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Dual-Mode Bipolar Resistance Switching in the HfO_2 RRAM Device

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***Abstract*–Studies on the TiN/HfO_2/TiN structure reveal a dual-mode bipolar resistance switching behavior. The device is found to exhibit both positive-set/negative-reset and negative-set/positive-reset switching modes. The change-over from one switching mode to another is effected by extending the range of voltage-sweep on the side of the polarity which initially resulted in a set. A reset would subsequently occur after which the device could only be set by a voltage-sweep of the opposite polarity. The behavior may be consistently ascribed to the rupture of the conductive filament at the cathode interface following the reconnection of the filament at the anode interface during the initial set. The dual-mode characteristic enables three distinct operating states to be realized as compared to the usual two for the single bipolar mode.**

Introduction – Transition metal oxides, such as HfO_x[1-3], NiO_x[4], TaO_x[5,6], etc. have been studied for RRAM application. Among them, HfO_x is promising due to its established compatibility with the CMOS technology. To-date, various resistance switching modes, such as unipolar[1], bipolar[2] and non-polar[2,3] (i.e. co-existence of the former two) have been observed on HfO_x RRAM devices. In this paper, we report a dual-mode bipolar resistive behavior of the TiN/HfO_2/TiN structure. A possible explanation is proposed.

Experimental Details – The process flow for test device fabrication and a schematic cross-section diagram of the test device are shown in Fig. 1. The HfO_2 dielectric was grown via atomic layer deposition, using Tetrakis(dimethylamino) hafnium as the precursor and H_2O as the oxidizing agent. Two different stacks were examined: (A) TiN/HfO_2 (6 nm)/TiN and (B) TiN/HfO_x (3 nm)/HfO_2 (3 nm)/TiN. In the latter, the oxygen deficient HfO_x layer was achieved by increasing the precursor pulse while keeping the H_2O pulse fixed. High-resolution transmission electron microscopy confirms the dielectric thickness to be ~6 nm in both stacks (Fig. 2). Electrical measurements were performed at room temperature with the voltage applied to the top TiN electrode or TE (the bottom TiN electrode or BE was always grounded). As stack B was found to exhibit more stable dual-mode switching behavior as compared to stack A, most of the results presented here are for the former unless stated otherwise. The advantage of stack B over stack A will be discussed.

Results and Discussion – Single mode bipolar switching behavior can be realized under both forming polarities (Fig. 3), by virtue of the symmetrical electrode configuration. The dual-mode bipolar switching behavior is demonstrated in Fig. 4, for the case of positive forming. The alphanumerical labels denote the sequence of measurements. Curves 1a, 1b and 2a depict the typical negative-reset/positive-set bipolar switching behavior following the positive forming. It is interesting to point out that after the positive-set step (curve 2a), a positive voltage-sweep to larger voltages yielded a subsequent reset at ~+1.3 V. The ensuing positive-voltage sweep confirms the reset (curve 2c). It should be emphasized that in curve 2c, the set transition seen previously in curve 2a is no longer observed. Instead, the device can now only be set using a negative voltage-sweep (curves 3a, 3b) and reset by a positive voltage-sweep (curves 4a, 4b). Clearly, the previous bipolar switching mode comprising positive set/negative reset has been changed to a complementary mode involving negative set/positive reset. The absence of a set transition following the prior reset in the same polarity domain (cf. curves 2b, 2c) distinguishes the dual-mode switching behavior from the non-polar behavior of the Pt/HfO_2/Pt device[2,3]. Moreover, the reset voltage is smaller than the set voltage in the latter whereas it is the reverse for the TiN/HfO_x/HfO_2/TiN device.

Consistent switching characteristics are achieved by repeatedly 'toggling' the device between the two bipolar modes (Fig. 5). A dual-mode switching behavior is also observed after negative forming (Fig. 6(a)) and for the TiN/HfO_2/TiN device (Fig. 6(b)). But unlike the TiN/HfO_x/HfO_2/TiN device for which stable resistance switching remains after several hundreds of dc sweep cycles, the switching performance of the TiN/HfO_2/TiN device deteriorates rapidly. In the latter, the lack of a substantial oxygen-deficient interfacial layer at the TE (Fig. 1) fails to provide a 'reservoir' that facilitates the consistent movement of oxygen ions to and from the CF[7]. Improved performance has been achieved via the incorporation of a Ti or Hf oxygen-gettering layer[8,9].

Fig. 7 provides a plausible explanation for the dual-mode bipolar switching behavior. A negative voltage favors the transport of oxygen ions from TE into the CF, reoxidizing the part of the CF near the TE interface (1). As most of the voltage in the subsequent positive sweep will be absorbed across this high resistance part of the CF, oxygen ions can be drawn back to the TE at a relatively low voltage, thus restoring the low resistance state (2). So long as the positive voltage is limited, bipolar switching behavior involving the alternate rupture and reconnection of this part of the CF is realized. A further increase of the positive voltage now draws in oxygen ions from the BE, causing the rupture of the CF near the BE interface as shown (3). Following this, the reconnection of this part of the CF cannot happen again under the same polarity sweep. To achieve a set transition again, an opposite (negative) polarity sweep is needed to drive the oxygen ions in the reoxidized part of the CF back to the BE. When this happens, the ruptured CF at the BE interface is reconnected again. As a result of the change in the location where the CF is ruptured, the previous positive set/negative reset mode is changed into a negative set/positive reset mode. It is believed that the relatively thick oxygen-deficient interfacial layers at both TE and BE in the HfO_x/HfO_2 stack facilitate the transport of oxygen ions between the electrodes and CF, thus improving the dual-mode switching performance. The different locations at which the rupture/ reconnection of the CF occur can provide three distinct states for RRAM operation, corresponding to the following scenarios: (1) fully connected CF; (2) CF ruptured at the top interface; (3) CF ruptured at the bottom interface. The location of CF rupture may be distinguished by applying a small positive TE voltage to observe if a set could occur (with the original data preserved elsewhere). If the CF could be reconnected, then the rupture occurs at the top interface (i.e. positive set/negative reset); otherwise the rupture occurs at the bottom interface (i.e. negative set/positive reset).

Summary – Results of our study on the TiN/HfO_2/TiN RRAM device show that the voltage polarities for the set and reset transition can be reversed, constituting the presence of a complementary bipolar switching mode. The changeover from one mode to another is effected by extending the voltage sweep for set transition to higher values, which triggers a reset that can now only be set again by an opposite polarity sweep. The dual-mode behavior enables the device to be operated in three distinct states, believed to arise from a change in the location of filament rupture/formation from one electrode interface to another.

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References: [1] Long, *et al.*, IEEE EDL, 34, 623-625, 2013. [2] Cabout, *et al.*, Thin Solid Films, 533, 19-23, 2013. [3] Jousseaume, *et al.*, Solid-State Electronics, 58, 62-67, 2011. [4] Lelmini, *et al.*, Nanotech., 22, 254022, 2011. [5] Lee *et al.*, Nature Mat., 10, 625-630, 2011. [6] Tong *et al.*, J. Appl. Phys., 52, 04CD01, 2013. [7] Bertaud, *et al.*, Appl. Phys. Lett., 101, 143501, 2012. [8] Lee, *et al.*, IEDM Tech. Dig., 2008, 297-300. [9] Govoreanu, *et al.*, IEDM Tech. Dig., 2011, 729-732.

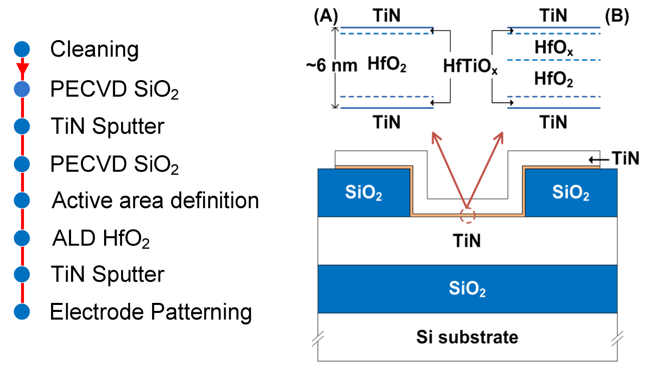

Fig. 1. Processing flow (left) and schematic cross-sectional diagram (right) of the test device. Two dielectric splits were realized: (A) a near-stoichiometric HfO_2, bounded by interfacial $HfTiO_x$ layers at the top and bottom TiN electrodes. A thicker $HfTiO_x$ is expected at the bottom interface, as this interface was subjected to a higher thermal budget. (B) a similar stack but with a HfO_x ($x < 2$) layer inserted between the top TiN electrode and the HfO_2 layer. This structure was achieved by first depositing a ~3 nm near-stoichiometric HfO_2 layer, followed by a ~3 nm oxygen deficient HfO_x layer via increasing the Hf precursor to H_2O pulse ratio.

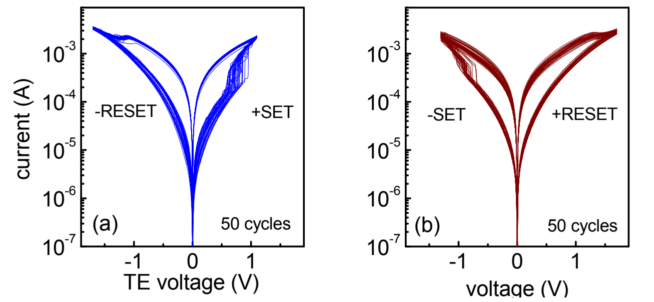

Fig. 5. Current-voltage curves for 50 bipolar set/reset cycles. Consistent resistive switching behavior can be observed for each mode: (a) positive set/negative reset; (b) negative set/positive reset.

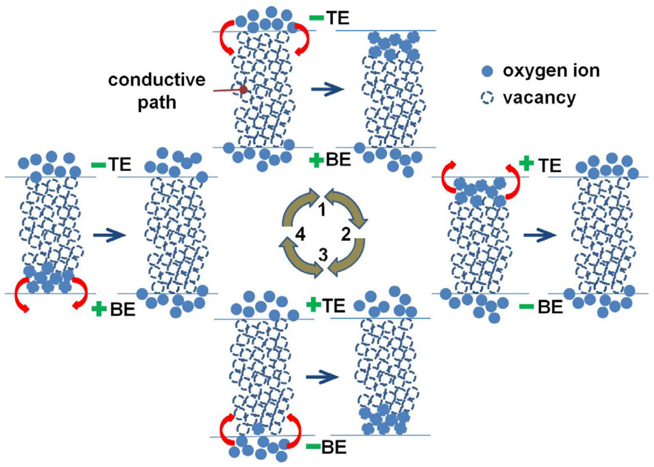

Fig. 7. Schematic illustration of the proposed mechanism for dual-mode resistive switching, for the case of positive forming. (1) and (2) depicts the conventional negative reset/positive set behavior: during a negative voltage sweep (applied to the top electrode or TE), the conductive path near the TE is reoxidized by the oxygen ions drawn in, causing a reset to the high resistance state (cf. Fig. 4, curve 1a). A positive voltage sweep depletes the oxygen ions from the same region, causing a set to a low resistance state (curve 2a). (3) Increasing the positive voltage, however, would result in oxygen ions being drawn in from the bottom electrode (BE), leading to the lower part of the conductive path being reoxidized as shown. This explains the reset observed at ~+1.3 V (curve 2b). (4) A subsequent negative voltage sweep pushes the oxygen ions back to the BE and restores the low resistance state (curve 3a). Extending the voltage sweep range in turn induces a reset, when the top part of the conductive path is reoxidized (curve 5a).

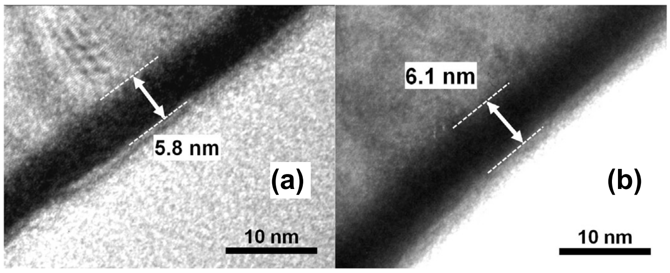

Fig. 2. High resolution cross-sectional transmission electron micrograph of the (a) $TiN/HfO_2/TiN$ and (b) $TiN/HfO_x/HfO_2/TiN$ RRAM structures.

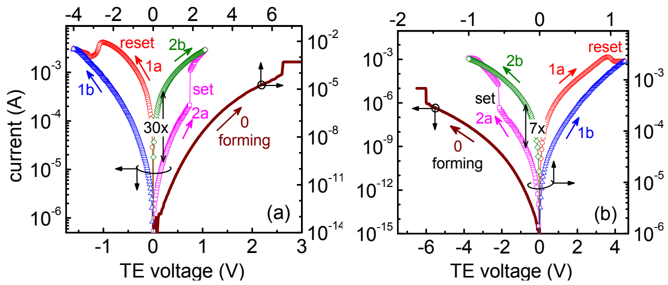

Fig. 3. Current-voltage (@top electrode TE) curves for forming and subsequent bipolar set and reset operations on the $TiN/HfO_x/HfO_2/TiN$ RRAM device. (a) Positive forming with the current compliance set at 0.5 mA; (b) Negative forming with the current compliance set at 10 μA. The order of the measurements performed after forming (0) is denoted by the numbers as shown.

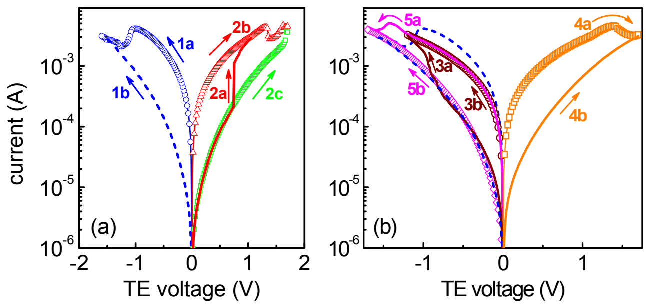

Fig. 4. A set of current-voltage curves illustrating the existence of a dual-mode resistive switching behavior after positive forming. The order of measurements is as indicated by the numbers. (a) Curve 1a, 1b and 2a show the conventional negative reset, post-negative-reset and positive set measurements. Extending the voltage range during the post-positive-set induces a reset at ~+1.3 V (curve 2b). The reset is confirmed by the lower current seen in curve 2c, for which the set previously present in curve 2a is now absent. (b) The set can now only be induced by a negative voltage sweep (curves 3a, 3b) and positive voltage sweep only produces a reset (curves 4a, 4b). The results clearly show a changeover from a positive set/negative reset to a negative set/positive reset mode. Extending the negative voltage sweep (after the negative set) induces a reset (curves 5a, 5b) and a change back to the positive set/negative reset mode. Also shown are curves 1a and 1b (dashed lines) from (a).

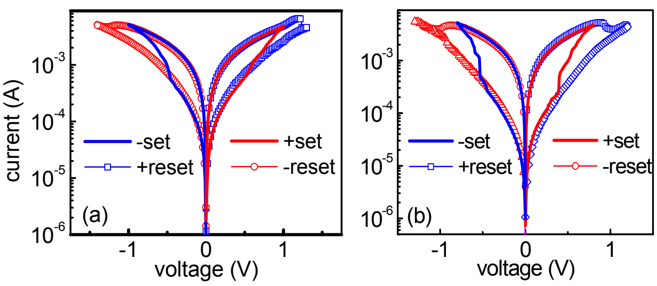

Fig. 6. (a) An illustration of dual-mode resistive switching in the $TiN/HfO_x/HfO_2/TiN$ stack subjected to negative forming. Similar to the case depicted in Fig. 4, a changeover from the conventional negative set/positive reset to positive set/negative reset can be triggered via extending the range of the post-negative-set measurement. (b) Similar observation is obtained for the $TiN/HfO_2/TiN$ stack.