TiO₂ memory devices are fabricated on a plastic substrate at room temperature. The metal-insulator-metal (MIM) structure is grown on polyimide (PI). Several metals with different ductilities, such as Al, W, Cu and Ag, are selected as electrode. The test results show that the samples have stable resistive switching behaviors, and the electric characteristics can stay stable even after the radius of substrate is bent up to 10 mm. After 10³ times of substrate bending, the memory cells with W as bottom electrode on PI still show stable resistive switching characteristics and low switching voltages. The set voltage and reset voltage can be as low as 0.9 V and 0.3 V, respectively.

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Resistive random access memory (RRAM) has been widely investigated for its simple structure, high speed operation, low power consumption, high packing density, etc.^[1] For most of the RRAM devices, metal oxides, such as NiO, ZnO and TiO₂, are adopted as the insulator layer, which show good electrical performance^[2]. Recently, flexible material is applied in many fields, such as electronic paper, sensors and solar cells^[3]. The innovative devices including transparent RRAM and flexible RRAM have been proposed^[4-8]. Indium tin oxide (ITO) was usually employed as the electrode^[9, 10]. In addition, a flexible RRAM device using a solution processed ZnO thin film was fabricated on plastic substrates^[11]. The relatively unsmooth surface and an additional annealing process over 200 °C both make this method not so favorable. The dispersions of the resistance lead to device failure after several times of substrate bending. Therefore, there is a serious issue on how to minimize the dispersions of the resistance values on ON-state and OFF-state.

In this paper, the magnetron sputtering method is applied to deposit the TiO₂ thin film on the polyimide (PI) substrate (DuPont). TiO₂ thin film is deposited on different bottom electrodes. The resistive switching behaviors of the samples are tested with semiconductor parameter analyzer. After several times of substrate bending, the performance of the samples with different bottom electrodes is evaluated, and the characteristics and the ductilities of the electrodes are discussed.

The metal-insulator-metal (MIM) capacitor structure

was fabricated on a PI substrate. To reduce the surface roughness, the PI substrate was dehydrated in vacuum at 200 °C. The bottom electrodes of different materials, such as Al, W, Cu and Ag, were directly deposited on the PI substrate at room temperature. Subsequently, the TiO₂ thin film was deposited using a Ti target under 1 Pa at room temperature. Fig.1 shows the schematic diagram of the TiO₂ RRAM cell. The thickness of TiO₂ layer is about 100 nm. Finally, a Cu top electrode with a thickness of 100 nm was formed on top of TiO₂ film by thermal evaporation using photolithography and a lift-off process. The current-voltage (*I-V*) characteristics of the devices are obtained using a semiconductor parameter analyzer (Agilent B1500).

To characterize the memory device on a PI substrate, the TiO₂ thin film was fabricated on different electrodes with the same deposition conditions. In the devices, TiO₂ thin films were deposited with the same process at room temperature. The flexible TiO₂-based devices exhibit electrical switching with memory characteristics which match the electrical behavior previously reported on resistive switching memory.

Fig.2 shows *I-V* characteristics of typical TiO₂ memory devices fabricated on different electrodes. The devices present low threshold voltage and stable switching *I-V* curves. For example, RRAM device with Cu electrode starts in the high resistance state (HRS) on the first voltage sweep. When the bias is increased to 0.7 V, the current increases abruptly, and the device is transformed

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to the low resistance state (LRS). This state remains stable until a bias of about 0.4 V is applied, resulting in a transition back to high resistance state. A current compliance is employed to keep the devices on the PI substrate from electrical breakdown.

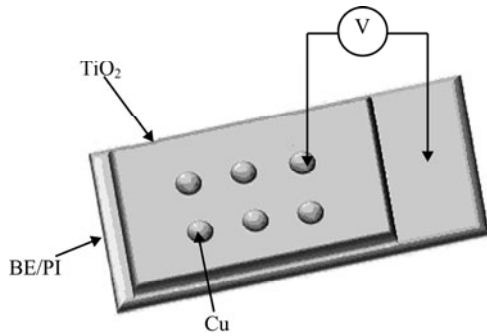


Fig.1 Schematic diagram of the TiO₂ RRAM device

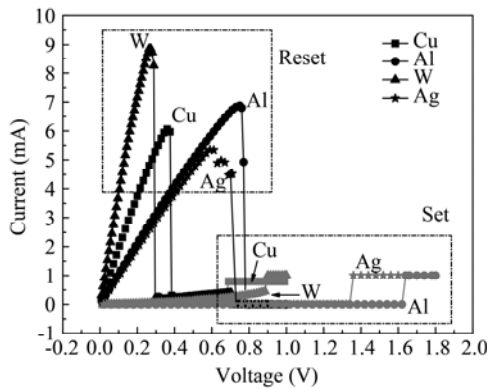
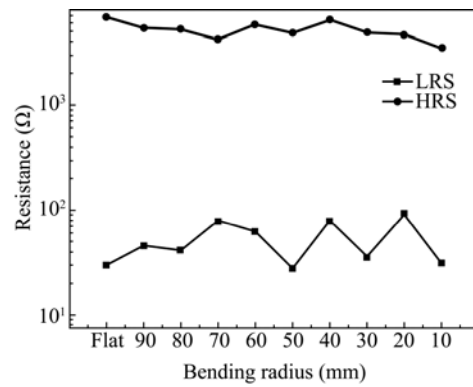


Fig.2 Current-voltage (*I-V*) curves of the TiO₂ memory devices with different bottom electrodes on flexible substrate

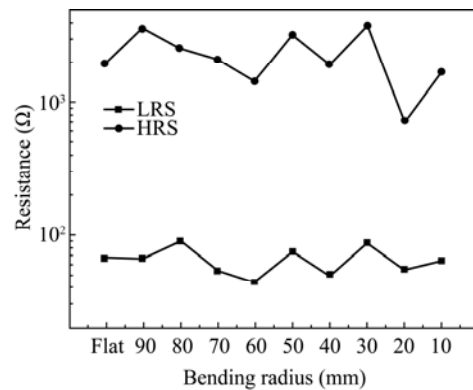
A mechanical bending test of the RRAM on a flexible substrate is performed in order to confirm the mechanical stability of the device for flexible memory applications, and the results are presented in Fig.3. The resistance is measured at 0.1 V after the set process and the reset process. Because of the good ductility of the bottom electrode, the performance of resistive switching does not degrade, and the ratio of the high state to low state remains at least 100, even when the substrate is bent up to 10 mm radius.

Fig.4 demonstrates that even after being flexed for 1000 times, the devices retained an adequate state ratio for memory applications.

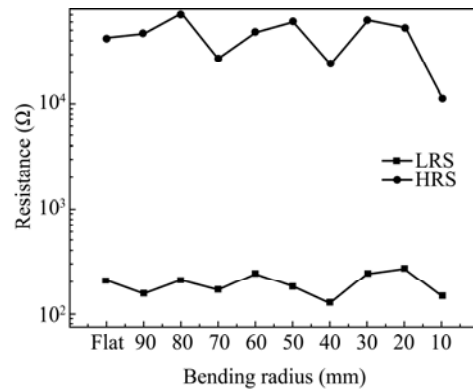
After the mechanical bending test, the flexible memories based on TiO₂ with different bottom electrodes show stable resistive switching characteristics, but the degrees of the decline are different. The switching margin in cell structure of TiO₂/Cu remains stable for 500 cycles, and it starts to decrease as the mechanical bending test continues. Similar phenomenon is also observed in TiO₂/Al and TiO₂/Ag structures, while the bending cycles for declination are 600 and 700, respectively. As in TiO₂/W struc-



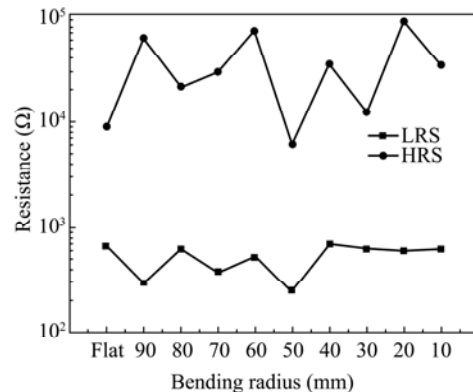
(a) Cu



(b) Al



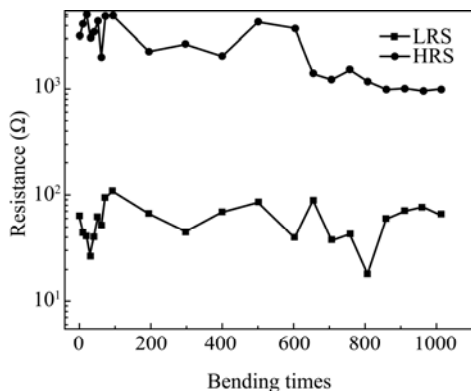
(c) W



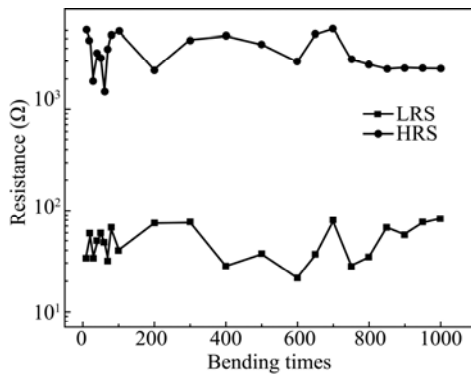
(d) Ag

Fig.3 Resistance variation as a function of bending radius with different bottom electrodes

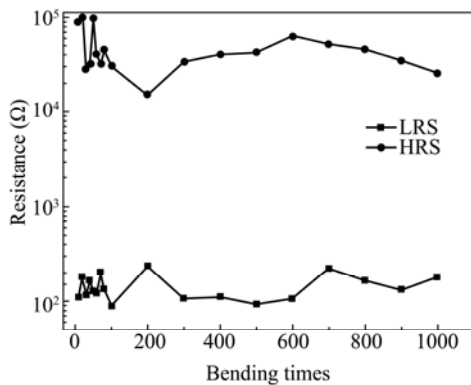
ture, the cell shows stable switching characteristic even after being bent for 1000 times. It may be due to the nature of the electrode or the contact mode between electrode and the TiO₂ film. We attribute the difference in stability of cell structures with different electrodes to the metal characteristics of the bottom electrodes. After the bending process, Cu bottom electrode is more possible to be oxidized than the same structure without being bent, and it affects the switching characteristics of the structure. It is reported that W showed stable characteristics when contacted with O₂, therefore the switching structure with W bottom electrode could keep a relatively stable switching margin even after being bent for thousands of times.



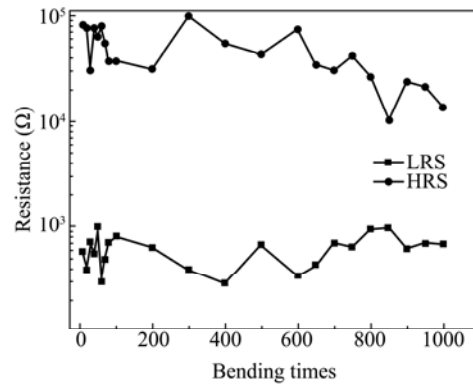
(a) Cu



(b) Al



(c) W



(d) Ag

Fig.4 Resistance variation as a function of bending times with different bottom electrodes

In summary, we demonstrate the non-volatile memory characteristics of flexible TiO₂ memory devices fabricated on different electrodes. Because of the nature of the electrode and different flexibilities, the resistive switching characteristics have different degrees of decline as the bending radius decreases and the times of bending increase. The TiO₂ memory device fabricated on W electrode shows a more stable resistive switching behavior. These devices have high potential for application as flexible memory components.

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