Supporting Information

Memristors Based on (Zr, Hf, Nb, Ta, Mo, W) High Entropy Oxides

*Minhyung Ahn, Yongmo Park, Seung Hwan Lee, Sieun Chae, Jihang Lee, John T. Heron, Emmanouil Kioupakis, Wei Lu, Jamie Phillips**

M. Ahn and Y. Park contributed equally.

M. Ahn, Y. Park, Dr. S. H. Lee, W. Lu
Department of Electrical Engineering and Computer Science, University of Michigan, 1301 Beal Avenue, Ann Arbor, MI 48109-2122, USA
E-mail: jphilli@udel.edu

S. Chae, J. Lee, J. T. Heron, E. Kioupakis
Department of Materials Science and Engineering, University of Michigan, 2300 Hayward St, Ann Arbor, MI 48109-2117, USA

J. Phillips
Department of Electrical and Computer Engineering, University of Delaware, Newark, DE 19716, USA

Keywords: memristors, high entropy oxides, pulsed laser deposition, neuromorphic, first-principle calculations

1. XPS analysis of HEO thin film

In addition to the XPS spectra of Nb, Mo, and W core levels (**Figure 3**), the XPS spectra of the other three elements (Zr, Hf, and Ta) are presented in **Figure S**1. **Table S**1 lists the peak positions of the decomposed peaks and their line shapes used in XPS fitting analyzed by CASA XPS software. All spectra are calibrated to match the C 1s peak originated from adventitious carbon with 284.8 eV. The identified peaks agree with previous reports for Zr,[1] Hf,[2] Nb,[3] Ta,[4] Mo,[5] and W.[6] The analysis of the HEO film was especially challenging due to peak overlap from a large number of elements. The Nb 3d core level spectrum overlaps with the Hf^{4+} $4d_{5/2}$ peak. The Mo 3d core level spectrum overlaps with the Hf^{4+} $4d_{5/}2$ and the two Ta 4d peaks with 11.24 eV of spin-orbit coupling.[7] Possibly due to the large number of elements or the lattice distortion variance in the HEO thin film, the energy difference of the same type of peaks between the vacuum and 30 mTorr spectra are significant, 0.32 eV in Zr 3d spectra for instance, although the charge neutralizer of the XPS system was turned on.

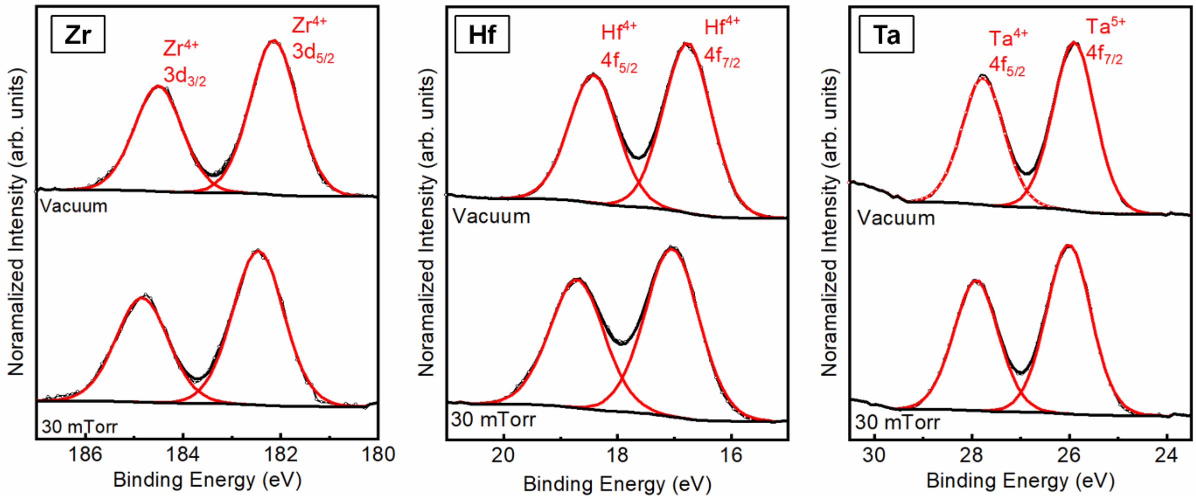

Figure S1. XPS spectra of HEO thin film deposited in a vacuum and in 30 mTorr of oxygen partial pressure.ore level spectra of Zr 3d, Hf 4f, and Ta 4f are presented.

Table S1. Peak positions and line shapes of the XPS spectraThe line shape denotes the assumed line shape and their command functions in CASA XPS software. The core levels with Δ_{so} indicate the fixed spin-orbit coupling energy were assumed during XPS fitting.

Core level	Line shape	Peaks	Vacuum (eV)	30 mTorr (eV)
Zr 3d	Gaussian-Lorentzian, GL(30)	Zr^{4+} $3d_{5/2}$	182.14	182.46
		Zr^{4+} $3d_{3/2}$	184.51	184.84
Nb 3d (Δ_{so} = 2. 75 eV)	Gaussian-Lorentzian, GL(30)	Nb^{5+} $3d_{5/2}$	206.95	207.10
		Nb^{4+} $3d_{5/2}$	205.07	205.18
		Hf^{4+} $4d_{5/2}$	212.96	213.35
Mo 3d (Δ_{so} = 3.1 eV)	Gaussian-Lorentzian, GL(30)	Mo^{5+} $3d_{5/2}$	231.75	232.10
		Mo^{4+} $3d_{5/2}$	228.63	228.60
		Ta^{5+} $4d_{3/2}$	241.23	241.40
		Ta^{5+} $4d_{5/2}$	229.99	230.16
		Hf^{4+} $4d_{3/2}$	223.77	224.02
Hf 4f	Gaussian-Lorentzian, GL(30)	Hf^{4+} $4f_{7/2}$	16.77	17.04
		Hf^{4+} $4f_{5/2}$	18.42	18.71
Ta 4f	Gaussian-Lorentzian, GL(30)	Ta^{4+} $4f_{7/2}$	25.90	26.01
		Ta^{4+} $4f_{5/2}$	27.77	27.91
W 4f (Δ_{so} = 2.17 eV)	Asymmetric Lorentzian, LA(1.33,2.44,69)	W^{6+} $4f_{7/2}$	35.34	35.40
		W^{4+} $4f_{7/2}$	31.90	32.33
		W $4f_{7/2}$	30.07	30.51
		W $5p_{3/2}$	40.07	41.07

2. Additional electrical characterization results of HEO-based memristors

The characteristics of memristors should be consistent with continuous set/reset DC switching. HEO-based memristors show good cycle-to-cycle characteristics by demonstrating 0.021 V of standard deviation in set voltage (**Figure S2**d) with low operation voltage (<1 V, **Figure S2**a and b). The memristors with the HEO thin film deposited in a vacuum shows less cycle-to-cycle variation compared to the in-oxygen deposited device. The resistive switching curve of Ta_2O_{5-x} based memristors with the same device structure except switching medium (Pd/Ta_2O_{5-x}/Ta/Pd) is presented in **Figure S2**c, presenting a higher forming voltage (1.5 V) than HEO-based memristors. **Figure S2**f shows excellent retention capability of HEO-based memristors by demonstrating the maintained resistivity state more than 20 hours at 100 ℃.

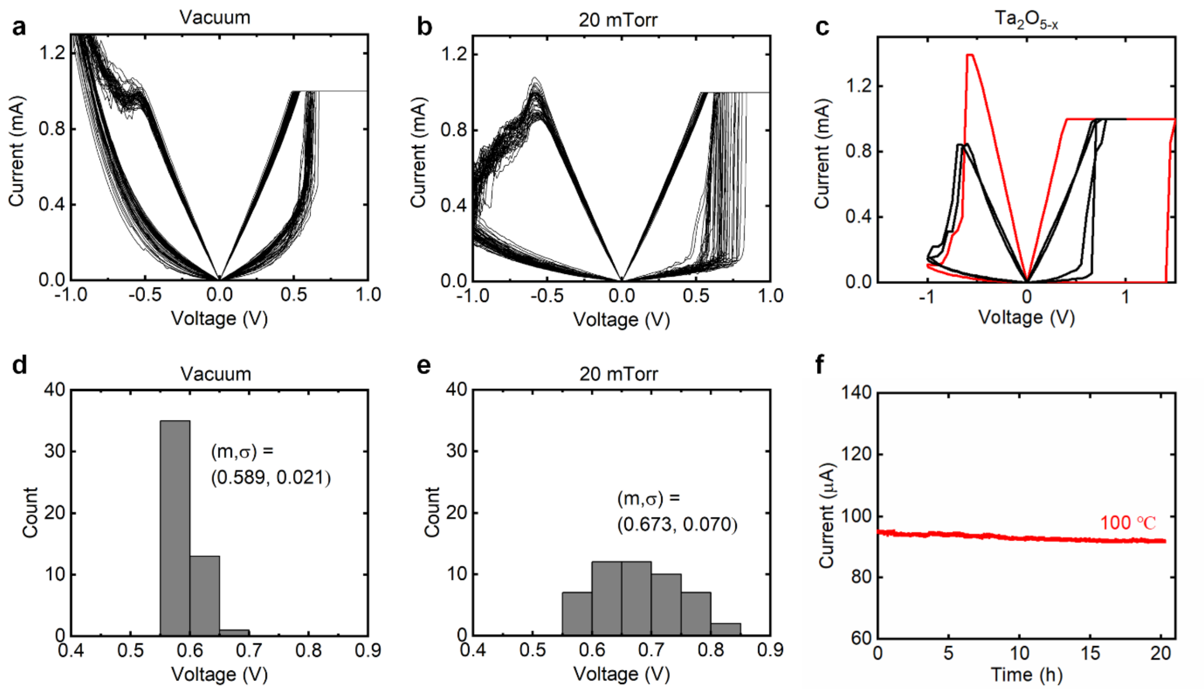

Figure S2. Overlapped resistive switching curves of 50 set/reset operations and corresponding histograms of the set voltages of HEO-based memristors where the thin film was deposited a, d) in a vacuum and b, e) in 20 mTorr of oxygen partial pressure. Mean (m) and standard deviation (σ) are presented in the figure. c) Forming and resistive switching curves of the memristors using Ta_2O_{5-x} as a switching medium. f) Long term retention test at 100 ℃. The memristor was set as LRS at the beginning and read by 0.05V of a read pulse for every 10 seconds. The measurement was intentionally stopped after 20 hours

3. Computational details

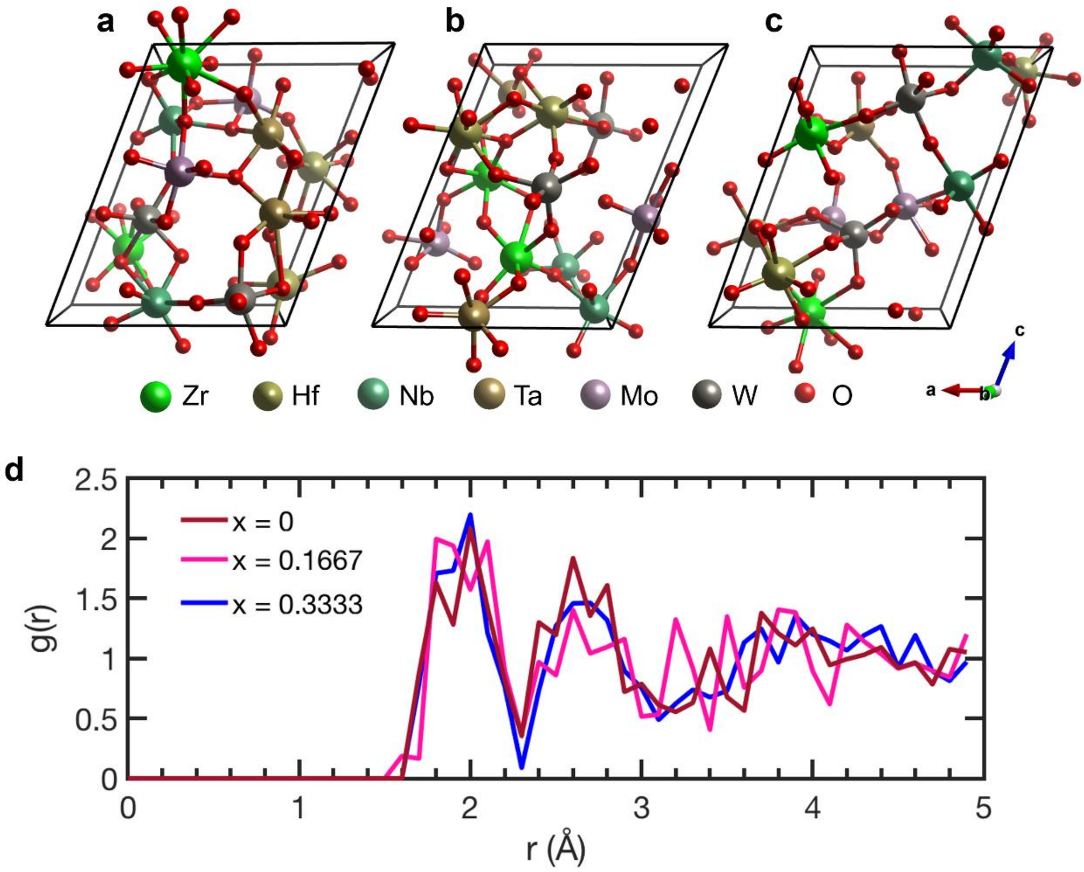

Figure S3. a-c) Crystal structures of amorphous (Zr,Hf,Nb,Ta,Mo,W)$_2$O$_{5-x}$ with a) x = 0, b) x = 0.1667, and c) x = 0.3333. d) Radial distribution function of the amorphous (Zr,Hf,Nb,Ta,Mo,W)$_2$O$_{5-x}$ with varied oxygen composition.

References

[1] Y. Mi, J. Wang, Z. Yang, Z. Wang, H. Wang, S. Yang, *RSC Adv.* **2014**, *4*, 6060.

[2] X. Luo, Y. Li, H. Yang, Y. Liang, K. He, W. Sun, H. H. Lin, S. Yao, X. Lu, L. Wan, Z. Feng, *Crystals* **2018**, *8*, 248.

[3] A. S. Trifonov, A. V Lubenchenko, V. I. Polkin, A. B. Pavolotsky, S. V Ketov, D. V Louzguine-Luzgin, *J. Appl. Phys.* **2015**, *117*, 125704.

[4] C. Mannequin, T. Tsuruoka, T. Hasegawa, M. Aono, *Appl. Surf. Sci.* **2016**, *385*, 426.

[5] J. Baltrusaitis, B. Mendoza-Sanchez, V. Fernandez, R. Veenstra, N. Dukstiene, A. Roberts, N. Fairley, *Appl. Surf. Sci.* **2015**, *326*, 151.

[6] F. Y. Xie, L. Gong, X. Liu, Y. T. Tao, W. H. Zhang, S. H. Chen, H. Meng, J. Chen, *J. Electron Spectros. Relat. Phenomena* **2012**, *185*, 112.

[7] F. Ji, J. P. Xu, Y. Huang, L. Liu, P. T. Lai, *IEEE Trans. Electron Devices* **2014**, *61*, 3608.