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Selectorless resistive switching memory: Non-uniform dielectric architecture and seasoning effect for low power array applications

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ABSTRACT
In this work, the nonlinear (NL) characteristics of bi-layer high-k/low-k dielectrics structure, i.e. high-k layer with the low-k layer, are for selectorless oxide-based resistive random-access memories (RRAM) memory array application. It has been shown that such structure enhances the read currents at full read voltage ($\sim 10^{-3}$ A) as compared to the bi-layer low-k/low-k structure ($\sim 10^{-4}$ A), reduces low-voltage current, increases I-V nonlinearity and thereby suppresses the sneak path currents in the selectorless RRAM. Improved seasoning effect has also been demonstrated using the bilayer dielectric structure. The Fowler-Nordheim tunneling behavior has been found in the first RESET process (-0.45 to -1.25 V) as followed by the high self-rectifying characteristics that enlarge the immunity to the sneak path current and reduce the read errors in the array applications. The breakdown controllability of the forming process dominates the followed seasoning cycles which leads to two different performances in bilayer stacks i.e. efficient seasoning and inefficient seasoning, which provides an intrinsic design of selectorless RRAM devices. The device characteristics with current transport mechanisms have also been investigated. Our results provide additional insights into ways to achieve high performance and excellent reliability of built-in nonlinearity in selectorless RRAM (NL > 120, memory window > 100, sub-μs switching speed, and NL retention) for the future low-power RRAM memory array configurations.

INTRODUCTION
In recent years, resistive random access memory (RRAM) has drawn much interest as a promising candidate for next-generation nonvolatile emerging memory due to its potential scalability beyond 10 nm feature size (4F$^2$ design rule), compatibility with a crossbar structure with CMOS integration, intrinsic fast switching speed (<10 ns), femto-joule operating power, and excellent reliability (10$^{12}$ endurance cycles with 10 year retention at 85$^\circ$C capacity$^6$). With simplifying memory array design by crossbar architecture, however, the sneak-path current is a major problem from neighboring unselected cells (USC), which significantly affects the read operation on the selected cell. To solve the sneak path issue, a selector or access device integrated with a memory unit has been developed.$^5$–$^8$ Unfortunately, these additional selector devices, i.e. 1S-1R configurations considerably increase fabrication process, circuit design complexity, and additional cost per chip. Therefore, a selectorless memory i.e. 1R-only design architecture with nonlinear nature is desirable for high-density RRAM array applications. The built-in nonlinear nature can alleviate the sneak path current because the on-state of the selected cell can be read at a “full-voltage region”, while the sharp conductance drops at “lower-voltage region” effectively.
suppress sneak path current through unselected cells in reading schemes (e.g. V/2 and V/3 read schemes). In other words, the sneak path current can be avoided by taking advantage of nonlinearity in the self-rectifying current-voltage (I-V) characteristics. In our previous work, we have reported the intrinsic nonlinearity in bilayer selectorless devices, i.e. HfO$_x$/graphite stacks, can be optimized by inserting a low-k layer i.e. graphite and graphite oxide formation with manipulating the SET compliance current limits (CCL), the so-called “gap design method”. However, the mechanism and characteristics role of the high-k materials e.g. HfO$_x$ in enhancing the nonlinearity of stacked RRAM devices has not yet been investigated. In this work, it has been found that the high-k layer was utilized as the oxygen reservoir with higher oxygen concentration, which improves the nonlinearity by efficiently increasing the read current at the full-read voltage ($V_{\text{read}}$); while the identical low-k layer used for suppressing the low-voltage current i.e. HfO$_x$/graphite (bi-layer high-k/low-k dielectrics structure) and SiO$_x$/graphite devices (bi-layer low-k/low-k dielectrics structure). Also, the low-k layer quality has been re-examined here by analyzing 1st RESET process electrically after electroforming process. The results indicate that less overshoot damage in lower forming voltage induced Fowler–Nordheim (F-N) tunneling as compared to higher forming voltage devices (no F-N tunneling), which determine the nonlinearity and selectorless device reliability i.e. seasoning effect. Our results provide additional insights into ways to achieve high performance and excellent reliability of built-in nonlinearity in 1R-only selectorless RRAM (Ni > 120, memory window > 100, sub-μs switching speed, and multilevel operation, and NL retention) for the future bilayer selectorless RRAM low-power memory array configurations.

**FABRICATION PROCESS**

The starting substrates were heavily-doped N+ Si wafers. Titanium nitride (TiN) of 200 nm was deposited as the bottom electrode. Then, 5 nm of graphite and followed by 7 nm of HfO$_x$, or 7 nm of SiO$_x$ were deposited as resistive switching dielectric layers for realizing the bilayer selectorless structures by radio frequency (RF) sputtering. The graphite oxide was formed after HfO$_x$ deposition as reported in our previous work. Platinum of 165 nm was then deposited as top electrodes, as followed by lift-off method for RRAM devices (Fig. S1). The HfO$_x$ (11 nm) single layer devices, SiO$_x$ (10 nm) single layer, and HfO$_x$ (4 nm)/SiO$_x$ (9 nm) bilayer devices are used as references. For simplifying the device notications, the abbreviation of HfO$_x$ as “H”, SiO$_x$ as “S”, and graphite as “G” are used following by the thickness of thin films. An Agilent B1500 and Lakeshore probe station were used for electrical characterization of the RRAM devices.

**RESULTS AND DISCUSSION**

To initiate the resistive switching in these devices, a one-step single sweep electroforming process was used with a current-limited voltage-sweep to induce a soft breakdown and formed a conductive filament the low resistance state (LRS). To switch to high resistance state (HRS), a negative voltage was applied, and the filament was ruptured. Here, the soft-breakdown process was performed by single sweeping the voltage until current abruptly increased to a compliance current limit (CCL) of 1 mA, as shown in Figure 1(a). In general, this CCL is required to prevent permanent hard-breakdown of oxide layers during the forming process and to increase the “electroforming yield” for RRAM devices, i.e. % of the switchable device after electroforming. The forming voltage of H7G5 (~3.4 V) is smaller than which of S7G5 (~5.2 V), which suggests the higher oxygen vacancies and higher oxygen ions concentration in HfO$_x$ than in SiO$_x$.

Figure 1(b) shows the bipolar resistive switching I-V characteristics during DC voltage sweeps and HfO$_x$ (7 nm)/graphite (5 nm) (H7G5) and SiO$_x$ (7 nm)/graphite (5 nm) (S7G5) bilayer RRAM devices. Voltage was applied to the bottom electrode (TiN) with the top electrode (Pt) connected to ground. After the electroforming process, the resistive switching performance was stabilized by 30 DC voltage sweep cycles. The SET process i.e. switching from HRS to LRS took place in positive polarity, while the RESET occurred in negative polarity.

The SET process for graphite-based RRAMs was performed by applying to 3 V forward/reverse double sweep with 1 mA CCL to program to LRS. The RESET process was done by sweeping to -2.1 V, where current decreased as the voltage was swept from around RESET voltage, and the devices were then programmed into HRS. The nonlinearity is defined as the current at the read voltage ($V_{\text{read}}$) divided by the current at the one third read voltage ($1/3 V_{\text{read}}$) with V/3 scheme. The on-state of the selected cell (SC) is read at a “high-voltage” region, while the sharp conductance decreases at “low-voltage region” (i.e. 1/3 $V_{\text{read}}$) effectively suppresses the sneak current through the unselected cells (USC). The nonlinearity of H7G5 stacked device exhibits ~6 times of improvement over that of S7G5 device with SET CCL of 1 mA, which suggests a significant

![Figure 1](https://example.com/figure1.png)

**FIG. 1.** (a) I-V characteristics of forming process for H7G5 and S7G5, (b) I-V characteristics of bipolar RS operation in the selectorless HfO$_x$ (7 nm)/graphite (5 nm) (red, H7G5) and SiO$_x$ (7 nm)/graphite (5 nm) (green, S7G5) stacked RRAM (median of cycles).
increased current at $V_{\text{read}}$ by inserting the high-k layer i.e. HfO$_x$ in bilayer devices, with nearly similar current at 1/3 $V_{\text{read}}$ ($\sim 10^{-5}$ A) for both structures. The high-k layer i.e. HfO$_x$ in H7G5 is shown to enhance the higher currents at full read voltage ($I_{V_{\text{read}}}$ $\sim 10^{-3}$ A) than those of S7G5 ($I_{V_{\text{read}}} \sim 10^{-4}$ A), where the same low-k layer (i.e. reduces the current at 1/3$V_{\text{read}}$) and same SET CCL of 1 mA (i.e. switching gap in low-k layer) are utilized.

Figure 2 shows the transmission electron microscopy (TEM) image of H7G5 stacked device and the energy dispersive X-Ray spectrum (EDX) results of H7G5 device. Meanwhile, as-deposited graphite in a (221) crystalline plane has been examined by the X-ray diffraction pattern (data not shown) and found to be rhombohedral structure. The EDX analysis i.e. median of five spots was conducted with the beam size of 1.5 nm for H7G5 and S7G5 devices, respectively. The element compositions in at% and wt% have been calculated by the ESVision software. The oxygen-to-carbon ratio (O/C) is $\sim 10$x higher in H7G5 than in S7G5 devices. This indicates that the HfO$_x$ layer acts as an oxygen reservoir layer with higher oxygen vacancies and oxygen ions. In addition, the oxygen affinity of HfO$_x$ is larger than SiO$_x$. In other words, oxygen concentration is higher in HfO$_x$; which is related to the Gibbs free energy of HfO$_x$ ($\Delta G^0 = -266, 435$) and SiO$_x$ ($\Delta G^0 = -215,600$) under the same atmosphere with the spontaneous oxidation process. The high-k materials, acting as an oxygen reservoir layer has higher vacancy concentrations ($V_{V_{\text{ox}}}$) than low-k materials. This leads to higher $I_{V_{\text{read}}}$ and higher NL. With HfO$_x$ as an oxygen reservoir layer in the bilayer device, the 30 cycles median of operating voltage i.e. SET ($\sim 1.28$ V) and RESET ($\sim -0.74$ V) voltages are smaller than in SiO$_x$ stacks (SET: $\sim -1.35$ V; RESET: $\sim -1.2$ V). A plausible explanation is the higher oxygen vacancy and oxygen ion concentrations provided by high-k layer integration (Figure 2(c), left). The switching power, defined as the switching voltage multiplied with switching current, is higher in S7G5 than in H7G5 (Figure 2(c), right). A smaller switching voltage is obtained with increasing oxygen vacancy (or oxygen ions) concentrations. Thus, the high-k layer integration is desirable for the bilayer engineering in reducing the read error with higher NL, especially for higher $I_{V_{\text{read}}}$ as a comparison to the low-k/low-k stacked devices. In addition, the current transport characteristics have been studied by the low-temperature measurements in both HfO$_x$/graphite and SiO$_x$/graphite stacks. The trap depth of HfO$_x$/graphite ($\sim 0.16$ eV) has been extracted as shallower than which of SiO$_x$/graphite ($\sim 0.5$ eV), which resulted in the higher $I_{V_{\text{read}}}$ with the high-k layer under the same bias condition (Fig. S2).

To investigate the stability of selectorless devices, Figure 3 shows the examination process for low-k layer quality determination by analyzing forming and 1$^{\text{st}}$ RESET processes in detail (HfO$_x$ (4 nm)/SiO$_x$ (9 nm) structure as an example). The I-V characteristics with high electroforming voltage and leaky post-forming resistance (Figure 3(a)) did not result in the nonlinear characteristics as
compared to the I-V characteristics with low electroforming voltage and resistive post-forming resistance one (Figure 3(b)). The nonlinearity with cycles, high-voltage current, and low-voltage current are investigated (Fig. S3). This indicates that the potential hard breakdown induced by higher voltage forming process is undesired for the nonlinearity and selectorless device reliability. Note that the devices with low forming voltage have resistive post-forming resistance (read at -0.5V), and the 1\textsuperscript{st} RESET process show a sharp nonlinear increasing region from the low-voltage response, named as “sharp increase” region on current transport behaviors.

Figure 4 compares two cases mentioned in Figure 3, namely, the inefficient seasoning and the efficient seasoning. Inefficient seasoning is a condition for which it takes extensive amount of time to achieve nonlinearity due to leaky of 1/3 read region. For efficient seasoning, nonlinearity is quickly approached to stable state driven by to resistive of 1/3 read region, i.e. suppressed low-voltage current and high nonlinearity. Note that more robust low-k layer with less forming process damage can determine the nonlinearity and selectorless device reliability and stability under the fixed SET current compliance limitation (SET CCL=1 mA). In other words, the device-to-device (D2D) variation results from the early stage operation e.g. electroforming and first RESET should be considered even followed by the identical operation schemes. The four cases are included for the relationship between the 1\textsuperscript{st} RESET and the seasoning performance i.e. nonlinear 1\textsuperscript{st} RESET (green arrow (i-ii)) and linear 1\textsuperscript{st} RESET (blue arrow (iii-vi)). Figure 4(b) shows the statistics of the correlation between the 1\textsuperscript{st} RESET and nonlinearity. The strong seasoning correlations have been presented for the case (i) and case (vi), which including 20 devices for H7G5 and 20 devices for H4S9 bilayer stacked structures have been tested. Chu et al. have also observed similar phenomena of charge quantity is the critical factor for forming process.\textsuperscript{17} The over-forming would lead to device damage i.e. hard breakdown as well as increasing the quantity of charge through the switching layer. The formation of the conducted path can be mitigated by the ultrafast pulse electroforming further to form a discontinuous conduction path in the low-k layer and better nonlinearity.

Current in the high-voltage region (-0.5 V) exhibits different characteristics than current in the low-voltage region (named “sharp increase” behaviors) (See inset of Figure 5 and Figure 3(b)). Transport in this voltage range is found to fit well to the Fowler-Nordheim (F-N) tunneling formula (red region and zoom-in plot of Figure 5 inset) with scientifically accepted accuracy ($R^2 = 99\%$), which showed that less overshoot damage in lower forming voltage may induce Fowler–Nordheim (F-N) tunneling, as compared to which with higher forming voltage devices. The results also confirm that the seasoning effect is related to nonlinearity improvement by robust low-k layer quality and less forming process damage can improve the nonlinearity and selectorless device reliability.
Finally, the benchmarks of current developed bilayer selectorless RRAMs are summarized (Fig. S4) by nonlinearity as a function of memory window (read at 0.28 V), and switching energy (pulse width of 100 ns), showing that the H7G5 is an excellent candidate for bilayer selectorless RRAM with high nonlinearity (~120), good memory window (~10^2), and low switching energy (~40 pJ/bit) for low power applications.

CONCLUSION

In summary, intrinsic nonlinearity characteristics have been demonstrated for the bilayer selectorless 1R-only RRAM without additional selectors. The nonlinearity in HfO2 stacked RRAM devices has been presented, where the high-k layer deposition results in enhancing the read current at the full-read voltage (10^3 A) for improving the NL and reducing the read error, as compared to the low-k layers integration (~10^4 A). Furthermore, the trap depth (~0.16 eV) of HfO2/graphite stacks has been found by investigating the current transport mechanism, which is shallower and contributed to the enhanced read current with higher nonlinearity. The seasoning effect determination with nonlinearity NL is examined for the built-in nonlinear characteristics of low power operating one-resistor selector-less RRAM by stacking engineering. In summary, intrinsic nonlinearity characteristics have been demonstrated for the bilayer selectorless 1R-only RRAM without additional selectors. The nonlinearity in HfO2 stacked RRAM devices has been presented, where the high-k layer deposition results in enhancing the read current at the full-read voltage (10^3 A) for improving the NL and reducing the read error, as compared to the low-k layers integration (~10^4 A). Furthermore, the trap depth (~0.16 eV) of HfO2/graphite stacks has been found by investigating the current transport mechanism, which is shallower and contributed to the enhanced read current with higher nonlinearity. The seasoning effect determination with nonlinearity NL is examined for the built-in nonlinear characteristics of low power operating one-resistor selector-less RRAM by stacking engineering. In summary, intrinsic nonlinearity characteristics have been demonstrated for the bilayer selectorless 1R-only RRAM without additional selectors. The nonlinearity in HfO2 stacked RRAM devices has been presented, where the high-k layer deposition results in enhancing the read current at the full-read voltage (10^3 A) for improving the NL and reducing the read error, as compared to the low-k layers integration (~10^4 A). Furthermore, the trap depth (~0.16 eV) of HfO2/graphite stacks has been found by investigating the current transport mechanism, which is shallower and contributed to the enhanced read current with higher nonlinearity. The seasoning effect determination with nonlinearity NL is examined for the built-in nonlinear characteristics of low power operating one-resistor selector-less RRAM by stacking engineering.

SUPPLEMENTARY MATERIAL

See supplementary material for the fabrication process, device structures, nonlinearity equation derivation, and electrical characteristics of bilayer selectorless RRAMs.

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FIG. 5. Fowler-Nordheim (F-N) tunneling fitting in the high voltage region of efficient cycling as seasoning cycles on the selectorless memory device. (Inset shows the 1st RESET I-V characteristics and fitting region).