Metal Cation Motion Induced Resistance Switching in Highly Reliable Hafnium Oxide based Memristive Devices

Hao Jiang[1], Lili Han[1,2], Huolin Xin[2] and Qiangfei Xia[1,*]
[1]Nanodevices and Integrated Systems Laboratory, Department of Electrical and Computer Engineering, University of Massachusetts, Amherst, MA 01003
[2]Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973
[*]Email: qxia@ecs.umass.edu

Memristive or also called resistive switching (RS) devices have attracted extensive interest because of their potential applications in the next generation nonvolatile memory and computing. Hafnium oxide is one of the most promising switching materials because of its CMOS compatibility and reliable performance even when scaled down to 10 nm [1]. Here, we developed a Ta/HfO_2/Pt memristive device that has low programming voltage, fast switching speed (≤ 5 ns), robust endurance (≥1.2×10^{11} cycles) and reliable retention (extrapolated to be >> 10 years at 85 °C). We directly observed the migration of Ta into the HfO_2 layer that formed a conduction channel. Our results suggest that although oxygen anions migration is widely considered as the switching mechanism for valence change memories (VCM) [2], reactive metal cations migration also plays an important role for the resistive switching.

Fig. 1a shows an optical image of the 10 × 10 μm^2 cross point structure used in this study. After photolithography, 1.5 nm Ti/20 nm Pt were deposited onto a SiO_2/Si substrate sequentially by electron beam evaporator, followed by lift-off. A 5 nm HfO_2 blanket layer was prepared by atomic layer deposition (ALD) at 250 °C. 50 nm Ta as the top electrode (TE) was defined by a second set of photolithography, metallization and liftoff. After electroforming, the device was brought to low resistance state (LRS). It can be reset to high resistance state (HRS) with a negative bias and set back to LRS with a positive bias. Fig. 1b shows 50 consecutive DC-sweep cycles with typical Vset and Vreset being about 0.65 and -1.10 V, respectively.

The device can also be switched reliably between HRS and LRS using 5 ns electrical pulses of 2.2 V for set and – 4 V for reset (Fig. 2a) (faster than 5 ns speed could be measured with a shorter pulse). We achieved over 1.2×10^{11} open-loop switching cycles with 100 ns pulses (1.3 V for set and – 3.05 V for reset, Fig. 2b). This is the highest reported endurance for a memristive device with a single oxide layer as the switching material. The device retained their resistance states (both LRS and HRS) after over one month without noticeable degradation at room temperature. We measured the retention properties at higher temperature and the extrapolated retention time is 3.7×10^4 years at 85 °C and beyond 10 years at 160 ºC (Fig. 2c). The retention of our Ta/HfO_2/Pt device is much better than that usually observed in other reported HfO_2 devices, while comparable to that for TaO_x devices. This strongly implies Ta cations have migrated into the HfO_2 layer and directly contributed to the formation of conduction channel(s).

To observe the metal migration and verify our hypothesis, we conducted scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) analyses for our Ta/HfO_2/Pt device. Fig. 3a shows the STEM image of a conduction channel identified around the deformation sites. The conduction channel is Ta-rich and O-deficient confirmed by EELS (Fig. 3b and c). We believe the switching is attributed to the channel composition modulation through motions of both Ta cations and O anions. The current work offers another dimension of device engineering to achieve desired electrical performance of memristive devices for different applications.

[1]. B. Govoreanu et al., in Proc. IEEE IEDM, 2011, pp. 730-732.
[2]. J. J. Yang er al., Nature nano, 2013, 8, 13.

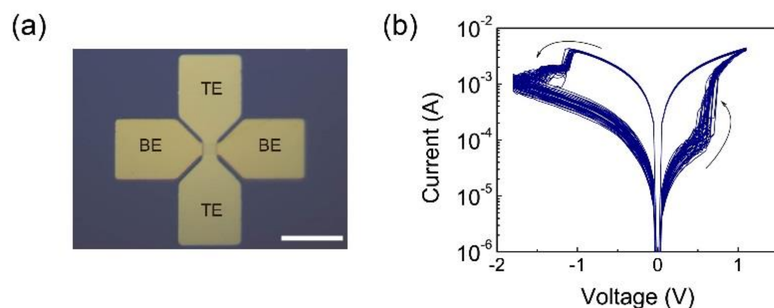

Figure 1. DC performance of the $Ta/HfO_2/Pt$ memristive devices. (a) An optical image of the 10 × 10 μm^2 cross point structure used throughout the studies. Scale bar: 50 μm. (b) I-V curves for 50 consecutive switching cycles after electroforming. The black arrows show the polarity.

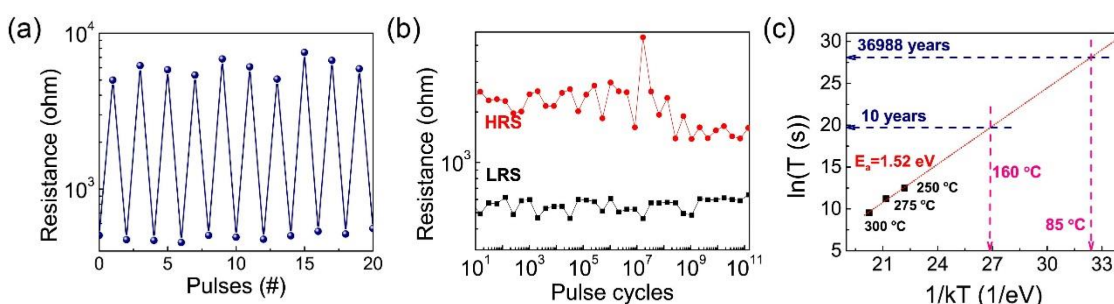

Figure 2. Fast switching speed, robust endurance and reliable retention of the $Ta/HfO_2/Pt$ memristive devices. (a) The device can be repeatably switched between HRS and LRS with 5 ns pulses (set: 2.2 V; reset: - 4 V) indicating faster than 5 ns switching speed. (b) 120 billion switching cycles have been demonstrated with pulses of 1.3 V/100 ns for set and - 3.05 V/100 ns for reset. (c) Retention time measured at 250, 275 and 300 ^{0}C. The dotted red line is the Arrhenius fitting which yields an activation energy 1.52 eV. The extrapolated retention time at 85 ^{0}C is 36988 years, and is 10 years even at 160 ^{0}C.

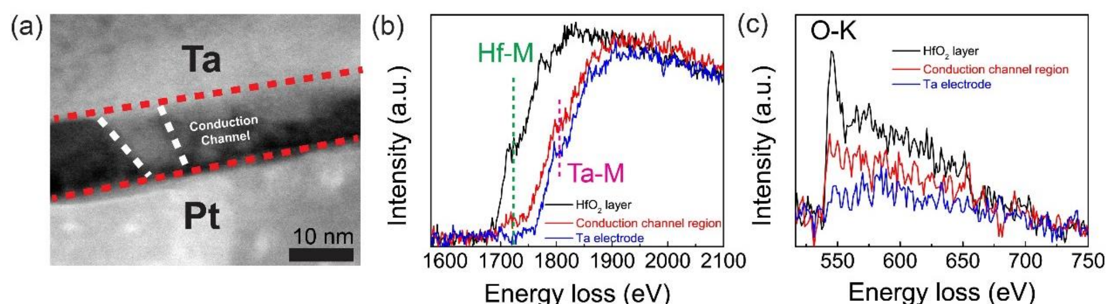

Figure 3. Direct observation of a Ta-rich and O-deficient conduction channel in the $Ta/HfO_2/Pt$ memristive device. (a) HAADF-STEM image shows a sub-10 nm conduction channel connecting Ta top and Pt bottom electrodes. The conduction channel is brighter in the image, which means it contains more atoms with large atomic numbers (Ta here). (b) Comparison of core-loss EELS spectra collected at the pristine HfO_2 layer, conduction channel region and Ta electrode. It indicates the conduction channel is Ta-rich. (c) O-K edge EELS spectra taken at three areas, which clearly show the conduction channel is also O-deficient.