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

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Enhanced stability of complementary resistance switching in the TiN/HfO₅/TiN resistive random access memory device via interface engineering

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This study shows that a majority (70%) of TiN/HfO₅/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/HfO₅ 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/HfO₅ or both TiN/HfO₅ 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 HfO₅. © 2016 AIP Publishing LLC.

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HfO₅-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 problem, processing complexity is increased. A recent work proposed a one-transistor-n-resistors (1TnR)¹⁶,¹⁷ configurations can solve the sneak-path current problem. In this manner, the sneak-path current problem can be solved without having to integrate an inert metal (e.g., Pt), underscoring the impact interfacial oxide 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 HfO₅ layer in the TiN/HfO₅/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 HfO₅. 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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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 HfOx 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/HfOx/TiN, TiN(top)/Al2O3/HfOx/TiN, and TiN/Al2O3/HfOx/Al2O3/TiN. The thickness of HfOx and Al2O3 in the respective samples is shown in Figs. 1(b), 1(c), and 1(d). The 4 nm thick IL, seen between HfOx and the bottom TiN electrode (Fig. 1(b)), was due to the oxidation of the TiN oxidation during the fabrication process.

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_p,pk) would eventually draw enough oxygen from the bottom IL into the adjacent filament region to re-oxidize it, resetting 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 back to the LRS.

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

FIG. 2. Complementary resistance switching in the TiN/HfOx/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 $V_{n, pk}$ causes the re-oxidized filament region at the BE interface to be re-formed 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 HRSSs. 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 $\pm 0.2$ V, is typically >100, much larger than the ratio of $\sim$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/HfOx/TiN device, which commonly displays a bipolar switching behavior. On the other hand, a large non-polar reset is usually found in devices with a Ni or Pt electrode (e.g., Ni/HfOx/p-Si, Pt/HfOx/Pt) 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. 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, it is shown that the ILs at the TiN/HfOx 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/HfOx/Pt structure only displays the conventional bipolar resistance switching. The failed CRS in the majority of the TiN/HfOx/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 TiOx film, reactively sputtered on a metal electrode and annealed at 600°C, is $\sim 3$ MV/cm. Considering the thickness dependence of $E_b$ ($\propto t_{ox}^{-2}; \alpha \sim 0.5–1$), 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 TiOx formed at a lower temperature (250°C). Thus, it is likely to also suffer a breakdown following the breakdown of the HfOx (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. 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. 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/HfOx interfaces (i.e., TiN/Al2O3/HfOx/TiN, TiN/Al2O3/HfOx/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 HfOx. 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 HfOx; the theoretical $E_b$ of Al2O3 is ~13 MV/cm, whereas that of HfOx is ~5 MV/cm. 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. In addition, Al2O3 has a larger oxygen-vacancy formation energy and migration barrier energy as compared to HfOx. In these regards, it is expected that the thin Al2O3 layer would be able to sustain the forming voltage upon filament formation in the HfOx, until the forming process is interrupted.
The testing results support our proposition. The percentage of devices, with a 3-nm Al₂O₃ layer inserted between the TE and HfOₓ, 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 Al₂O₃ layer at both TiN/HfOₓ interfaces, devices displaying a large reset loop and failed CRS are totally eliminated. With two Al₂O₃ layers, a smaller voltage load appears across each layer, reducing the probability of Al₂O₃ breakdown. For devices with an Al₂O₃ 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 Al₂O₃ layer is situated directly next to the TiN cathode and could therefore effectively suppress the surge in current and Ti migration. However, the stoichiometric TiOₓ interfacial layer is a much poorer barrier against the electron wind and Ti migration under positive-voltage forming. 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 HfOₓ is marginally reduced in the device that has the Al₂O₃ layer included at the TE interface but a much greater reduction is obtained in the device that has Al₂O₃ layers incorporated at both interfaces.

Based on the experimental results, a possible explanation for the high percentage of TiN/HfOₓ/TiN devices that fail to display CRS after forming is proposed (Fig. 5). Because of the higher permittivity of the TiOₓ ILs, the major portion of the applied voltage is initially developed across the thicker HfOₓ layer. When the formation of a low-resistance path occurs in the HfOₓ due to the build-up of vacancy defects to a critical level, the bulk of the applied voltage would now be transferred to the TiOₓ ILs. Owing to the relatively low breakdown field of the TiOₓ, 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)). Due to the random nature of oxide breakdown and ion migration, breakdown regions 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, 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. From molecular dynamics simulation, a significant decrease of the melting point to <450 °C is found for Ti nanowires. It has been estimated that the local filament temperature due to Joule heating may approach hundreds of degree Celsius for several milliampere of current. 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 HfOₓ 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 TiN/HfOₓ/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 TiN/HfOₓ/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/HfOₓ 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.

FIG. 4. Energy-dispersive X-ray analysis of the Ti element concentration within the HfOₓ layer of the TiN/HfOₓ/TiN, TiN/Al₂O₃/HfOₓ/TiN, and TiN/Al₂O₃/HfOₓ/Al₂O₃/TiN devices after positive-voltage forming. The evidently lower Ti element concentration, especially for the device with a thin Al₂O₃ incorporated at both TiN/HfOₓ interfaces, implies that the Al₂O₃ 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 HfOₓ 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.