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Enlarged read window in the asymmetric ITO/HfO\textsubscript{x}/TiN complementary resistive switch

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The narrow read-window of most complementary resistive switches proposed to-date poses a significant challenge to array-level implementation, as inherent variations in the set and reset voltages result in an unacceptably small read margin. In this work, we present the asymmetrical ITO/HfO\textsubscript{x}/TiN complementary resistive switch, with a significantly enhanced positive read window of 1.6 V as compared to the much narrower window of 0.5 V of the symmetrical TiN/HfO\textsubscript{x}/TiN switch. A read margin of 1.1 V is obtained after accounting for statistical variations, representing a significant improvement over the 0.1 V margin of the symmetrical counterpart. Analyses show that the enlarged read window may be ascribed to two important attributes: (1) the stronger affinity of ITO for oxygen, which leads to a reduced positive set voltage and (2) a larger write function of the ITO, resulting in an increase in the positive reset voltage. Published by AIP Publishing.

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The resistive random access memory (RRAM) has shown the potential in becoming the future universal memory, due to its fast switching time (~ns), low switching energy (~pJ), and high write endurance (~10\textsuperscript{12} cycles).\textsuperscript{1–8} For high-density memory integration, RRAM cells are usually deployed in the form of a crossbar array. However, a major issue with a crossbar array is the sneak-path current, a parasitic current which arises from neighboring RRAM cells programmed to the low-resistance state (LRS).\textsuperscript{9} A typical way to solve the sneak-path current is to connect each RRAM cell in series to a selector device, which serves to isolate the cell from its neighbours.\textsuperscript{10–13} To preserve the packing density and three-dimensional stacking advantages of the crossbar architecture, recent effort is mainly centered on oxide-based thin-film selectors\textsuperscript{14–16} having the same metal-insulator-metal structure as the RRAM cell. But for a selector to be effective, it must have a low off-state current and a highly non-linear, i.e., steep turn-on current-voltage curve. The attainment of both characteristics has remained a difficult challenge.\textsuperscript{17}

On the other hand, complementary resistance switching (CRS)\textsuperscript{9} offers the promise of a selector-less crossbar RRAM array free of the sneak-path current problem. In this approach, two distinct high-resistance states (HRS) are used to represent the binary memory data, as opposed to the usual low- and high-resistance states. Only one of the two high-resistance states would switch to a low-resistance state during the read process, thus allowing them to be distinguished electrically. Because a selector is not needed, CRS enables a more straightforward realization of RRAM on flexible substrates.\textsuperscript{18} Since the introduction of the idea in 2010 based on two anti-serially connected cells,\textsuperscript{9} CRS has been reported in single RRAM cells with a bilayer oxide stack,\textsuperscript{19–22} and also in cells having a single oxide layer.\textsuperscript{23–26} However, a major obstacle of CRS implementation lies in the generally small “read window,” i.e., the difference between the set and reset voltages (\(V_{\text{set}}\) and \(V_{\text{reset}}\)) for one of the high-resistance states.\textsuperscript{9,19–28} Coupled with inherent variations in \(V_{\text{set}}\) and \(V_{\text{reset}}\), the resultant array-level read margin becomes unacceptably narrow. Attempt to increase the read window has been made through multi-layer stack engineering.\textsuperscript{18}

A recent study has found that CRS in the TiN/HfO\textsubscript{x}/TiN RRAM cell is due to an oxygen exchange between the vacancy-type conducting filament in HfO\textsubscript{x} and the reactive TiN electrodes.\textsuperscript{23,29} The exchange enables the position of filament rupture to be alternated between the electrode interfaces, thus giving rise to a CRS behavior. On the one hand, this finding indicates that a cell with the same top and bottom electrodes would tend to have a small read window, due to a similar interaction between the filament and the electrodes.\textsuperscript{23} On the other hand, it suggests the possibility of enlarging the read window through electrode interface engineering. In this work, we report the CRS characteristics of the ITO/HfO\textsubscript{x}/TiN RRAM cell, with different top and bottom electrodes. A significant improvement in the positive read window to 1.6 V is obtained. The resultant read margin is 1.1 V after accounting for \(V_{\text{set}}\) and \(V_{\text{reset}}\) variations. On the other hand, the negative read window is comparable to that of the TiN/\ HfO\textsubscript{x}/TiN. The results may be consistently ascribed to the difference in oxygen affinity and work function of the ITO and TiN electrodes.

Figure 1(a) shows a scanning electron micrograph of the asymmetric ITO/HfO\textsubscript{x}/TiN crossbar device. Electron-beam lithography (EBL) was first performed on a pre-cleaned SiO\textsubscript{2}/Si substrate, followed by DC reactive magnetron sputtering for TiN deposition (Ti:N ratio of 1:1) and lift-off to form the bottom electrode. Atomic layer deposition (ALD) of the HfO\textsubscript{x} layer at 250 °C was then carried out with tetrakis (dimethylamino) hafnium as the precursor and H\textsubscript{2}O as the oxidizing agent. After the second EBL step, ITO deposition

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(via physical sputtering of a commercial ITO target with \(\sim 5\) wt. % Sn in an argon-only ambient) followed by lift-off. High-resolution cross-sectional transmission electron microscopy of the test device revealed a 7 nm thick HfO\(_x\) [Fig. 1(b)]. The bright shade between the HfO\(_x\) and TiN may refer to an interfacial oxide formed by the oxidation of the exposed TiN surface during initial ALD cycles.\(^{23}\) For comparison, symmetric TiN/HfO\(_x\)/TiN devices, only substituting the top ITO electrode by TiN, were also fabricated. To facilitate later discussion, the former will be referred as the ITO device, while the latter as the TiN device. DC voltage-sweep testing was performed at room temperature (27 °C) using a Keithley SCS4200 parameter analyzer. The voltage-bias was applied to the top ITO or TiN electrode with the bottom TiN electrode always grounded.

Figure 2 shows typical CRS behaviors of the ITO and TiN devices. Forming was carried out using a positive-voltage sweep (not shown) to create a conductive filament within the HfO\(_x\) layer so that the subsequent resistive switching effect could be observed. For the ITO device [Fig. 2(a)], a positive-voltage sweep triggers a high to low resistance (HRS1) or set transition @ \(V_{\text{set}}^+ \sim 0.2\) V. If the voltage sweep is stopped after this set transition, the device can only be reset by a negative-voltage sweep (@ \(V_{\text{reset}}^- \sim -1\) V), i.e., it exhibits a typical positive set/negative reset bipolar switching behavior. However, if the positive-voltage sweep is further extended, a reset subsequently happens @ \(V_{\text{reset}}^- \sim -1.5\) V, bringing the device to a different high-resistance state (HRS2). Following this reset, the device can no longer be set again using a positive-voltage sweep. Instead, it can only be set by a negative-voltage sweep (@ \(V_{\text{set}}^- \sim -0.4\) V) and reset by a positive-voltage sweep (@ \(V_{\text{reset}}^+ \sim 1.5\) V), i.e., the device now operates in a complementary switching mode (negative set/positive reset). An extension of the negative-voltage sweep yields a reset @ \(V_{\text{reset}}^- \sim -1\) V to HRS1, after which the device is changed back to the positive set/negative reset mode. The device may be alternated between the two switching modes by extending the voltage sweep beyond the initial set transition (Fig. S1, supplementary material). A similar behavior is obtained for the TiN device [Fig. 2(b)]. An oxygen-exchange mechanism between the oxygen vacancies in the conducting filament formed in the HfO\(_x\) and the ITO or TiN electrode, adopted from our earlier study on the CRS behavior of the TiN/HfO\(_x\)/TiN device,\(^{23}\) may also be used to explain the CRS behavior in the ITO device. A conducting filament, comprising oxygen vacancies, is generated in the HfO\(_x\) after forming.\(^{30–35}\) A negative-voltage sweep drives oxygen from the top ITO interface region to the adjacent vacancy sites in the filament, rupturing the filament and causing a reset to HRS1. A subsequent positive-voltage sweep reconnects the filament and causes a set by reversing the oxygen migration process. An extended positive-voltage sweep would draw oxygen from the bottom TiN interface region into the adjacent filament and in turn ruptures the filament there, resetting the device to HRS2 (see Fig. S2 in the supplementary material for a schematic illustration).

A comparison of the CRS characteristics of the ITO and TiN devices reveals two major differences. First, for most of the ITO devices tested, the resistance of HRS1 is significantly higher than that of HRS2 [cf. Fig. 2(a)]. The respective resistance distributions differ by a factor of \(>10^3\) at the median value [Fig. 3(a)]. This is in contrast to the comparable HRS1 and HRS2 of the TiN device [Fig. 3(b)]. Clearly, the lower HRS2 resistance of the ITO device limits the memory window. But it is pertinent to clarify that this lower HRS2 resistance (or higher current) of the ITO device would not pose any problem for array-level CRS operation. Electrically, HRS1 and HRS2 are not distinguished by the difference in their current or resistance values but by their different responses to a read voltage bias. A positive voltage larger than \(V_{\text{set}}^+\) would trigger a HRS1 \(\rightarrow\) LRS transition [Fig. 2(a)], since the ruptured filament next to the ITO interface is reconnected to the ITO (via oxygen migration from the ruptured filament to the ITO). However, it has no effect if the device is in the HRS2 state, since the voltage polarity does not favor oxygen migration from the ruptured filament back to the adjacent TiN electrode. Similarly, a read voltage more negative than \(V_{\text{reset}}^-\) would trigger a HRS2 \(\rightarrow\) LRS transition but has no effect if the device is in the HRS1 state.

Second, the \(V_{\text{set}}\) and \(V_{\text{reset}}\) of the ITO device show a larger difference of 1.6 V (median) in the positive-voltage
regime as compared to 0.7 V in the negative-voltage regime [Fig. 4(a)], whereas they differ comparably (0.5 V) in both voltage regimes for the TiN device [Fig. 4(b)]. After accounting for the spread in voltages, the difference between the upper end of $V_{\text{set}}^+$ and the lower end of $V_{\text{reset}}^+$ distributions (defined as the read margin) in the positive-voltage regime is 1.1 V for the ITO device, substantially larger than 0.13 V for the TiN device. On the other hand, the read margin in the negative-voltage regime is comparable for both devices (0.2 V versus 0.15 V). Table I summarizes, for both devices, the median $V_{\text{set}}$ and $V_{\text{reset}}$ values for the positive- and negative-voltage regimes, together with the filament change that occurred for each voltage, and a notation denoting the direction of oxygen transfer between the filament and the electrode. Take the $V_{\text{set}}^+$ of the ITO device for instance, which corresponds to the reconnection of the ruptured filament next to ITO [Figs. 2(a) and S2]. This change arises from the migration of oxygen from the ruptured filament (HfO$_x$) to the ITO, and the process is denoted as O$_{\text{HfOx}}$ → ITO. At $V_{\text{reset}}^+$ the filament next to TiN is ruptured and the oxygen transfer process is denoted as O$_{\text{TiN}}$ → O$_V$ (O$_V$ denotes the vacancy sites of the filament). It is clear from Table I that the enlarged positive read window of the ITO device is due to the reduction in $V_{\text{set}}$ and the increase of $V_{\text{reset}}^+$ relative to those of the TiN device. The analysis implies that (1) it is easier for oxygen to migrate from the ruptured filament to ITO ($V_{\text{set}}^+ = 0.2$ V) than to TiN ($V_{\text{set}}^+ = 0.6$ V); (2) it is more difficult for oxygen to migrate from the bottom TiN to adjacent vacancy sites of the filament in the ITO device ($V_{\text{reset}}^+ = 1.8$ V) than in the TiN device ($V_{\text{reset}}^+ = 1.1$ V).

Since both devices have the same bottom TiN electrode, the above differences may be ascribed to the different top electrodes. To understand point (1), X-ray photoelectron spectroscopy (XPS) measurement was made on separately prepared test samples with a 7-nm HfO$_x$ blanket-deposited over either a bottom TiN or ITO electrode (Fig. S3, supplementary material) to check the effect of the electrode material on the HfO$_x$ stoichiometry. Details on the XPS test samples, measurement, and data analysis are provided in the supplementary material. The Hf 4f and O 1s core-level spectra, and their corresponding constituent component spectra, are shown in Fig. S4. Analysis revealed a Hf:O ratio of 1:1.4 for the HfO$_x$ layer in the HfO$_x$/ITO stack, as compared to a ratio of 1:1.7 in the HfO$_x$/TiN stack. The lower oxygen ratio for the HfO$_x$/ITO stack indicates that oxygen in the HfO$_x$ may have been “scavenged” by the bottom ITO layer. Studies$^{36,37}$ have found that an ITO film sputter-deposited in an argon-only (i.e., oxygen-absent) ambient has a high concentration of oxygen vacancies, which give the film an n-type conductivity. An oxygen deficient ITO layer in turn promotes the migration of oxygen from the HfO$_x$ layer,$^{38}$ thus making the latter also more oxygen deficient. The XPS analysis shows that the ITO electrode has a stronger affinity for oxygen than the TiN electrode. This may explain the smaller $V_{\text{set}}^+$ of the ITO device.

Next, we turn our attention to point (2). It should be noted that the $V_{\text{reset}}^+$ of the TiN device (1.1 V) is smaller than that of the ITO device (1.8 V), despite in both cases, the reset involves the rupture of filament due to oxygen migration from the bottom TiN electrode. The large difference between HRS1 and HRS2 of the ITO device provides a clue on the effect of the ITO electrode on electrical conduction through the stack. To shed further light, a study on the current conduction mechanism was made. Among the various transport models (Poole-Frenkel, Schottky, space-charge limited, and quantum point contact) proposed for RRAM current conduction in HRS, the Schottky model is found to give the best fit to the experimental data. According to the Schottky conduction model, the current density $J$ may be expressed as

$$J = A^* T^2 \exp \left( -\frac{q (\phi_B - \sqrt{qE/4\pi\varepsilon})}{kT} \right)$$

$$= C_1 \exp \left( -\frac{q \phi_B}{kT} + C_2 \sqrt{V} \right),$$

where $C_1 = A^* T^2$ and $C_2 = \frac{1}{kT} \sqrt{\frac{q}{4\pi\varepsilon}}$ are constants for a given interface structure and temperature $T$ ($A^* = 120$ A cm$^{-2}$K$^{-2}$) is the Richardson constant; $k$ is the Boltzmann constant; $q$ is the electronic charge; $d$ is the effective barrier thickness; and $\varepsilon$ is the permittivity and $q \phi_B$ is the Schottky barrier (in eV). As is apparent in Fig. 5, a very good least-square linear regression fit ($R^2 > 0.98$) to the experimental data can be obtained on a ln $I$ versus $V^{1/2}$ plot, implying that conduction in HRS1 and HRS2 is limited by Shockley emission. The extracted Shockley barrier is 0.49 eV and 0.17 eV for the ITO/HfO$_x$ and HfO$_x$/ITO interface, respectively. The substantially lower current (or higher resistance) for HRS1 may thus be explained by the larger Shockley barrier at the ITO/HfO$_x$ interface. Studies on the tunneling current characteristics of ITO/HfO$_2$/Si and TiN/HfO$_2$/Si structures have also found a larger ITO/HfO$_2$ Schottky barrier.$^{32,43}$ The

<table>
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<th>Device</th>
<th>Median switching voltage</th>
<th>Filament change</th>
<th>Oxygen transfer</th>
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<tr>
<td>ITO/HfO$_x$/TiN</td>
<td>$V_{\text{set}} = 0.2$ V</td>
<td>Reformed @ITO</td>
<td>O$_{\text{HfOx}}$ → ITO</td>
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<td></td>
<td>$V_{\text{reset}} = 1.8$ V</td>
<td>Ruptured @TiN</td>
<td>O$_{\text{TiN}}$ → O$_V$</td>
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<tr>
<td></td>
<td>$V_{\text{set}} = -0.3$ V</td>
<td>Reformed @ITO</td>
<td>O$_{\text{HfOx}}$ → TiN</td>
</tr>
<tr>
<td></td>
<td>$V_{\text{reset}} = -1.1$ V</td>
<td>Ruptured @ITO</td>
<td>O$_{\text{TiN}}$ → O$_V$</td>
</tr>
<tr>
<td>TiN/HfO$_x$/TiN</td>
<td>$V_{\text{set}} = 0.6$ V</td>
<td>Reformed @TiN$_{\text{not}}$</td>
<td>O$<em>{\text{HfOx}}$ → TiN$</em>{\text{not}}$</td>
</tr>
<tr>
<td></td>
<td>$V_{\text{reset}} = 1.1$ V</td>
<td>Ruptured @TiN$_{\text{not}}$</td>
<td>O$_{\text{TiN}}$ → O$_V$</td>
</tr>
<tr>
<td></td>
<td>$V_{\text{set}} = -0.6$ V</td>
<td>Reformed @TiN$_{\text{not}}$</td>
<td>O$<em>{\text{HfOx}}$ → TiN$</em>{\text{not}}$</td>
</tr>
<tr>
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<td>Ruptured @TiN$_{\text{not}}$</td>
<td>O$_{\text{TiN}}$ → O$_V$</td>
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\[ q \frac{\phi_B}{kT} + C_2 \sqrt{V} \]
from the ruptured filament to TiN. But this difference in ruptured filament at the TiN interface, by oxygen migration despite in both cases, the set involves reconnection of the work function, the polarity of \( \psi \) is needed to cause a reset, which explains the increase in positive applied voltage means that a more positive voltage with respect to the TiN. The opposition between the low-resistance states [Fig. 5(c)]. Because of the larger ITO composition and shape. Variation in \( \psi \) across the structure is represented by a simplified linear variation of the vacuum level \( E_{F,\text{ITO}} \) and \( E_{F,TiN} \) denote the Fermi level of the ITO and TiN electrode, respectively.

The larger Schottky barrier at the ITO/HfO\(_x\)/TiN interface implies that the ITO electrode has a larger work function than the TiN electrode. This inference is in general agreement with the work function of ITO and TiN reported elsewhere; e.g., 5.3 eV for ITO\(^{44}\) and 4.5 eV for TiN.\(^{45}\) Due to the work function difference, a Volta potential, \( \Delta \psi \), exists between the ITO and TiN electrodes in both the high- and low-resistance states [Fig. 5(c)]. Because of the larger ITO work function, the polarity of \( \Delta \psi \) is such that it opposes (reinforces) a positive (negative) voltage applied to the ITO with respect to the TiN. The opposition between the \( \Delta \psi \) and positive applied voltage means that a more positive voltage is needed to cause a reset, which explains the increase in \( V_{\text{reset}}^+ \) of the ITO device. An increase in \( V_{\text{set}}^- \) should also be expected but the stronger oxygen affinity of ITO may have offset the increase, resulting in an overall decrease relative to the TiN device. A comparison of \( V_{\text{set}}^- \) and \( V_{\text{reset}}^+ \) of the two devices (Table I) also consistently reflects the possible role of \( \Delta \psi \) in the resistive switching voltages of the ITO device in the negative-voltage regime. The \( V_{\text{set}}^- \) of the ITO device is \(-0.3 \) V, less negative than that of the TiN device (\(-0.6 \) V), despite in both cases, the set involves reconnection of the ruptured filament at the TiN interface, by oxygen migration from the ruptured filament to TiN. But this difference in \( V_{\text{set}}^- \) of the two devices is smaller than the difference in \( V_{\text{reset}}^+ \). The reason for this discrepancy is not clear and is a subject of further investigation. As for \( V_{\text{reset}}^- \), a more negative value should be expected for the ITO device, in view of the stronger oxygen affinity of ITO and hence a greater difficulty for oxygen to migrate from ITO back to the filament. However, the \( V_{\text{reset}}^- \) of both devices is similar (1.1 V), implying that the Volta potential in the ITO device may have helped reduce the reset voltage (as it reinforces the negative applied voltage). On the other hand, no Volta potential should exist in the symmetric TiN/HfO\(_x\)/TiN stack and thus the TiN device shows identical set and reset voltages in both voltage regimes (Table I).

Our explanation on the effect of the electrode work-function difference on the switching operation of the ITO device is supported by the study of Hadi et al.,\(^{46}\) who reported a set-voltage increase for the W/CeO\(_x\)/SiO\(_2\)/n\(^+\)Si stack relative to the W/CeO\(_x\)/SiO\(_2\)/p\(^+\)Si stack, arising from a decrease in the work function of the n\(^+\) Si electrode relative to the top W electrode.

In summary, highly asymmetrical CRS characteristics are observed in the ITO/HfO\(_x\)/TiN RRAM device. These behaviors are manifested in the significant difference (by a factor of \( >10^3 \)) in the two high-resistance states (arising from the different interface barriers) and the much wider positive read margin of 1.1 V as compared to the negative read margin of 0.2 V. The former elucidates the important role of the interface barrier in the memory window, while the latter represents an important improvement over the much narrower read margin of 0.1 V obtained for the symmetric TiN/HfO\(_x\)/TiN as well as other CRS devices reported to-date, and it may be ascribed to a combination of two effects: (1) a reduced set voltage due to the greater oxygen affinity of ITO and (2) an increased reset voltage due to an opposing Volta potential arising from the larger work function of ITO, as evidenced by the larger ITO/HfO\(_x\) interface barrier. From the insights achieved, any attempt to modulate the HfO\(_x\)/TiN interface barrier for increasing the memory window should be made in the light of a possible impact on the read margin.

See supplementary material for a figure showing the repeated CRS switching cycles (Fig. S1) and a schematic illustration of the proposed mechanism for CRS (Fig. S2) in the ITO/HfO\(_x\)/TiN RRAM device. Details on XPS measurement (Fig. S3) and data analysis (Fig. S4) are also provided.

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1R. Waser and M. Aono, Nat. Mater. 6, 833 (2007).
6P. Lin, S. Pi, and Q. Xia, Nanotechnology 25, 405202 (2014).


