Homogeneous barrier modulation of TaO$_x$/TiO$_2$ bilayers for ultra-high endurance three-dimensional storage-class memory
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Abstract

Three-dimensional vertical resistive-switching random access memory (V-RRAM) is the most anticipated candidate for fulfilling the strict requirements of the disruptive storage-class memory technology, including low bit cost, fast access time, low-power nonvolatile storage, and excellent endurance. However, an essential self-selecting resistive-switching cell that satisfies these requirements has yet to be developed. In this study, we developed a TaO$_x$/TiO$_2$ double-layer V-RRAM containing numerous highly desired features, including: (1) a self-rectifying ratio of up to 10$^3$ with a sub-$\mu$A operating current, (2) little cycle-to-cycle and layer-to-layer variation, (3) a steep vertical sidewall profile for high-density integration, (4) forming-free and self-compliance characteristics for a simple peripheral circuit design, and (5) an extrapolated endurance of over 10$^{15}$ cycles at 100 $^\circ$C. Furthermore, the switching and self-rectifying mechanisms were successfully modeled using oxygen ion migration and homogeneous barrier modulation. We also suggest the new possibility of monolithically integrating working and storage memory by exploiting a unique tradeoff between retention time and endurance.

Keywords: storage-class memory, resistive-switching random access memory, three-dimensional memory, current conduction mechanism, self rectification

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(Some figures may appear in colour only in the online journal)

1. Introduction

Inefficient memory and storage hierarchy based on dynamic random access memory (DRAM) and hard disks has become a major challenge in designing large-scale, high-performance computer systems. Using the existing hierarchy, the projected exascale computing requires impractical energy consumption, space usage, and cost [1]. This inefficiency is largely attributed to the access time gap of five orders of magnitude between hard disks (>10 ms) and DRAM (<100 ns). Storage-class memory (SCM) has been proposed to narrow or even eliminate the access time gap and greatly improve system performance [1, 2]. The basic requirements for SCM include low cost per bit, fast read and write access time, low-power nonvolatile storage, and excellent write endurance. However, none of the existing or emerging memory technologies can fulfill all of the requirements for SCM simultaneously. Solid-state drives based on NAND flash nonvolatile memory (NVM) are considered an early version of SCM. Recent advances in three-dimensional (3D) vertical NAND (V-NAND) technology may eventually realize SCM at a bit cost comparable to that of hard disks [3, 4]. However, slow access time and poor write endurance
Figure 1. (a) Illustration of 3D V-NAND and V-RRAM arrays for realizing high-bit-density SCM. Unit cells for both 3D V-NAND and V-RRAM on the vertical sidewalls are shown for comparison. (b) Cross-sectional TEM image of the 3D double-layer V-RRAM, showing a steep sidewall profile. (c) Enlarged picture of the Ta/TaOₓ/TiO₂/Ti MIIM unit cell as indicated in (b). The thicknesses of TiO₂ and TaOₓ on the vertical sidewalls are 40 nm and 20 nm, respectively. (d) EDX elemental profiling of the MIIM cell.

may limit the full potential of NAND-based SCM. Phase-change memory (PCM) is considered an alternative SCM possessing a faster access time than NAND. However, the high programming current of PCM is the main concern for high-density integration [2]. Although a programming current as low as 1 µA was recently demonstrated by using carbon nanotubes as nanoscale electrodes [5, 6], a high-density integration scheme as competitive as 3D V-NAND has yet to be developed. Emerging resistive-switching random access memory (RRAM) [7–12] is another strong candidate for high-performance SCM. The latest RRAM array prototypes have demonstrated a fast access time, closer to that of DRAM [13], endurance of over 10⁷ cycles [14], and a high integration density of 32 Gb by using the 24-nm technology [15]. Furthermore, 3D vertical RRAM (V-RRAM) technology, analogous to the V-NAND counterpart, is being actively developed to fabricate high-density memory in an extremely cost-effective manner [16–18]. Figure 1 illustrates the representative cell structures of V-RRAM and V-NAND. Both V-RRAM and V-NAND use multiple thin-film deposition and minimal photolithography and etching steps. Oxide/nitride/oxide (ONO) layers, used for local charge storage, and resistive-switching (RS) layers are deposited on the vertical sidewalls of V-NAND and V-RRAM, respectively. Requiring no serial Si transistors in the memory core of V-RRAM not only enables fast random access in a cross-point configuration, but also allows ultimate scalability beyond the conventional transistor scaling limits. In addition, the insufficient number of stored electrons (less than 100) is a known physical limit of NAND technology below 20 nm [19]. By contrast, RRAM has shown promising scalability beyond 10 nm [20].

Two critical challenges remain for V-RRAM in becoming a legitimate SCM candidate. First, self-selecting or self-rectifying characteristics involving a highly nonlinear resistance are required in high-density cross-point V-RRAM to suppress the sneak current in read and write operations [21–23]. Otherwise, the sneak current through the neighboring unselected cells would degrade readout signals, attenuate voltage propagation, and increase read/write power consumption [24–26]. The V-RRAM devices reported in the literature either lacked sufficient selectivity [16, 17] or were incompatible with semiconductor fabrication owing to their use of noble metal electrodes such as Pt [18]. Furthermore, the physical mechanism and design principles used to realize the desired selectivity are not comprehensively understood. Second, although far superior to flash, a write endurance of RRAM that satisfies the demanding requirements for replacing DRAM as working memory (>10¹⁵ cycles) has yet to be achieved. Recently, a self-rectifying RRAM based on a TaOₓ/TiO₂ bilayer structure has exhibited numerous highly desirable features for implementing high-density cross-point arrays [23]. In this paper, we report on a Ta/TaOₓ/TiO₂/Ti V-RRAM which demonstrates a substantial self-rectifying ratio of 10³ with a sub-µA operating current and extrapolated endurance of over 10¹⁵ cycles at 100 °C. The RS and self-rectifying mechanisms were successfully modeled using oxygen ion (O²⁻) migration in TaOₓ, corresponding homogeneous barrier modulation, and asymmetric tunnel barriers at the Ta/TaOₓ and TaOₓ/TiO₂ interfaces. Furthermore, a tradeoff between retention time and endurance may enable the monolithic integration of DRAM-like and NVM-like SCM using identical V-RRAM technology.
Nanotechnology difference between top-layer and bottom-layer cells. The effective device area at the vertical sidewall is 0.2 µm². The device demonstrates a sub-µA operating current and an RR of 10⁵ at ±2 V. Multiple resistance states controlled using a gradual RESET process. Devices comprise varied sidewall lengths from 0.6 to 20 µm and a fixed Ti thickness of 100 nm (effective areas of 0.12–4 µm²). Both the LRS and HRS currents are scaled according to the device area.

2. Experimental details

We fabricated a double-layer V-RRAM, similar to that shown in figure 1. Multiple Ti horizontal electrodes and SiO₂ isolation layers were sequentially deposited onto 550-nm-thick SiO₂ substrates. For the Ti electrodes, 100-nm-thick Ti was deposited using dc magnetron sputtering with a Ti (99.99%) target at a deposition rate of 1 nm s⁻¹. For the SiO₂ isolation layers, 100-nm-thick SiO₂ was deposited using plasma-enhanced chemical vapor deposition (PECVD) at 320 °C and tetraethyl orthosilicate (TEOS) as a silicon source at a deposition rate of 1.7 nm s⁻¹. Vertical pillar structures with a sidewall width of 0.5 µm were patterned using a lithography process, followed by etching multiple Ti and SiO₂ layers, with the etchants HBr₆ and CCl₄, respectively, until the SiO₂ substrates were reached. To prepare the bilayer TaOₓ/TiO₂, 60-nm-thick TiO₂ and 40-nm-thick TaOₓ were sequentially deposited by means of reactive dc magnetron sputtering at room temperature using Ti (99.99%) and Ta (99.95%) targets, respectively, in an Ar and O₂ mixture. The Ar to O₂ gas flow ratio and the deposition rate for TiO₂ were 2:1 and 0.006 nm s⁻¹, whereas those for TaOₓ were 20:3 and 0.04 nm s⁻¹. Two additional lithography and dry etching steps were performed to open the contacts to the Ti horizontal electrodes for the top and bottom cells. Finally, the Ω shape of the Ta vertical electrodes with a thickness of 250 nm and various sidewall lengths from 0.2 to 20 µm were deposited using dc magnetron sputtering with a Ta (99.95%) target at a deposition rate of 0.1 nm s⁻¹, followed by a lift-off process completing the Ta/TaOₓ/TiO₂/Ti metal–insulator–insulator–metal (MIIM) RRAM unit cell on the vertical sidewalls.

A transmission electron microscopy (TEM) image of the double-layer V-RRAM is shown in figure 1(b). In contrast to the tapered sidewall with a Pt bottom electrode [18], using the fab-friendly Ti horizontal electrode formed a steep sidewall profile, which is critical in reducing the pitch size between vertical pillars in a high-density array with a large number of vertically stacked layers. Because of the nonconformal deposition of the sputtered films, the film appeared to be thinner on the vertical sidewall (20-nm TaOₓ and 40-nm TiO₂) but thicker on the top of the pillar structure. An enlarged TEM image of the TaOₓ/TiO₂ bilayer is shown in figure 1(c). The Ti and TiO₂ films were highly crystalline, with an amorphous 20-nm-thick interfacial layer formed by oxidizing the Ti electrode during the reactive sputtering process. The crystallinity of the Ta and TaOₓ films was greatly enhanced at the sidewall, thereby forming columnar grains with the TiO₂ underlayer. The elemental analysis by energy-dispersive x-ray spectroscopy (EDX) shown in figure 1(d) reveals a nearly stoichiometric TiO₂ layer, an oxygen-deficient TiOₓ (x < 2) interfacial layer, and a TaOₓ layer with a gradient substoichiometric composition. The TaOₓ became more oxygen-deficient toward the Ta top electrode, suggesting a strong oxygen scavenging ability of Ta because of its low electronegativity. The results of a separate analysis using x-ray photoelectron spectroscopy (XPS) were consistent with the EDX results (figure S1, supporting information available at stacks.iop.org/Nano/25/165202/mmedia).

3. Results and discussion

Figure 2(a) shows the typical bipolar resistive switching (BRS) characteristics of the MIIM V-RRAM with a sub-µA operating current. The effective device area at the vertical sidewall was 0.2 µm². The device operation required neither electrical forming nor current compliance, which greatly reduces the complexity of the peripheral circuit design. We observed little switching variation and no apparent difference between the top-layer and bottom-layer cells. Excessive switching variability is known to be a major bottleneck of the typical filamentary RRAM because of the stochastic nature of the percolation-based SET process [27, 28]. A previous study reported that the variability became even more severe in a sub-µA filamentary RRAM because of the unavoidable random fluctuation of very few ions moving at SET/RESET in the filament constriction [29]. By contrast, the results of this study support the possibility of developing a low-power RRAM with minimal variability. A tenfold resistance change in a high resistance state (HRS) and a low resistance state (LRS) could be read only at a negative (forward) bias because the current–voltage (I–V) curves completely overlapped at a positive (reverse) bias. A rectifying ratio (RR) of an LRS at
±2 V that exceeds three orders of magnitude may effectively suppress the sneak current in high-density 3D arrays. Although the rectifying LRS resembled that of typical one diode–one resistor (1DIR) cells, this self-rectifying RBS device provided a wider programming margin by using opposite polarities of SET and RESET voltages compared with the unipolar resistive switching (URS) of 1DIRs.

Figure 2(b) shows a gradual RESET process that enables multiple resistance states to be precisely controlled using an appropriate RESET voltage, ranging from −4 to −6 V, and a SET voltage of 5 V. The gradual RESET is a signature of increasing tunnel distance in the HRS, most often involving O\(^{2−}\) migration in the RS layers [30]. Figure 2(c) shows the BRS curves of V-RRAM with varied sidewall lengths from 0.6 to 20 μm and a fixed Ti thickness of 100 nm. Both the LRS and HRS currents showed an apparent area dependence, thereby supporting a homogeneous transport mechanism that is substantially different from the filamentary conduction often observed in RRAM devices [31–34].

To elucidate the RS mechanism of the Ta/TaO\(_x\)/TiO\(_x\)/TaO\(_x\)/Ti devices, we fabricated several planar devices with various combinations of TaO\(_x\) and TiO\(_x\) thicknesses by using a short-loop shadow-mask process. Both the Ta/TiO\(_x\)/Ti and Ta/TaO\(_x\)/Ti devices with only a single dielectric layer were highly conductive at both polarities without RS (figure S2, supporting information available at stacks.iop.org/Nano/25/165202/mmedia). TaO\(_x\)/TiO\(_x\) is known as an extremely active metal that easily reacts with deposited metal oxides [35]. Therefore, separate devices of Ti/TiO\(_x\)/Pt and Ta/TaO\(_x\)/Pt were fabricated using inert Pt bottom electrodes to investigate the roles of the Ti/TiO\(_x\) and Ta/TaO\(_x\) interfaces in RS. As shown in figure 3(a), both devices exhibited rectifying I−V because of the asymmetric Schottky barriers at the Ti/TiO\(_x\) (Ta/TaO\(_x\)) and TiO\(_x\)/Pt (TaO\(_x\)/Pt) interfaces. A higher forward current in the Ti/TiO\(_x\)/Pt device indicates that the Ti/TiO\(_x\) interface formed a more ohmic-like transparent barrier [33, 35] compared with that of the Ta/TaO\(_x\) interface [36]. After electrical forming occurred at a positive bias with a current compliance of 1 mA, only the Ta/TaO\(_x\)/Pt device demonstrated reproducible BRS with gradual RESET characteristics, as shown in the inset of figure 3(a). In addition, figure 3(b) shows the BRS I−V of Ta/TaO\(_x\)/TiO\(_x\)/Ti devices with various TaO\(_x\) thicknesses. Reducing the TaO\(_x\) thickness increased both the forward and reverse currents. The increase in the reverse current was more dramatic and, thus, the RR was degraded when a thinner TaO\(_x\) film was used. The resistance ratio between the HRS and LRS also reduced when a thinner TaO\(_x\) film was used. By contrast, the effect of the TiO\(_x\) thickness on device currents was secondary, as shown in figure 3(c). However, a sufficient TiO\(_x\) thickness was necessary to achieve RS and self-rectifying. Otherwise, the device would behave like the Ta/TaO\(_x\)/Ti structure, possibly because of the strong oxygen scavenging ability of Ti (figure S3, supporting information available at stacks.iop.org/Nano/25/165202/mmedia).

We proposed a plausible physical model, as shown in figure 4(a), to explain the experimental findings. The TiO\(_x\)/Ti interface is believed to be a transparent ohmic contact. Therefore, electron injection from the Ti electrode at a positive bias is limited mainly by the conduction band offset at the TaO\(_x\)/TiO\(_x\) interface. In addition, electron injection from the Ta electrode at a negative bias is controlled by the TaO\(_x\)/Schottky interface formed by immobile shallow donor-like dopants. Varying charge distributions near the Ta/TaO\(_x\) interface affect the tunnel width of the Schottky barrier at a negative bias, corresponding to multiple resistance states, but have little influence on the tunnel width of the TaO\(_x\)/TiO\(_x\) barrier at a positive bias. Because of the homogeneous nature of current conduction, a one-dimensional (1D) numerical simulation of O\(^{2−}\) migration and homogeneous barrier modulation was performed to verify the proposed physical model. The detailed simulation method is discussed in the supporting information (available at stacks.iop.org/Nano/25/165202/mmedia). Figures 4(b) and (c) show the calculated band structures of the LRS and HRS at ±2 V and the corresponding V\(_0\) and O\(^{2−}\) concentration profiles,
Figure 4. (a) Schematic diagrams showing $O^{2−}$ migration in the $V_O$-rich (oxygen-deficient) layer near the top Ta electrode during bipolar SET and RESET operations and (c) corresponding $V_O$ and $O^{2−}$ concentration profiles. Varying charge distributions near the Ta/TaO$_x$ interface affect the tunnel width of the Ta/TaO$_x$ Schottky barrier at $−2$ V but not the tunnel width of the TaO$_x$/TiO$_2$ barrier at $+2$ V. (d) Calculated $I$–$V$ curves of the Ta/TaO$_x$(20 nm)/TiO$_2$(60 nm)/Ti MIIM, displaying multiple resistance levels. (e) Calculated $I$–$V$ curves of several MIIM devices with various TaO$_x$ and TiO$_2$ thicknesses, showing good qualitative agreement with the experiments (figures 3(b) and (c)) using a single set of parameters.

which confirm the presence of $O^{2−}$ migration, Schottky barrier modulation at the Ta/TaO$_x$ interface, and asymmetric tunnel barriers at positive and negative polarities. Note that the homogeneous barrier modulation involving a large number of interface defects in the entire device area overcomes the limitation of the stochastic percolation statistics and random fluctuation of very few ions in the filament constrictions and is, thus, the key to realize deterministic BRS. Maintaining a gradient TaO$_x$ composition (i.e., more oxygen-deficient near the Ta/TaO$_x$ interface but less so near the TaO$_x$/TiO$_2$ interface) is critical for achieving the desired resistance ratio and the asymmetric charge distribution necessary for self rectification. In the filamentary RRAM, the composition profile is often tuned by the additional forming process, but in this forming-free device it is believed to be controlled by the oxygen scavenging ability of Ta and Ti and the appropriate design of the TaO$_x$ and TiO$_2$ thicknesses. Furthermore, figure 4(d) shows the calculated multiple resistance states on varying the RESET stop voltages. All resistance states exhibited negligible difference at a positive bias. Figure 4(e) shows the BRS characteristics associated with various TaO$_x$ and TiO$_2$ thicknesses, which are in good qualitative agreement with the $I$–$V$ curves in figures 3(b) and (c). Because the TaO$_x$ layer is the main tunnel barrier of current conduction, regardless of bias polarities, reducing the TaO$_x$ thickness results in a significant current increase.

Long-term device reliability characteristics, such as retention time and endurance, are critical for SCM applications. The planar shadow-mask devices were used in this investigation because they are less prone to unoptimized process variations in the V-RRAM, thus facilitating the collection of statistical data with high confidence. Figure 5(a) shows the typical retention failure behavior of the MIIM self-rectifying cell at room temperature. Multiple LRSs and HRSs were programmed by dc SET and RESET operations, respectively, at various voltages. Both the LRS and HRS resistances increased as the retention time increased, eventually saturating in a much higher resistance state of 1 GΩ. Therefore, we defined the retention failure criterion as the point when the LRS resistance increases by a factor of ten and becomes indistinguishable from the lowest HRS resistance before performing the retention test.
Figure 5. In a shadow-mask Ta/TaOx (10 nm)/TiO2 (30 nm)/Ti MIIM, (a) typical retention failure behaviors of the LRSs obtained by varying SET voltages and the HRSs obtained by varying RESET voltages at room temperature. (b) Arrhenius plot of the LRS retention time as a function of SET voltage. Retention failure is defined as occurring when the LRS resistance increased by a factor of ten. (c) Typical pulse endurance of over \(10^{12}\) cycles achieved using ac SET and RESET pulses of 100 ns at \(\pm 6\) V and a read voltage of \(-2\) V at room temperature. (d) Arrhenius plot of the endurance cycle as a function of the magnitude of SET pulses of 100 ns. A fixed RESET pulse of 100 ns at \(-6\) V was used.

The resistance increase may be explained by the increase in the tunnel width of the Ta/TaOx Schottky barrier as O\(^2^-\) diffused away from the interface possessing a high O\(^2^-\) concentration into the TaOx film even with no external electric field present. Figure 5(b) shows the Arrhenius plot of the LRS retention time obtained at varied SET voltages and baking temperatures from 25 to 175 °C. Thirty cells under each condition were measured. Using higher SET voltages yielded slightly lower LRS resistances and improved retention time because additional O\(^2^-\) was driven toward the Ta/TaOx interface. Furthermore, the extracted activation energy of O\(^2^-\) migration, \(E_A \approx 0.7\) eV, was relatively insensitive to SET voltage. All of the other devices with various TaOx/TiO2 thicknesses produced a similar \(E_A\) value (figure S4, supporting information available at stacks.iop.org/Nano/25/165202/mmedia). This \(E_A\) value agrees with that used in the 1D O\(^2^-\) migration model, thus supporting the O\(^2^-\) diffusion mechanism for retention failure.

Figure 5(c) shows the typical endurance characteristics of the MIIM self-rectifying cell at room temperature on using ac SET and RESET pulses of 100 ns, which is close to the access time requirement of DRAM and may be further improved by optimizing the RC delay in the vertical RRAM structure. Higher pulse amplitudes than dc SET and RESET voltages were used because of the shorter pulse time. An extremely high endurance of over \(10^{12}\) cycles without device wear-out is on a par with that of the best RRAM device previously reported [37]. For DRAM-like SCM applications, excellent device endurance must be guaranteed in a worst-case scenario of a non-stop operating condition for ten years (i.e., endurance of over \(10^{15}\) cycles for a pulse width of 100 ns). We performed an acceleration test using elevated temperatures to project a device endurance beyond \(10^{15}\) cycles. Figure 5(d) shows the Arrhenius plot of the endurance cycle obtained at varied SET pulse magnitudes and baking temperatures from 150 to 250 °C. Ten cells under each condition were measured. All of the failed devices remained in an LRS of 200 \(\Omega\), which was much lower than that of the initial LRS, and were completely lacking in self-rectifying behavior, which is similar to the characteristics of a normal RRAM device after undergoing electrical forming. Therefore, we attributed the failure mode to the irreversible hard breakdown of the rectifying TaOx/TiO2 interface. Although using a high SET voltage improves retention time, it degrades device endurance. A SET pulse of 8 V easily destroyed the interface within tens of cycles, whereas \(10^{15}\) endurance cycles at 100 °C may be achieved by lowering the SET pulse to 6 V. The extracted activation energy of irreversible breakdown, \(E'_A\), shown in figure 5(d), was much higher than the \(E_A\) of O\(^2^-\) migration, indicating that the irreversible hard breakdown was not induced by the migration of existing O\(^2^-\) but rather by the generation of new O\(^2^-\) and VO defects near the TaOx/TiO2 interface under electrical stress. A much higher value of \(E'_A\) compared with that of \(E_A\) is required to ensure robust device endurance. As shown in figure 5(d), the apparent voltage dependence on the time to irreversible hard breakdown and \(E'_A\) also agrees with the occurrence of a dielectric
breakdown event [38]. On-going research is being conducted to quantitatively investigate the voltage dependence.

The tradeoff between retention time and endurance presents a challenge in choosing an appropriate SET voltage for an ideal SCM with a NVM-like retention and a DRAM-like endurance. However, this tradeoff also presents a new opportunity to implement a monolithic SCM with multiple retention and endurance specifications. A SCM chip comprising an identical array architecture and peripheral read and write circuits may be divided into distinct subareas by applying various SET voltages depending on their applications. For example, by applying a lower SET voltage, a working memory with an unlimited endurance but a retention time of minutes to hours could be a low-power alternative to volatile DRAM. By applying a higher SET voltage, a nonvolatile storage cache with a limited but reasonable endurance and a retention time of hours to days could expedite the slow process of acquiring data directly from disk drives and considerably reduce energy consumption. Furthermore, this SCM technology is compatible with 3D V-RRAM technology, which exhibits superior scalability, thereby ensuring an extremely low bit cost.

4. Conclusions

In summary, we present a promising SCM technology based on a TaOx/TiO2 V-RRAM structure and a homogeneous barrier modulation mechanism. The remarkable properties demonstrated in this device differ substantially from those of the prevalent filamentary RRAM, including a high self-rectifying ratio at a low operating current, negligible cycling variation, forming-free and self-compliance characteristics, and an extremely high endurance, capable of realizing working memory applications. Therefore, this class of homogeneous barrier modulation RRAM is optimal for realizing high-performance and ultra-high-density SCM and is, thus, deserving of more attention in future RRAM research. Several aspects of device fabrication and materials require further investigations. For example, other conformal deposition techniques such as atomic layer deposition (ALD) would benefit the thickness scaling of the RS films and the pitch-size scaling of 3D arrays; however, this may require developing substoichiometric ALD films. In addition, improvements in retention time might be possible by tailoring the TaOx compositions or inserting barrier layers to suppress O2− diffusion. Device scalability below 10 nm and the further reduction of operating voltages should also be investigated.

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