Asymmetric bipolar resistive switching in solution-processed Pt/TiO₂/W devices

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Abstract

The resistive switching characteristics of Pt/TiO₂/W devices in a submicrometre via-hole structure are investigated. TiO₂ film is grown by the sol–gel spin coating technique. The device exhibits reversible and reproducible bistable resistive switching with a rectifying effect. The Schottky contact at the Pt/TiO₂ interface limits electron injection under reverse bias resulting in a rectification ratio of >60 at 2 V in the low-resistance state. The switching mechanism in our device can be interpreted as an anion migration-induced redox reaction at the tungsten bottom electrode (W). The rectifying effect can significantly reduce the sneak path current in a crossbar array and provide a feasible way to achieve high memory density.

(Some figures in this article are in colour only in the electronic version)

Oxide-based resistive random access memory (RRAM) has attracted a great deal of attention for non-volatile memory applications due to its structural simplicity, fast switching speed, low power consumption and high-density integration [1–3]. The crossbar-array-type resistive memory is ideal for realizing the highest memory density with the smallest cell size ($4F^2$, F —minimum feature size) [2–4]. However, selecting a designated cell within a passive crossbar array without encountering the interference of leakage current through neighbouring cells is the biggest hindrance to the realization of high-density memory cell arrays. Because typical current–voltage (I – V) curves for the low resistance state (LRS) of resistive memories are almost symmetrical (resistor-like), a cell in the high resistance state (HRS) will be misread when the surrounding cells in the LRS form an unexpected sneak current path [5]. In the worst-case scenario, all of the unselected cells are in the LRS. With increase in memory density, the number of sneak current paths is huge, which makes the read operation difficult without employing any selection devices in the crosspoint application. Several types of oxide-based selection devices, such as 1D–1R type, have been proposed for unipolar-type resistive switching [6, 7].

However, the switching uniformity of a unipolar RRAM is much worse compared with bipolar interface-type switching due to the random formation and rupture of filaments [8]. The conventional p–n junction diode cannot be used as a selection device for a bipolar-type RRAM because the current flow through the diode under a reverse bias condition is extremely low. Another option is the utilization of a Zener diode, which allows current in the forward direction (like a regular diode), but also in the reverse direction if the voltage is higher than the breakdown voltage (Zener voltage) [9]. However, the basic requirements, such as a high forward/reverse (FR) current ratio and high current density, are difficult to simultaneously satisfy with a single Zener diode [10]. An asymmetric LRS under different polarities can reduce the sneak path current and does not require any kind of selection device, thereby enabling the realization of the highest density with the smallest cell size [5, 10]. It has recently been reported that a nanoscale resistive memory with intrinsic diode characteristics in an amorphous Si-based memory cell eliminates the misreading problem in crossbar arrays [11]. Zuo *et al* proposed a self-rectifying feature in Au nanocrystal-embedded ZrO₂-based resistive memory to alleviate the crosstalk problem [10]. Jo *et al*

reported that a self-formed Schottky barrier at the Al/PCMO interface can act as a selection device for crosspoint memory applications [12]. Linn *et al* successfully demonstrated a complementary resistive switch that can eliminate the sneak path problem in passive crossbar arrays [13].

In this paper, we report the resistive switching characteristics of TiO₂ thin films on a 250 nm via-hole substrate grown by the sol–gel spin coating technique. Among the various methods available to deposit oxide films, the sol–gel process is advantageous because of its simplicity, low cost of fabrication, and ease of control of the stoichiometry and doping levels [14]. We investigated the effect of annealing temperature and top electrodes (TEs) in order to obtain a reliable rectifying effect and resistive switching. Shima *et al* reported the rectifying and resistive switching behaviour in a Pt/TiO_x/Pt device [15]. Recently, Huang *et al* have reported the transition of stable rectification to resistive switching in Ti/TiO₂/Pt devices [16]. Yang *et al* demonstrated a family of reconfigurable electronic devices by combining the properties of memristive switching and non-linear rectification in a Pt/TiO₂/Pt stack [17]. Similarly, we observe both resistive switching and stable rectification in our Pt/TiO₂/W devices. On the basis of our findings, we suggest a feasible method for alleviating the read disturbance problem in crosspoint arrays.

The TiO₂ sol was prepared using titanium isopropoxide (TTIP) as the source material and ethanol as the solvent. The detailed preparation method of the sol is described elsewhere [18]. The thin films were prepared on a submicrometre (250 nm) W/SiO₂/Si via-hole substrate by spin coating. Each layer was preheated at 150 °C for 5 min. This procedure was repeated until the desired film thickness was achieved. Thin films were annealed at 250 or 400 °C for 60 min. X-ray diffraction results confirm that the 250 °C annealed sample is amorphous in nature whereas the 400 °C sample exhibits a polycrystalline anatase phase [18]. Finally, different TEs, such as Pt, W, Al and Ti of 100 nm thickness, were deposited by radio-frequency (RF) magnetron sputtering. The TEs were patterned using conventional photolithography. The electrical characterization of the device was carried out using a standard parameter analyser (Agilent 4155C). All biases were applied to the top electrode (TE) whereas the bottom electrode (BE) was grounded. Figure 1(a) presents the device structure and the measuring conditions. A positive bias was defined as a flow of current from the TE to the BE. The formation of the TiO₂ layer was confirmed by x-ray photoelectron spectroscopy (XPS). The surface core-level spectra of Ti 2p and O 1s are depicted in figures 1(b) and (c), respectively. Figure 1(b) illustrates that the oxidation state of titanium consists of Ti⁴⁺ at the surface. The Ti 2p_{3/2}, Ti 2p_{1/2} and O 1s peaks are observed at binding energies of around 459.3 eV, 465.1 eV and 531.0 eV respectively, which are very close to those observed in the case of bulk TiO₂ [19]. No other sub-oxides were detected on the surface. However, the presence of sub-oxides was detected after sputter etching which may be due to the low annealing condition for the film preparation. Also, it may be possible that sputter etching can change the oxidation states of Ti⁴⁺ [20]. The O 1s spectra were deconvoluted into two peaks corresponding to the Ti–O and oxygen induced defects.

Figure 1. (a) The typical current–electric field (I – E) measurement condition, (b) XPS core-level spectra of Ti 2p and (c) O 1s.

Several authors have reported that the shoulder peak around 532 eV corresponds to the non-lattice oxygen [21]. Another possibility is that it may be due to adsorbed water vapour on the surface. A shoulder peak is evident along the depth, indicating that it may correspond to the non-lattice oxygen.

Figure 2(a) depicts the typical current–field (I – E) characteristics for the Pt/TiO₂/W memory devices. The field was scanned as follows: $0 \rightarrow +E_{\text{max}} \rightarrow 0 \rightarrow -E_{\text{max}} \rightarrow 0$ (indicated by arrows). Resistive switching from the HRS to the LRS is induced by sweeping the applied electric field in the positive direction which is known as the set process. The reset operation is carried out by sweeping the electric field in the negative direction. The device then switches back to the HRS. We observed a reproducible resistive switching behaviour with the application of appropriate bias voltages in our Pt/TiO₂/W memory device. Figure 2(b) depicts the endurance characteristics of the memory devices. The states were read at a voltage around 2 V, and the memory margin was maintained at above 10 for 100 cycles. A forming-type process is required to obtain the memory window as shown in the inset of figure 2(a) (a-1). The initial resistance state of the film was close to the HRS. A stable memory window was only observed after sweeping the electric field in the negative direction. A positive sweep did not open the hysteresis window. Additionally, with increasing switching cycles, we could observe the appearance of a ‘hump’ in the negative bias region, as depicted in the inset of figure 2(a) (a-2). With the increase in the number of cycles, the ‘hump’ became wider. Several authors have attributed this to negative differential resistance (NDR), which is caused by the motion of oxygen ions at the oxides and the reactive electrode interface [22]. In this study, we did not observe any kind of soft breakdown-like process that generates permanent conducting channels in

Figure 2. (a) Typical I - E characteristics of the Pt/TiO₂/W resistive memory. The arrow indicates the electric field sweep direction. The inset shows (a-1) forming process and (a-2) I - E curve under negative bias in the linear scale. (b) LRS and HRS were read at 2 V. (c) The endurance performance of the LRS read at 2 V and -2 V.

the device [1]. The forming process observed in our devices drives oxygen ions to the W BE. During the initial stages, W oxidizes locally and as the switching cycle increases it oxidizes the entire surface. The LRS current increases slightly with an increase in the number of switching cycles (figure 2(b)). This suggests that the resistance at the LRS decreases due to the larger number of oxygen vacancies in the TiO₂ layer with the increase in switching cycles. The Pt/TiO₂/W memory cells exhibited a high device yield of more than 90%. The operating voltage required to switch our memory device is slightly higher (20 V) [23]. The higher voltage requirement for the operation might be due to the larger thickness (~ 160 nm) and amorphous nature of our film. It is known that the migration of oxygen is much faster along the grain boundaries. It is also evident that the inherent stability of W necessitates the use of a higher voltage for oxidation, and also the current level under negative polarity is very low. It is worth noting that the thinner films also exhibit rectifying memory characteristics with low operating voltages (~ 10 V). However as the film thickness is reduced, some devices short-circuited. During annealing, the organics are evaporated, generating pinholes in the TiO₂ films that leads to a poor device yield. Figure 2(a) reveals that the device exhibits a pronounced rectifying effect in the LRS. In the LRS, the current under a positive bias is much higher than that under a negative bias. With this FR current ratio in the

LRS, the read disturbance in crossbar structure arrays can be avoided. This kind of rectifying resistive memory exhibits potential to be used in crossbar structure arrays. There is no need to add any additional selection device to the rectifying resistive memory. An endurance test was carried out after the device was set to the LRS. The current was recorded at 2 V and -2 V readout voltages, respectively, as illustrated in figure 2(c). Although the resistance at -2 V fluctuates initially, after a few switching cycles the FR current ratio remains almost unchanged. This reproducible and reliable rectifying effect can effectively reduce the misreading in crossbar architectures.

The retention performance of the memory cells at room temperature is depicted in figure 3(a). Limited variations were observed in the current of LRS and HRS over 10^5 s, confirming the non-volatile nature of the device. After the device was switched to the LRS or HRS, no electrical power was needed to subsequently maintain the resistance of a given state. Initially, the LRS displays a tail region (inset of figure 3(a)) that might be due to oxygen vacancy relaxation [23, 24]. The pulse switching characteristics are illustrated in figure 3(b). A positive pulse of approximately 20 V for 10 ms sets the device in the LRS whereas a negative pulse resets the device (-20 V, 10 ms). After each switching, the junction current is measured at a voltage of 2 V. The current level reveals that the HRS-to-LRS ratio is approximately 10 over 5000 switching cycles, indicating that our device is reliable. The ON/OFF ratio is reduced to 6 as the pulse width is reduced from 10 ms to 1 ms. Slow switching might be due to the amorphous nature and larger thickness of the film. Shen *et al* reported a switching speed of 0.1 s for barium strontium titanate (BST) with W as the TE. Switching is attributed to reversible oxidation and reduction in the WO_x layer at the W-BST interface [25]. Recently Jeong *et al* have reported a switching speed of 5 ms for amorphous TiO₂ stacked between Al electrodes [26].

To determine the origin of asymmetry in the I - E curves, we investigated our memory device under different TEs and annealing conditions. It was observed that more symmetric I - E curves were obtained when we used W, Al and Ti as TEs. Figure 4 depicts the typical I - E curves obtained for the film annealed at 400 °C with W and Pt as the TE (solid line). For comparison, the I - E curve obtained for the TiO₂ films annealed at 250 °C (dashed line) is also depicted. All devices exhibit counter-clockwise switching irrespective of the TE and annealing conditions. No forming-type process is required for the film annealed at a high temperature (400 °C). Increasing the annealing temperature also leads to an increase in the leakage currents. However, the voltage required to switch the device on/off is significantly reduced. Voltage in the range ± 10 V is sufficient to switch the device on/off (Pt/TiO₂/W). This might be due to the fact that a higher annealing temperature leads to the crystallization of TiO_x films. Additionally, as W is utilized as the TE, the reset voltage can be reduced even further (8/-6 V). Hence we believe that a higher current in the negative bias may enhance the oxidation of W electrode by Joule heating phenomena. When a metal and an oxide are brought into contact, the atomic positions and charge distributions at the surface can change due to oxidation and reduction reactions at the interface. In the case of TiO₂

Figure 3. (a) Retention characteristics of Pt/TiO₂/W memory device measured at room temperature. Inset shows the initial degradation of LRS in linear scale. (b) Pulse endurance of Pt/TiO₂/W memory devices.

Figure 4. I - E characteristics of Pt/TiO₂/W and W/TiO₂/W devices (solid line) where TiO₂ was annealed at 400 °C. The dotted line depicts the I - E curves for the film annealed at 250 °C. Inset shows the band structure of the Pt/TiO₂/W under different biases.

based memory devices, interface oxidation was reported when reactive elements were used as the electrode material [26, 27]. Analogously, the occurrence of a WO_x layer was reported at the interface between BST and W [25].

Rectifying characteristics were observed with Pt TEs whereas nearly symmetrical I - E curves were obtained with W TEs (figure 4). The inset of figure 4 shows the band structure of Pt/TiO₂/W under different biases. When a negative voltage is applied to Pt, electrons are injected from Pt to TiO₂ and experience a substantial Schottky barrier. The work functions of Al, W and Pt are 4.28 eV, 4.55 eV and 5.65 eV, respectively. TiO₂ is a well-known n-type semiconducting oxide with an electron affinity of 4.0 eV; its electron-transport properties

are dominated by oxygen vacancies. It is evident from figure 4 that the Pt/TiO₂ junction has pronounced Schottky characteristics whereas in W/TiO₂ the Schottky barrier is less pronounced. Therefore, the barrier formed between Pt and TiO₂ film explains the rectifying effect. This indicates that the TE dominates the asymmetric I - E curve.

The mechanism for resistive switching in our devices is **oxygen migration-induced redox switching at the W electrode**. The switching might be due to a reversible oxidation and reduction in a WO_x layer at the TiO₂/W interface. During the forming process (negative bias to the TE) oxygen ions migrated to the BE (W). This may create a WO_x layer at the interface [25]. When a positive bias is applied to the Pt electrode, the oxygen can be released from the WO_x layer further. The resistance of the interface WO_x can be increased by reducing the number of oxygen vacancies. It is evident from the insets of figures 2(a) and (b) that the WO_x layer might have undergone more oxidation with an increasing number of switching cycles. Thus, the WO_x interface layer works like an oxygen sink and it stores and releases the oxygen during switching. Further investigation is required in order to understand the interface between W and TiO₂. Although the switching in our sample is dominated by the interface, the existence of conducting channels in TiO₂ films may be possible. Recently, using conducting atomic force microscopy, Huang *et al* have demonstrated that conduction through a Schottky barrier is inhomogeneous in nature because of localized oxygen migration [16]. In addition, for practical applications, the rectification ratio still needs to be improved and the operating voltage further reduced. Investigations are currently being carried out to improve the performance of the device.

In conclusion, we describe bipolar resistive switching on a simple sol-gel TiO₂ film sandwiched between Pt and W electrodes. We observe stable and repeatable resistive

switching with a rectifying effect. Crosstalk issues can be significantly reduced by properly engineering the top electrode. This low-temperature process can be easily integrated into a 3D stackable crossbar array and does not require any kind of selection device.

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