Self-Rectifying Resistive Switching Memory with Ultralow Switching Current in Pt/Ta₂O₅/HfO₂-x/Hf Stack

Haili Ma¹, Jie Feng¹*, Hangbing Lv², Tian Gao¹, Xiaoxin Xu², Qing Luo², Tiancheng Gong² and Peng Yuan²

Abstract
In this study, we present a bilayer resistive switching memory device with Pt/Ta₂O₅/HfO₂-x/Hf structure, which shows sub-1 μA ultralow operating current, median switching voltage, adequate ON/OFF ratio, and simultaneously containing excellent self-rectifying characteristics. The control sample with single HfO₂-x structure shows bidirectional memory switching properties with symmetrical I–V curve in low resistance state. After introducing a 28-nm-thick Ta₂O₅ layer on HfO₂-x layer, self-rectifying phenomena appeared, with a maximum self-rectifying ratio (RR) of ~4 × 10³ observed at ±0.5 V. Apart from being a series resistance for the cell, the Ta₂O₅ rectifying layer also served as an oxygen reservoir which remains intact during the whole switching cycle.

Keywords: RRAM, Crossbar, Leakage current issue, Self-rectifying

Background
The long time issue faced by semiconductor industry was searching for efficient methods to overcome the fundamental scaling limits of charge-based information storage devices. One of the promising methods is to use crossbar architecture to increase integration density. However, the sneak-path issue (shown in Fig. 1a) acts as a disturbing problem in reading the correct information [1]. Various methods are developed to settle this urgent problem, including one MOSFET transistor-one resistor (1T1R), one diode-one resistor (1D1R), complementary resistive switch (CRS), one bidirectional selector-one resistor (1S1R), and one resistor with self-rectification (1R with S-R) [2]. Among these candidates, resistance random access memories (RRAMs) with self-rectifying characteristics in the low resistance state (LRS) has been receiving great attention in recent years owing to the feasibility of its realization in a simple one resistor structure. Typical bipolar resistive switching (RS) behavior of 1R with S-R cells, as indicated in Fig. 1b, reveals an asymmetric I–V characteristics in the LRS, which means that electrons can be easily injected or seriously blocked under different bias voltage. In this case, the ground scheme, where the selected word line (WL) is biased to Vread and all other WL/bit lines (BLs) are grounded, is generally adopted to mitigate leakage current (shown in lower right inset of Fig. 1b). The wealth of self-rectifying phenomena in different structures reported so far, while either too high switching voltage [3, 4] or insufficient ON/OFF window [5, 6] is exposed by most reports.

Presented in this work, therefore, is a material system that can provide ultralow operating current (<1 uA), sufficient ON/OFF window (~10²), median operating voltages (<6 V), as well as excellent self-rectifying functionality (RR >1000). In the bilayer stack, stoichiometric Ta₂O₅ and anoxic HfO₂-x were employed to be electrolytes, which contacted with high-work-function metal (Pt, 5.6 eV) and low-work-function metal (Hf, 3.9 eV), respectively [7]. The method can be generally stated as one layer (in this case, HfO₂-x) and works as the RS layer by trapping and detrapping the deep trap sites while the other dielectric layer (in this case, Ta₂O₅) remains intact during the whole switching cycle and creates a high Schottky barrier with Pt to constitute the rectifying functionality.

* Correspondence: jfeng@sjtu.edu.cn
¹Department of Micro/Nano Electronics, Key Laboratory for Thin Film and Micro Fabrication of Ministry of Education, Shanghai Jiao Tong University, Shanghai, China
Full list of author information is available at the end of the article

© The Author(s). 2017 Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.
Methods
We fabricated the Pt/Ta$_2$O$_5$/HfO$_2$-x/Hf devices by combining DC magnetron sputtering and oxygen plasma oxidation. The relevant fabrication process flow, equivalent schematic diagram, and cross sectional SEM image including relevant XPS data of our optimal sample are shown in Fig. 2. A bilayer of Ti and Hf, with a thickness of 3 and 60 nm, respectively, was deposited by DC magnetron sputtering on a SiO$_2$/Si substrate. The HfO$_{2-x}$ films were formed by directly oxidizing the metal Hf via oxygen plasma with the power of 50 W and different durations (i.e., 1300, 1600, and 1900 s). Whereas the 28-nm-thick Ta$_2$O$_5$ films were deposited by DC reactive magnetron sputtering using a Ta target in Ar/O$_2$ gas mixture (with excess volume of O$_2$ gas) at room temperature, the total pressure was ~0.28 Pa. For the electrode preparation, a large part of fresh metal Hf was reserved by covering aluminum foil in advance, and then the rest part was overlaid by inert Pt (30 nm) to fabricate the bottom-electrode Hf, while top-electrode Pt (50 nm) with a diameter of ~200 μm was deposited by DC magnetron sputtering using a metal shadow mask. For comparison, the stacks of Pt/HfO$_{2-x}$/Hf without Ta$_2$O$_5$ layer and Pt/Ta$_2$O$_5$(28 nm)/Hf without HfO$_{2-x}$ layer were also fabricated.

The cross sectional image was observed using a UKTRA-55 field emission scanning electron microscope (FESEM); and chemical status of films were examined using an X-ray photoelectron spectroscopy (XPS, Kratos Axis UltraDLD spectrometer, Kratos Analytical-A Shimadzu group company). For the XPS measurement, the Ar + ion beam energy was set to 1 keV during the sputter-etching. As to the electrical measurements, a low-noise Keithley 4200 semiconductor characterization system was conducted at room temperature, in voltage sweep mode. Each voltage sweep began from 0 V, and the bias was applied to the TE while the BE was grounded.

Results and Discussion
Figure 3 shows the typical I–V characteristics of our samples (deposited in the same batch). For simplicity, the device that possesses Pt/HfO$_{2-x}$/Hf stack but different oxidizing duration (i.e., 1300, 1600, and 1900 s) is denoted as Device01, Device02, and Device03, respectively. Whereas Device00 and Device28 denote Pt/Ta$_2$O$_5$/Hf
stack and the sample with Pt/Ta$_2$O$_5$(28 nm)/HfO$_{2-x}$(oxidizing 1600 s)/Hf structure, respectively. As indicated in Fig. 3a, Device02 behaved better bidirectional RS characteristics than Device01 and Device03; therefore, this condition was chosen to prepare the RS layer in our Pt/Ta$_2$O$_5$/HfO$_{2-x}$/Hf devices. Whereas rectifying properties (no RS behavior) was found in Device00, and the effect of their combination was reflected by Device28 (Fig. 3c). Additionally, it is worth noting from the XPS results in Fig. 2c that the binding energy of Ta 4f well coincided with the reported value of the Ta 4f peak (26.6 eV for Ta 4f7/2 and 28.4 eV for Ta 4f5/2) in Ta$_2$O$_5$ [3, 8]. For HfO$_{2-x}$, grown by directly oxidizing the metal Hf via oxygen plasma with a duration 1600 s, the core-level Hf 4f7/2–Hf 4f5/2 was observed at an energy corresponding to the non-stoichiometric HfO$_2$ (12.7–18.5 eV) [9], which indicated the presence of the neutral oxygen vacancy in our HfO$_{2-x}$ layer. Along with the I–V characteristics in Fig. 3, it was confirmed that HfO$_{2-x}$ layer plays the role of RS layer indeed, whereas stoichiometric Ta$_2$O$_5$ layer works as a rectifier with high resistance and only slight oxygen deficiency. Beyond that, the thickness of HfO$_{2-x}$ layer with oxidizing duration 1600 s approximates 30 nm.

When a positive voltage sweep with an $I_{\text{comp}}$ of 1 uA (to prevent the device hard breakdown) were firstly applied whereas their BE were grounded, then as-fabricated devices transform into the LRS (or ON state), i.e., the SET process (for Device02 and Device28). Particularly the electroforming was relieved since a large amount of oxygen vacancies ($V_O$) in the HfO$_{2-x}$ film (RS layer) [10, 11]. To turn the devices back into the HRS, i.e., the RESET process, a negative voltage sweep (−1.5 V for Device02 and −3.5 V for Device28) was required. Particularly, after stacking a 28-nm-thick Ta$_2$O$_5$ layer on HfO$_{2-x}$ film, a pronounced self-rectifying behavior appeared in Device28. Significantly, a $\sim 4 \times 10^3$-fold reduction in LRS current was observed at $-0.5 \text{ V}(V_{\text{read}})$ compared with the current at $0.5 \text{ V}(V_{\text{read}})$. In addition, a DC cycling and retention property test of Device28 were also implemented, the results are presented in Fig. 4. The high uniformity of RS performance and stable distribution of retention time data (baked at 85 °C up to $10^4$ s) indicate the high feasibility of the present structure as the RS element in crossbar.

To demonstrate the feasibility of settling the sneak-path issue by utilizing the observed self-rectifying behavior, numerical simulation of the maximum crossbar size has also been conducted for Device28 by the use of MATLAB. Figure 5 shows that the obtained self-rectifying property in this work can guarantee a maximum crossbar array size of $\sim 5 \text{ k bit}$ in the worst case scenario for reading (V scheme).

Now, we turn to discuss the switching and self-rectifying mechanism discovered in Device28 from the
viewpoint of energy band. Although the accurate energy band structure could not be depicted due to the lack of precise information on the band offset between the two dielectric layers and possible (larger) Schottky barrier at the HfO$_2$-x/Hf interface, a tentative schematic band diagram could be drawn as shown in Fig. 6a for the zero external bias condition. Here, the CB offset between Ta$_2$O$_5$ and HfO$_2$-x was taken as 1 eV considering the known electron affinities of both materials [12, 13], and contact potential at the HfO$_2$-x/Hf interface was taken as 1.3 eV based on their electron affinity and work function. As the band gap of Ta$_2$O$_5$ is lower than that of HfO$_2$-x (≈4.2 and ≈5.68 eV, respectively) [3], the electrons transported to Ta$_2$O$_5$ easily moved to Pt TE via the conduction within the CB of the Ta$_2$O$_5$ layer, so that the Ta$_2$O$_5$ layer kept intact under the positive bias condition. In addition, considering the high oxygen affinity of beneath metal Hf in the HfO$_2$-x/Hf stack, abundance of $V_O$ would be induced in bulk portion of HfO$_2$-x. It is believed that these $V_O$ values were dispersed within the HfO$_2$-x layer and acted as the deep trap sites (red dot lines drawn in Fig. 6b–e) for the injected carriers in both states [3]. (It must be noted that the trap depth of 1.0 eV well coincided with the energy distance between the $V_O$ and the CB edge in HfO$_2$-x [14]. Therefore, the trap positions of HfO$_2$-x layer occur near E$_c$ of Ta$_2$O$_5$ layer.)

When a small positive bias was applied to the Pt TE, a small amount of injected electrons, which tunneling from cathode to traps, were interfered with by the deep trap and transported through the HfO$_2$-x via hopping mechanism, so that the current flow under this circumstance must be much lower, as schematically shown in Fig. 6b. The observation of initially low current in Fig. 3b suggests that the deep trap levels were with the trap-empty configurations under low positive bias condition, which well coincided with the HRS. As the positive voltage increased, the carrier injection became higher and the energy band of electrolytes would be tilted further, so that traps started to be filled with major injected carriers, and the others would tunnel from Hf BE to the E$_c$ of HfO$_2$-x layer (F-N tunneling). Actually, the subsequent emission from traps to the E$_c$ of HfO$_2$-x layer is essentially

![Fig. 4](image)

**Fig. 4** a Distribution of the $I_{LRS}$ (at ±0.5 V) under DC sweeping mode for Device28 and b its retention property.

![Fig. 5](image)

**Fig. 5** a Schematic of data reading (V, V/2) and b comparison of calculated readout margins in $N \times N$ crossbar array integrating RRAM cells with and without self-rectifying behavior.
the Poole–Frenkel emission [15]. At the same time, the whole system switched to LRS (as indicated in Figs. 3b and 6c). The switching back from the LRS to HRS under the negative bias could be understood as follows.

After withdrawing the positive bias and applying a negative bias to the Pt TE, the electrons in the HfO$_2$-x traps started to detrap continually while the electron injection from the Pt TE was suppressed by the high Schottky barrier height. Fig. 6c shows the schematic diagram of this circumstance. When the traps became empty by the high negative bias, and bias was removed subsequently, the energy band diagram could be represented by Fig. 6e.

The most critical feature of the abovementioned switching mechanism is the change in the charge state of the electron traps, presumably VO with different oxidation states in HfO$_2$-x, not the variations in their local spatial distribution or concentration. Note that it is hopeful that improve the rectifying properties of our device if its active area can scaling further.

**Conclusions**

In summary, the RRAM device with ultralow operating current (<1 uA), sufficient ON/OFF ratio (~10$^5$), median operating voltages (<6 V), as well as excellent self-rectifying properties was prepared in a simple Pt/Ta$_2$O$_5$/HfO$_2$-x/Hf structure successfully. And satisfactory switching uniformity and retention performance are also demonstrated in it. In the stack, Ta$_2$O$_5$ layer works as a rectifier with high resistance and only slight oxygen deficiency, while HfO$_2$-x layer plays the role of the RS layer with more oxygen deficiency, lower dielectric constant, and higher energy band gap. These abovementioned merits manifest that the prototype Pt/Ta$_2$O$_5$/HfO$_2$-x/Hf devices could be used to effectively mitigate the sneak leakage in crossbar RRAM arrays.

**Acknowledgements**

The authors thank the Instrumental Analysis Center of Shanghai Jiao Tong University and Key Laboratory of Microelectronics Devices & Integrated Technology, Institute of Microelectronics of Chinese Academy of Sciences.

**Funding**

There is no funding source for this work.

**Authors’ Contributions**

HM and JF designed the experiments. HM and TG carried out the experiments. HM wrote the manuscript. JF and HL provided suggests for the experimental results analyzing and helped amend the manuscript. XX, QL, TG, and PY helped for the electrical tests and developed relevant analysis tools. All authors read and approved the final manuscript.

**Competing Interests**

The authors declare that they have no competing interests.

**Author details**

1Department of Micro/Nano Electronics, Key Laboratory for Thin Film and Micro Fabrication of Ministry of Education, Shanghai Jiao Tong University, Shanghai, China. 2Key Laboratory of Microelectronics Devices and Integrated Technology, Institute of Microelectronics, Chinese Academy of Sciences, Beijing, China.
References

1. Chang SH, Lee SB, Jeon DY, Park SJ, Kim GT, Yang SM, Chae SC, Yoo HK, Kang BS, Lee MJ, Noh TW (2011) Oxide double-layer nanocrossbar for ultrahigh-density bipolar resistive memory. Adv Mater 23:4063

2. Pan F, Gao S, Chen C, Song C, Zeng F (2014) Recent progress in resistive random access memories: materials, switching mechanisms, and performance. Mater Sci Eng RRep 83:1

3. Yoon JH, Song JS, Yoo JH, Seok JY, Yoon KJ, Kwon DE, Park TH, Hwang CS (2014) Highly uniform, electroforming-free, and self-rectifying resistive memory in the Pt/Ta2O5/HfO2/TiN structure. Adv Func Mater 24:5086

4. Li YT, Jiang XY, Tao CL (2013) A self-rectifying bipolar ram device based on Ni/HfO2/N(+)-Si structure. Modern Phys Lett B 28:389

5. Wang YF, Hsu CW, Wan CC, Wang IT, Lai WL, Chou CT, Lee YJ, Hou TH (2014) Homogeneous barrier modulation of Ta2O5/TiO2 bilayers for ultra-high endurance three-dimensional storage-class memory. Nanotechnology 25:165202

6. Kwong JY, Park JH, Kim TG (2015) Self-rectifying resistive-switching characteristics with ultralow operating currents in SiOxNy/AlN bilayer devices. Appl Phys Lett 106:223506

7. Michaelson HB (1977) The work function of the elements and its periodicity. J Appl Phys 48:4729

8. Song WD, Ying JF, He W, Zhuo YY-Q, Ji R, Xie HQ, Ng SK, Serene LG-NQ, Jiang Y (2015) Nano suboxide layer generated in Ta2O5 by Ar+ ion irradiation. Appl Phys Lett 106:031602

9. Kruchinin VN, Aliev VSH, Perevalov TV, Islamov DR, Gritsenko VA, Prosvirin IP, Cheng CH, Chin A (2015) Nanoscale potential fluctuation in non-stoichiometric HfOx and low resistive transport in RRAM. Microelectronic Eng 147:165

10. Tyapi P (2011) Ultrathin Ta2O5 film based photovoltaic device. Thin Solid Film 519:2355

11. Cho B, Song S, Ji Y, Lee T (2010) Electrical characterization of organic resistive memory with interfacial oxide layers formed by O2 plasma treatment. Appl Phys Lett 97:063305

12. Zeng W, Bowen KH, Li J, Dabkowska J, Gutowski M (2005) Electronic structure differences in ZrO2 vs HfO2. J Phys Chem A 109:11521

13. Lai BC-M, Kung NH-L, Lee J-Y-M (1999) A study on the capacitance–voltage characteristics of metal-Ta2O5–silicon capacitors for very large scale integration metal-oxide-semiconductor gate oxide applications. J Appl Phys 85:4087

14. Gavartin JL, Ramo DM, Shluger AL, Bersuker G, Lee BH (2006) Negative oxygen vacancies in HfO2 as charge traps in high-k stacks. Appl Phys Lett 89:082908

15. Wong H-SP, Lee HY, Yu S, Chen YS, Wu Y, Chen PS, Lee B, Chen FT, Tsai MJ (2012) Metal–oxide RRAM. Proc IEEE 100:1951