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Enhanced stability of complementary resistance switching in the TiN/HfO_x/TiN resistive random access memory device via interface engineering

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This study shows that a majority (70%) of TiN/HfO_x/TiN devices exhibit failed complementary resistance switching (CRS) after forming. In conjunction with the consistent observation of a large non-polar reset loop in the first post-forming voltage-sweep measurement, it is proposed that breakdown of the TiN/HfO_x interfacial oxide layers (crucial in enabling CRS) and the accompanied formation of Ti filaments (due to Ti migration from the TiN cathode into the breakdown path) resulted in CRS failure and the observed non-polar reset behavior. This hypothesis is supported by the significant reduction or complete elimination of the large non-polar reset and CRS failure in devices with a thin Al₂O₃ layer incorporated at the TiN-cathode/HfO_x or both TiN/HfO_x interfaces. The higher breakdown field of the thin Al₂O₃ enables it to sustain the forming voltage until the forming process is interrupted, thus enabling CRS via oxygen exchange with the adjacent vacancy-type filament formed in the HfO_x. © 2016 AIP Publishing LLC.

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HfO_x-based resistive random access memory (RRAM), by virtue of its high-density integration capacity, fast operation speed, and complementary-metal-oxide-semiconductor compatible fabrication process, is a leading contender for next-generation nonvolatile memory technology.^{1–4} In particular, the simple metal–insulator–metal structure and ease of scalability of the RRAM cell make it an ideal candidate for crossbar memory array implementation.^{5–10} However, the major issue with a crossbar array is the sneak-path current,¹¹ a parasitic current that flows through a neighboring cell in the low resistance state (LRS) when a read operation is performed on a designated cell in the high resistance state (HRS). This parasitic current is added to the read current of the designated cell, resulting in a read error. Although the one-diode-one-resistor (1D1R)^{12–15} and one-transistor-one-resistor (1T1R)^{16,17} configurations can solve the sneak-path current problem, processing complexity is increased. A recent work proposed a one-transistor-n-resistors (1TnR) configuration as a more cost-effective solution.¹⁸ In 2010, Linn *et al.*¹¹ proposed an alternative approach, coined the complementary switching RRAM. By connecting two conducting-bridge RRAM cells back-to-back, it is shown that whenever one cell is switched to the LRS, the other would be switched to the HRS. The major benefit of this approach is that the overall structure always remains in one of the two HRSs, distinguishable through their different current–voltage (I–V) curves. In this manner, the sneak-path current problem can be solved without having to integrate individual RRAM cells with a different selector.

Later works^{19–24} found complementary resistance switching (CRS) in a *single* device, paving the way for a simpler implementation of Linn *et al.*'s idea¹¹ by eliminating the common internal electrode that is prone to rapid degradation.

Examples include the Pd/Ta₂O_{5–x}/TaO_y/Pd^{20,21,24} structure consisting of an oxygen-deficient and oxygen-rich bi-layer oxide stack, and the TiN/HfO_x/TiN structure with a single oxide layer.^{19,22,23} The observation of CRS in the TiN/HfO_x/TiN structure is particularly important as both TiN and HfO_x are already widely deployed in mainstream manufacturing. In a recent study,²⁴ it is shown that the interfacial oxide layer at the HfO_x/TiN interface plays a crucial role in enabling CRS, via an oxygen exchange process with the adjacent conducting filament formed in the HfO_x. This mechanism allows the position of the re-oxidized filament to be alternated between the two TiN electrode interfaces, giving two distinct HRSs. The critical role of the interfacial layer (IL) is further supported by the observation that CRS ceases to exist when formation of one of the ILs is prevented by replacing the TiN electrode with an inert metal (e.g., Pt), underscoring the impact interface engineering may have on CRS. However, a systematic study in this respect is still lacking.

We show in this work that the forming process, which is needed to generate a conducting filament in the HfO_x layer in the TiN/HfO_x/TiN device, may compromise the integrity of the ILs, as these layers are also susceptible to breakdown during the forming transient. As a consequence of the IL breakdown, CRS is not observed, since there is now no proper IL that could facilitate oxygen exchange with the adjacent filament region in the HfO_x. It is shown that through the inclusion of a robust barrier oxide layer (BL) that is able to withstand the forming voltage until the process is interrupted, CRS failure may be eliminated.

The test devices were fabricated on SiO₂/p-Si substrates. First, a bottom TiN electrode (BE), of thickness 160 nm and with a Ti to N ratio of 1.1 to 1,²⁶ was prepared on a pre-cleaned SiO₂/p-Si substrate by DC reactive magnetron sputtering of a Ti target in a mixture of N₂ and Ar gases at 375 °C. The flow rates of N₂ and Ar were 30 and 8 sccm,

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FIG. 1. (a) Schematic cross-sectional diagram of the TiN/HfO_x/TiN test device. High resolution cross-sectional transmission electron micrographs of the (b) TiN/HfO_x/TiN, (c) TiN/Al₂O₃/HfO_x/TiN, and (d) TiN/Al₂O₃/HfO_x/Al₂O₃/TiN structures. The ~4 nm thick sub-stoichiometric TiO_x interfacial layer at the bottom interface is the result of TiN oxidation during the fabrication process.

respectively. Then, the deposition of SiO₂ serving as the isolation layer was carried out using tetraethyl orthosilicate (TEOS) via a chemical vapor deposition process. This was followed by standard photolithography and reactive ion etching (RIE) for active area definition. The wafer was then loaded into a Cambridge Nanotech Savannah S200 atomic layer deposition (ALD) system for Al₂O₃ (BL) and HfO_x growth at a temperature of 250°C and a pressure of 0.2 Torr. The respective metal precursors were trimethyl aluminum and tetrakis (dimethylamino) hafnium, while the oxidizing agent was H₂O vapor. For control samples, the deposition of Al₂O₃ was skipped. After the ALD process, a top TiN electrode (TE) (80 nm in thickness) was deposited under the same conditions as the bottom TiN electrode. This was followed by lithography and RIE to complete the metal-insulator-metal structures (Fig. 1(a)). To minimize the etching time, a thinner top TiN electrode was used. No post-deposition annealing was carried out.

The test devices have different oxide stack configurations: TiN/HfO_x/TiN, TiN(top)/Al₂O₃/HfO_x/TiN, and TiN/Al₂O₃/HfO_x/Al₂O₃/TiN. The thickness of HfO_x and Al₂O₃ in the respective samples is shown in Figs. 1(b), 1(c), and 1(d). The ~4 nm thick IL, seen between HfO_x and the bottom TiN electrode (Fig. 1(b)), was due to the oxidation of the TiN during the ALD process.²⁷ As previously shown,²⁵ this IL is the key to the existence of CRS in the TiN/HfO_x/TiN structure. Composition of the HfO_x was examined by X-ray photoelectron spectroscopy, and the Hf:O ratio is determined as 1:1.74.²⁵ Electrical measurements were performed on 50 × 50 μm² test devices at 300 K using a Keithley SCS4200 semiconductor parameter analyzer. The voltage bias was applied to the TE, and the BE was always grounded.

CRS in the single TiN/HfO_x/TiN device is characterized by the two sets of HRS I-V curves, each comprising two curves (symbol and thick line), in the positive- and negative-voltage regimes (Fig. 2). The respective set of curves only differs between (V_{p1}, V_{p2}) and (V_{n1}, V_{n2}),

similar to those obtained for the two-cell configuration.¹¹ Outside these voltage ranges, the curves are essentially indistinguishable. The CRS behavior may be attributed to the exchange of oxygen between the top and bottom IL and the respective adjacent filament regions (Fig. 4 of Ref. 25) as explained below. For instance, after forming using a positive-voltage ramp (not shown), the device is in the LRS and a negative-voltage sweep yields curve 1. A sufficiently negative voltage (≤V_{n,pk}) would drive oxygen (within the top IL) to the adjacent filament region and re-oxidize it, resetting the device to HRS as shown by the decreasing current. Repeating the negative-voltage sweep now yields the lower curve 2. The process can only be reversed by a positive-voltage sweep, which gives curve 3. When a sufficiently positive voltage (~V_{p1}) is developed across the re-oxidized part of the filament, oxygen in this region is driven back to the top IL and this part of the filament is reformed, setting the device back to the LRS. More importantly, a further increase of the positive voltage (≥V_{p,pk}) would eventually draw enough oxygen from the bottom IL into the adjacent filament region to re-oxidize it, resetting the device again to HRS, but a different one characterized by the re-oxidized part of the filament now being situated near the BE. Repeating the positive-voltage sweep yields curve 4, with a lower current level between V_{p1} and V_{p2}.

FIG. 2. Complementary resistance switching in the TiN/HfO_x/TiN device after positive-voltage forming. The order of the voltage-sweep measurements is denoted by the numbers shown.

A subsequent negative-voltage sweep would move the re-oxidized filament region back to the TE interface, when a voltage more negative than V_{n1} causes the re-oxidized filament region at the BE interface to be reformed and a voltage more negative than $V_{n,pk}$ results in the filament region at the TE interface to be re-oxidized (curve 5). The difference in the HRS I-V curves either between V_{p1} and V_{p2} or V_{n1} and V_{n2} may be used to denote two distinct memory states, with the read voltage set in between (V_{p1} , V_{p2}) or (V_{n1} , V_{n2}). It should be noted that the read operation is destructive for one of the two HRSs. For instance, if the re-oxidized filament region is at the TE, a read voltage between V_{p1} and V_{p2} would result in a set to the LRS, but this can be rectified with the subsequent application of a voltage more negative than $V_{n,pk}$. If the re-oxidized filament region is at the BE, the same read voltage would give a lower current, with no change to the filament configuration.

However, only a small fraction (less than 30%) of the tested devices (>30) exhibit the stable CRS (that can last several thousands of voltage-sweep cycles) shown in Fig. 2. The initial post-forming I-V curves for the rest of the devices are similar to the examples shown in Fig. 3, which evolve quickly to a switching failure. But a noteworthy feature should be mentioned. In every such device, a large reset loop (curve 1) can always be observed during the immediate sweep measurement made after forming, regardless of the voltage polarity. The switching ratio, defined as (I_{LRS}/I_{HRS} at ± 0.2 V), is typically >100, much larger than the ratio of ~ 10 –20 for devices that display stable CRS. This large reset loop is only seen once, and it is not reproduced again in later sweep measurements. An ensuing inverted-polarity sweep would typically yield a small current increase followed by a decrease (curve 2), which may appear similar to the set-then-reset feature of CRS. However, this behavior is also observed only once at the initial stage. Subsequent alternating sweeps would no longer yield any switching (curve 3).

It should be mentioned that the large non-polar reset seen in Figs. 3(a) and 3(b) is atypical of the TiN/HfO_x/TiN device, which commonly displays a bipolar switching behavior.²⁸ On the other hand, a large non-polar reset is usually found in devices with a Ni or Pt electrode (e.g., Ni/HfO₂/p⁺-Si,²⁸ Pt/HfO_x/Pt²⁹) and is often associated with the formation of a metal filament in the oxide, by the migration of metal ions from the electrode during the forming process. It is believed that such a filament may be melted by Joule heating, and therefore, a reset to the HRS can occur, during a voltage sweep involving either polarity.¹ The observation of a large

non-polar reset in Figs. 3(a) and 3(b) thus suggests that Ti filaments (since the test device has TiN electrodes) were generated during forming.

In an earlier study,²⁵ it is shown that the ILs at the TiN/HfO_x interfaces play a crucial role in enabling CRS. Eliminating the bottom IL by replacing the TiN with an inert Pt electrode also disables CRS; the resultant TiN/HfO_x/Pt structure only displays the conventional bipolar resistance switching. The failed CRS in the majority of the TiN/HfO_x/TiN devices thus suggests that the ILs might also have suffered a breakdown during forming. It has been reported that the average breakdown field E_b of a 10-nm TiO₂ film, reactively sputtered on a metal electrode and annealed at 600 °C, is ~ 3 MV/cm.³⁰ Considering the thickness t_{ox} dependence of E_b ($\propto t_{ox}^{-\alpha}$; $\alpha \sim 0.5$ –1),³¹ the breakdown field (voltage) of the 4-nm IL is likely to be < 7.5 MV/cm (< 3 V), given that it is a sub-stoichiometric TiO_x formed at a lower temperature (250 °C). Thus, it is likely to also suffer a breakdown following the breakdown of the HfO_x (the average forming voltage is 4.4 V). After the IL has suffered a breakdown, oxygen exchange with the adjacent filament region can no longer happen. In addition, as the breakdown of the ILs leads to a direct shorting of the TiN electrodes, the resultant current surge may cause the migration of Ti from the cathode into the breakdown path (supported by later results). *Ab-initio* simulation has shown that the energy barrier for metal-ion migration in an oxide is reduced in a region with a high vacancy defect concentration.³² Thus, Ti migration into the breakdown path, aided by the electron “wind,” may easily occur. A large non-polar reset loop (Figs. 3(a) and 3(b)) then occurs during a post-forming voltage sweep when the Ti filament is ruptured by a local heating effect.¹ Thus, to ensure CRS functionality, the ILs must be able to withstand the forming voltage, upon filament formation in the main oxide layer, until the forming process is interrupted.

To check our proposition, test devices with a thin layer of Al₂O₃ (~ 3 nm) incorporated at either one or both TiN/HfO_x interfaces (i.e., TiN/Al₂O₃/HfO_x/TiN, TiN/Al₂O₃/HfO_x/Al₂O₃/TiN) were fabricated and tested. The primary purpose of the Al₂O₃ is two-fold: (1) To “absorb” the forming voltage upon filament formation in the HfO_x. This would help reduce the electric field across the filament and the surge in the current. (2) To subsequently serve as a “reservoir” for oxygen exchange with the adjacent filament region for enabling CRS. To fulfill these roles, the Al₂O₃ must not breakdown during forming, and this constitutes the main consideration in its choice as elaborated below. With a lower permittivity, the E_b of Al₂O₃ is inherently higher than that of HfO₂; the theoretical E_b of Al₂O₃ is ~ 13 MV/cm, whereas that of HfO₂ is ~ 5 MV/cm.³³ In addition, it has been shown that the E_b of ALD Al₂O₃ is increased as its thickness is decreased; for a 3 nm Al₂O₃, the E_b is ~ 14 MV/cm, which corresponds to a breakdown voltage of ~ 4.2 V.³⁴ In addition, Al₂O₃ has a larger oxygen-vacancy formation energy and migration barrier energy as compared to HfO₂.³⁵ In these regards, it is expected that the thin Al₂O₃ layer would be able to sustain the forming voltage upon filament formation in the HfO_x, until the forming process is interrupted.

FIG. 3. Examples of large non-polar reset and failed complementary resistance switching seen in a majority ($\sim 70\%$) of the TiN/HfO_x/TiN devices. The order of measurements is indicated by the numbers. Both devices were formed by a positive-voltage sweep.

The testing results support our proposition. The percentage of devices, with a 3-nm Al_2O_3 layer inserted between the TE and HfO_x , which exhibits a large reset loop and failed CRS is reduced to 50% and 20%, respectively, for positive- and negative-voltage forming. More importantly, with the inclusion of a 3-nm Al_2O_3 layer at both TiN/HfO_x interfaces, devices displaying a large reset loop and failed CRS are totally eliminated. With two Al_2O_3 layers, a smaller voltage load appears across each layer, reducing the probability of Al_2O_3 breakdown. For devices with a Al_2O_3 layer included at the TE interface only, the significantly fewer cases of large non-polar reset and failed CRS under negative-voltage forming, as compared to positive-voltage forming, implies that Ti migration into the breakdown path originates from the cathode during the forming transient. This is because under negative-voltage forming, the Al_2O_3 layer is situated directly next to the TiN cathode and could therefore effectively suppress the surge in current and Ti migration. However, the substoichiometric TiO_x interfacial layer is a much poorer barrier against the electron wind and Ti migration under positive-voltage forming.³² These observations are consistent with the results from energy-dispersive X-ray analysis carried out on the test devices after positive-voltage forming. As shown in Fig. 4, Ti concentration in the HfO_x is marginally reduced in the device that has the Al_2O_3 layer included at the TE interface but a much greater reduction is obtained in the device that has Al_2O_3 layers incorporated at both interfaces.

Based on the experimental results, a possible explanation for the high percentage of $\text{TiN}/\text{HfO}_x/\text{TiN}$ devices that fail to display CRS after forming is proposed (Fig. 5). Because of the higher permittivity of the TiO_x ILs, the major portion of the applied voltage is initially developed across the thicker HfO_x layer.³⁰ When the formation of a low-resistance path occurs in the HfO_x due to the build-up of vacancy defects to a critical level, the bulk of the applied voltage would now be transferred to the TiO_x ILs. Owing to the relatively low breakdown field of the TiO_x ,³³ the ILs may breakdown before the forming process can be interrupted. Coupled with the surge in electron “wind,” the presence of a region of high concentration of vacancy defects next to the TiN cathode would in turn facilitate the migration of Ti into the breakdown path (Fig. 5(a)).³² Due to the random nature of oxide breakdown and ion migration, breakdown regions

FIG. 4. Energy-dispersive X-ray analysis of the Ti element concentration within the HfO_x layer of the $\text{TiN}/\text{HfO}_x/\text{TiN}$, $\text{TiN}/\text{Al}_2\text{O}_3/\text{HfO}_x/\text{TiN}$, and $\text{TiN}/\text{Al}_2\text{O}_3/\text{HfO}_x/\text{Al}_2\text{O}_3/\text{TiN}$ devices after positive-voltage forming. The evidently lower Ti element concentration, especially for the device with a thin Al_2O_3 incorporated at both TiN/HfO_x interfaces, implies that the Al_2O_3 remained intact and provides an effective barrier against Ti migration during forming transient.

FIG. 5. (a) The direct short between the top and bottom TiN electrodes, due to breakdown of the HfO_x and interfacial oxide layers (ILs), triggers a surge in electron wind (arrows) and accompanying migration of Ti ions from the cathode into the breakdown path, resulting in the formation of (b) a complete Ti filament and (c) a Ti-vacancy composite filament.

comprising complete Ti filaments (Fig. 5(b)) and composite Ti-vacancy filament (Fig. 5(c)) may be formed within the device area. During a subsequent voltage sweep, Joule heating causes the melting (rupture) of the Ti filaments,¹ when the local temperature exceeds the melting point. Although the melting point of bulk Ti is relatively high (1668°C), a remarkable dependence on size and structure has been observed.³⁶ From molecular dynamics simulation, a significant decrease of the melting point to $<450^\circ\text{C}$ is found for Ti nanowires.³⁶ It has been estimated that the local filament temperature due to Joule heating may approach hundreds of degree Celsius for several milliamperes of current.³⁷ It is thus possible for the Ti filaments to melt during the post-forming voltage-sweep measurement, resulting in the large reset loop observed (Figs. 3(a) and 3(b)). The gradual reset behavior may be ascribed to the size (hence melting temperature) distribution of the Ti filaments. Since the range of the applied voltage during post-forming measurement is restricted, reformation of the Ti filaments does not occur, and therefore, the large reset loop is not obtained again. With the ILs also suffered breakdown during forming, CRS is not observed since oxygen exchange with the adjacent filament region in the HfO_x cannot occur now. Possible redistribution of Ti ions and remnant oxygen ions in the Ti-vacancy composite filaments during the inverted-polarity sweep following the large reset may account for the minor current hysteresis seen in Figs. 3(a) and 3(b).

In summary, our study shows that a large percentage of the $\text{TiN}/\text{HfO}_x/\text{TiN}$ RRAM device fails to exhibit CRS after forming. These devices exhibit a large non-polar reset loop typical of devices for which the resistance reset is driven by Joule-heating induced dissolution of metal filaments. This has led us to propose IL breakdown as the cause of the metal (Ti) filament formation and CRS failure in the $\text{TiN}/\text{HfO}_x/\text{TiN}$ device. Our proposition is supported by experimental results of devices with a robust barrier oxide layer incorporated at either one or both the TiN/HfO_x interfaces. These devices show significantly reduced or zero CRS failure rate. The barrier oxide layer is chosen such that it is able to withstand the forming voltage (upon filament formation in the main oxide) until the forming process is interrupted. With the integrity of the barrier oxide layer ensured, stable CRS can be achieved.

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