Supplementary Information for

Engineering Incremental Resistive Switching in TaO_x Based Memristors for Brain-inspired Computing

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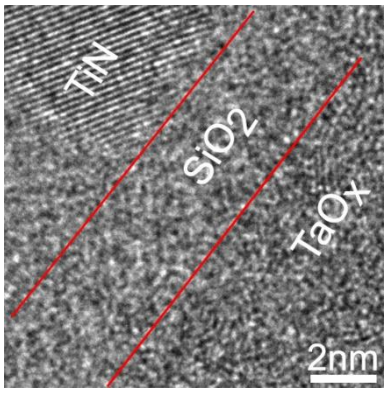

Fig. S1 HRTEM image of a TiN/SiO_2/TaO_x/Pt device. The nominal SiO_2 thickness was 4 nm.

Fig. S1 shows a HRTEM image of TiN/SiO_2-4nm/TaO_x/Pt device, where the TiN, SiO_2, and TaO_x layers can be clearly observed. The SiO_2 was found to have a denser microstructure compared with the TaO_x layer prepared by reactive sputtering. This microstructural attribute could lead to the retardation of oxygen diffusion in the SiO_2 layer. In addition, SiO_2 was reported to have a D_0 of 4.4 $\times 10^{-5}$–2.7 $\times 10^{-4}$ cm^2s^{-1} and an activation energy for diffusion (E_a) of 0.92–1.17 eV, corresponding to an oxygen diffusion constant (D) of 10^{-24}–10^{-20} cm^2s^{-1} at room temperature according to D =

$D_0\exp(-E_a/kT)$ (Refs. 31–33). This diffusion constant is 1–6 orders of magnitude lower than that in sub-stoichiometric TaO_x (Ref. 34). Therefore, the diffusion rate of oxygen ions is expected to decrease in SiO_2.

Figs. S2a–c exhibit the *I*–*V* characteristics of TiN/SiO_2/TaO_x/Pt devices with a SiO_2 thickness of 1, 2 and 4 nm, respectively. Before the reversible resistive switching can be obtained, the devices need to go through a high-voltage forming process, by sweeping the voltage to 5–6V, as shown in Fig. S3. This is different from the forming-free characteristic of TiN/TaO_x/Pt devices and can be due to the highly insulating nature of SiO_2. The reset current of TiN/SiO_2-4nm/TaO_x/Pt devices was unexpectedly increased compared with TiN/SiO_2/TaO_x/Pt devices with 1 and 2 nm SiO_2, which could be attributed to the current overshoot and uncontrolled filament growth in initial electroforming process. Such overshoot in current can be effectively mitigated by application of transient pulses, in agreement with the monotonously decreasing trend of device conductance when the SiO_2 thickness increases as shown in Figs. 4a,b.

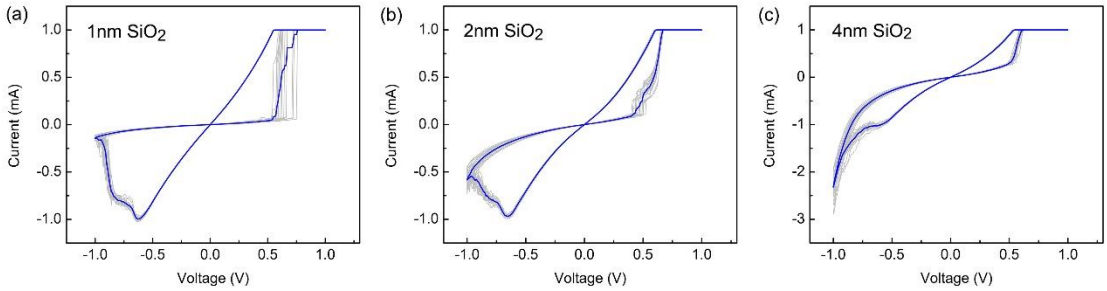

Fig. S2 20 consecutive *I*–*V* sweeps (gray) and averaged *I*–*V* curve (blue) of TiN/SiO_2/TaO_x/Pt devices with a SiO_2 thickness of (a) 1 nm, (b) 2 nm, and (c) 4 nm. 1 mA current compliance was adopted in the measurements to prevent hard breakdown.

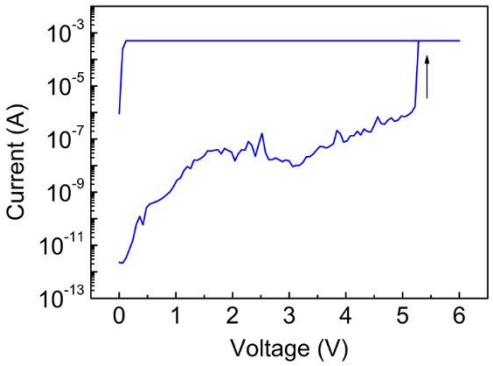

Fig. S3 A typical forming process in TiN/SiO_2/TaO_x/Pt devices, requiring a voltage of 5–6V.

Although a higher barrier is expected to exist at the TaO_x/Pt interface due to the higher work function of Pt (~5.5 eV) than TiN (~4.6 eV), this Schottky barrier could disappear and may not recover after the electroforming process due to irreversible accumulation of oxygen vacancies at the interface (Ref. S1), which is indeed the case for the TiN/SiO_2/TaO_x/Pt devices studied in this work. In order to verify this, Fig. S4 shows the *I*–*V* characteristics of the off state (–0.3~0.3 V) for TiN/SiO_2-1nm/TaO_x/Pt devices after forming. The repeatedly observed symmetric *I*–*V* characteristics imply the absence of Schottky barrier at the TaO_x/Pt interface. As a result, the resistive switching in the cell is likely to take place in the more stoichiometric and insulating SiO_2 layer that is in series with the sub-stoichiometric and more conductive TaO_x layer.

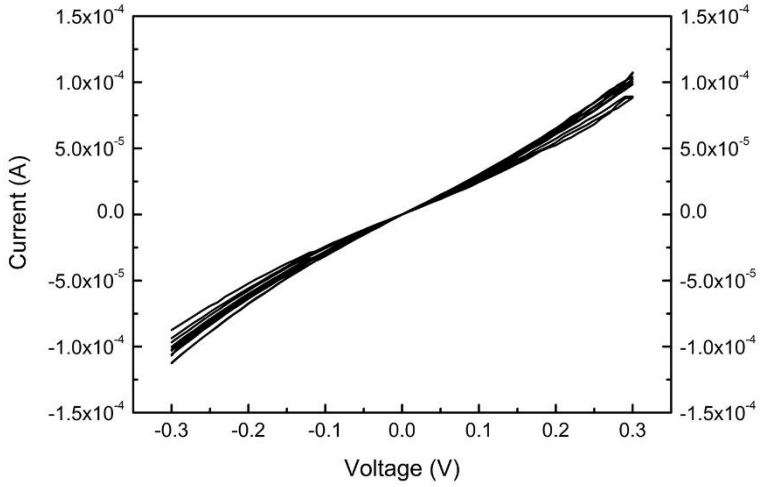

Fig. S4 *I*–*V* characteristics of the off state of 10 different TiN/SiO_2-1nm/TaO_x/Pt devices in the range of –0.3~0.3 V, where the devices have gone through forming.

The resistive switching in bilayer oxide based VCM cells is usually driven by the exchange of oxygen ions/vacancies, and as a result the switching polarity should be defined by the stacking sequence of the oxygen-rich and oxygen-deficient layers (Refs. S2-S5). This mechanism works typically for bilayer devices with two inert electrodes, where negligible redox reactions happen between the electrodes and the oxide, which is exactly the case for Refs. S2-S5. In the present case, however, TiN was used as the top electrode in TiN/SiO_2/TaO_x/Pt devices in order to make a fair comparison with the TiN/TaO_x/Pt control devices (Pt/TaO_x/Pt device was found to have a poor behavior due to its symmetric structure) so as to reveal the role of SiO_2 layer. Because TiN is a well-known oxygen reservoir material, the resistive switching in TiN/TaO_x/Pt devices should be driven

by the oxygen exchange and redox reactions between TiN and TaO_x, as widely reported in Refs. 24, 25 and S6 and in agreement with the switching polarity in Fig. 1 as well. Due to the coexistence of SiO_2/TaO_x oxide bilayer and TiN electrode, there are two competing switching mechanisms in $TiN/SiO_2/TaO_x/Pt$ devices, manifested as different switching polarities. Indeed, in addition to the switching polarity as shown in Figs. 3, 4 and S2, Figs. S5a–c show successful resistive switching with the opposite polarity in 3 different TiN/SiO_2-1nm$/TaO_x/Pt$ devices, whereas showing large fluctuations in both switching voltages and currents. Extensive measurements and comparisons have revealed that the switching behavior is more stable when the set/reset process is fulfilled by applying positive/negative voltage on TiN, as shown in Figs. 3, 4 and S2. When the applied voltage polarity is reversed, the switching uniformity is significantly affected, as can be seen from Fig. S5. Our study on incremental resistive switching was thus performed with the former switching polarity in consideration of its more reliable behavior.

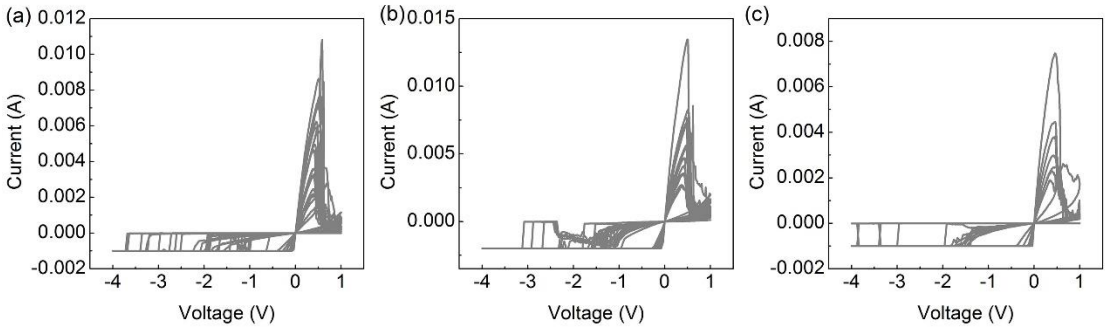

Fig. S5 Switching behavior of 3 different TiN/SiO_2-1nm$/TaO_x/Pt$ devices when the set/reset process is fulfilled by applying positive/negative voltage on Pt.

Fig. S6 shows the transient response of TiN/SiO_2-1nm$/TaO_x/Pt$ device using 1 V/20 ns set pulse and -1.5 V/20 ns reset pulse, demonstrating that the device can be successfully switched between the highest and the lowest conductance states within 20 ns, which is the resolution limit of our equipment. Compared with $TiN/TaO_x/Pt$ devices, the introduction of DLL has not significantly affected the operation speed of the devices, which suggests that the actual switching speed may be well below this time range and thus the influence of the DLL imposed on the operation speed was not reflected given the equipment capability.

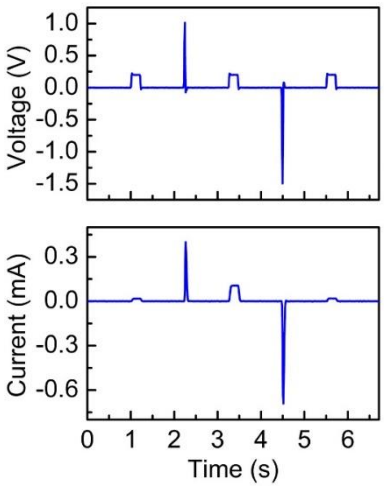

Fig. S6 Transient pulse measurements on TiN/SiO_2/TaO_x/Pt devices using 1 V/20 ns set pulse and –1.5 V/20 ns reset pulse, showing an operation speed of <20 ns.

Besides the operation speed, it was found that the device endurance was not significantly affected either after the introduction of SiO_2. We have performed endurance measurements on TiN/SiO_2/TaO_x/Pt device, and the results showed endurance up to 10^6, as shown in Fig. S7. This is a reasonably high value given the still not fully optimized switching current (~mA) of our devices. In fact, previous *in situ* TEM studies on a similar Pt/SiO_2/Ta_2O_{5-x}/TaO_{2-x}/Pt structure has shown that the resistive switching is enabled by the incorporation of tantalum oxide clusters in the SiO_2 layer during the forming process (Ref. 40), therefore implying the excellent performance of TaO_x-based memristors may be kept in the TiN/SiO_2/TaO_x/Pt devices.

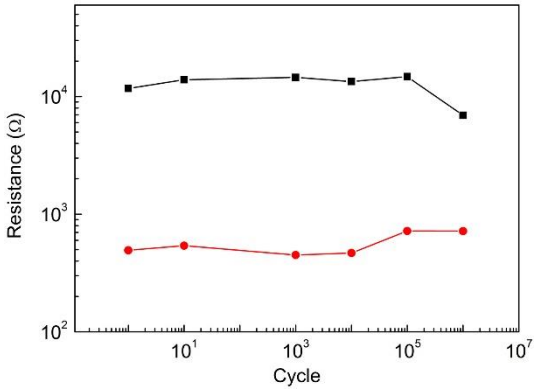

Fig. S7 Endurance test of TiN/SiO_2-1nm/TaO_x/Pt devices.

References

S1. J. -W. Yoon, J. H. Yoon, J. -H. Lee, and C. S. Hwang, Nanoscale 6, 6668 (2014).

S2. M.-J. Lee, C. B. Lee, D. Lee, S. R. Lee, M. Chang, J. H. Hur, Y.-B. Kim, C.-J. Kim, D. H. Seo, S. Seo, U. -I. Chung, I.-K. Yoo, and K. Kim, Nat. Mater. 10, 625 (2011).

S3. J. H. Hur, M. -J. Lee, C. B. Lee, Y. -B. Kim, and C. -J. Kim, Phys. Rev. B 82, 155321 (2010).

S4. Y. Yang, S. Choi, and W. Lu, Nano Lett. 13, 2908 (2013).

S5. Y. Yang, P. Sheridan, and W. Lu, Appl. Phys. Lett. 100, 203112 (2012).

S6. S. Y. Choi, M. K. Yang, S. Kim, and J. -K. Lee, Phys. Status Solidi RRL 4, 359 (2010).