

## Supporting information

### Interface Engineered reliable HfO<sub>2</sub>-based RRAM for Synaptic Simulation

Qiang Wang<sup>1</sup>, Gang Niu<sup>1\*</sup>, Sourav Roy<sup>1</sup>, Yankun Wang<sup>1</sup>, Yijun Zhang<sup>1</sup>, Heping Wu<sup>1</sup>, Shijie Zhai<sup>1</sup>,  
Wei Bai<sup>1</sup>, Peng Shi<sup>1</sup>, Sannian Song<sup>2</sup>, Zhitang Song<sup>2</sup>, Ya-Hong Xie<sup>3</sup>, Zuo-Guang Ye<sup>4</sup>, Christian  
Wenger<sup>5</sup>, Xiangjian Meng<sup>6</sup>, Wei Ren<sup>1,\*</sup>

1. Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, School of Electronic Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China
2. State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences 865 Changning Road, Shanghai 200050 China
3. Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California 90095, United States
4. Department of Chemistry and 4D LABS, Simon Fraser University, Burnaby, British Columbia, V5A 1S6, Canada
5. IHP-Leibniz-Institut für innovative Mikroelektronik, Im Technologiepark 25, 15236 Frankfurt (Oder), Germany
6. National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai, 200083 China

Table. S1. O<sub>3</sub> -induced changes of area, max intensity and FWHM from TiN, TiON and TiO<sub>2</sub> spectra.

O 3	TiN (455.28 eV)			TiON (457.48 eV)			TiO <sub>2</sub> (458.58 eV)		
	Peak val.			Peak val.			Peak val. FWHM		
	cycles (a.u.Area) ×10 <sup>4</sup>	(a.u.) ×10 <sup>4</sup>	FWHM (eV)	(a.u.) Area ×10 <sup>4</sup>	(a.u.) ×10 <sup>4</sup>	FWHM (eV)	(a.u.) Area ×10 <sup>4</sup>	(a.u.) ×10 <sup>4</sup>	FWHM (eV)
0	5.49	1.78	2.29	2.56	0.85	2.84	2.78	2	1.29
10	5.04	1.64	2.29	3.68	1.22	2.84	3.71	2.58	1.33
20	3.06	0.99	2.29		3.13	1.04	2.84	4.45	3.1
40									1.33

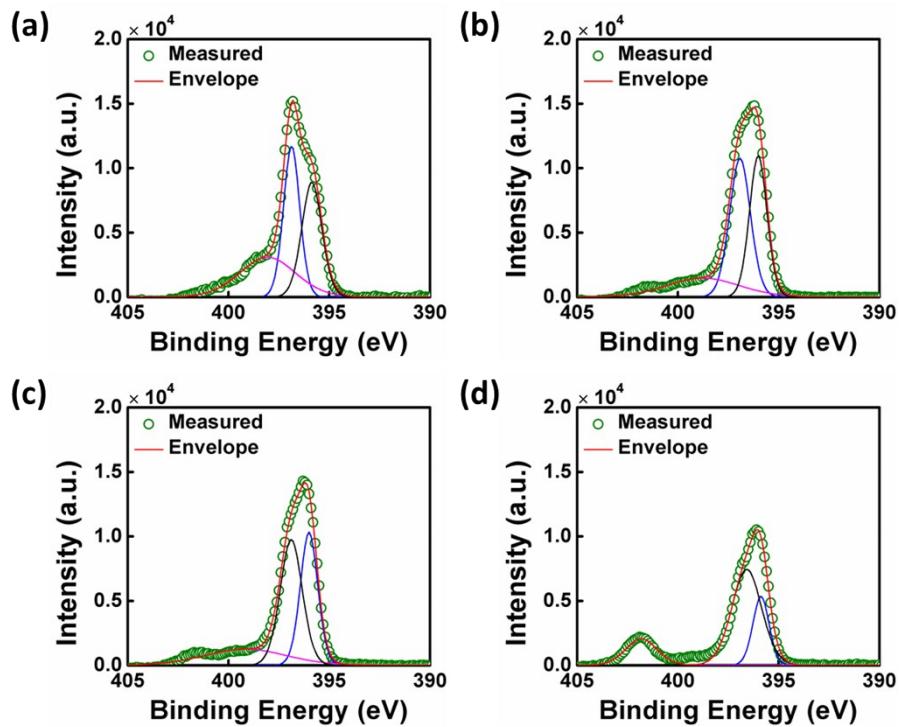


Fig.S1. N 1s spectra detected on the TiN surface with various O<sub>3</sub> treatment: (a) 0 O<sub>3</sub> Pulse, (b) 10 O<sub>3</sub> Pulses, (c) 20 O<sub>3</sub> Pulses and (d) 40 O<sub>3</sub> Pulses.

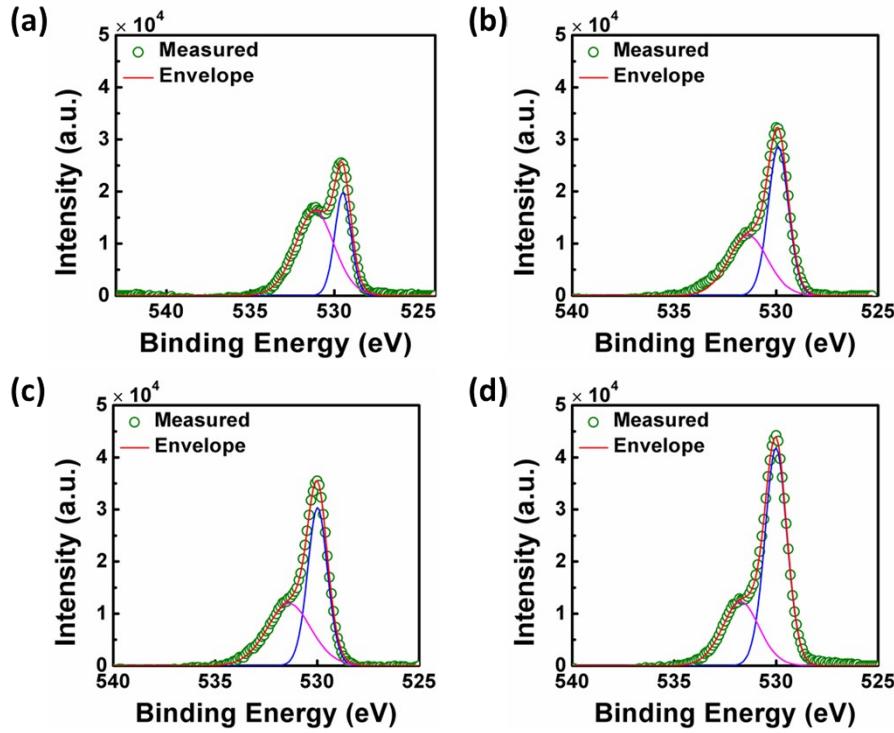


Fig.S2. O 1s spectra detected on the TiN surface with various O<sub>3</sub> treatment: (a) 0 O<sub>3</sub> Pulse, (b) 10 O<sub>3</sub> Pulses, (c) 20 O<sub>3</sub> Pulses and (d) 40 O<sub>3</sub> Pulses.

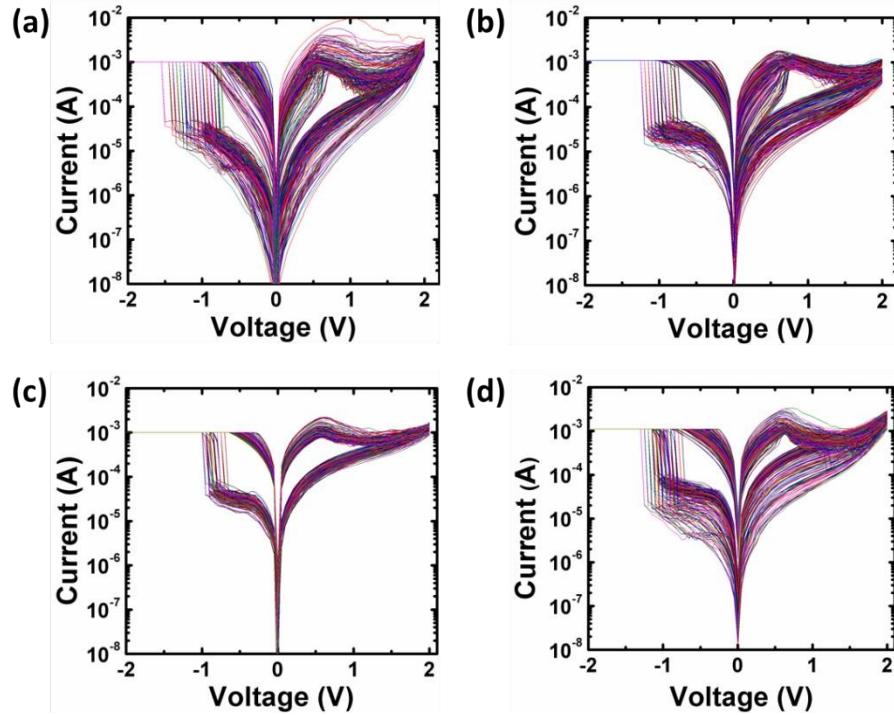


Fig.S3. 300 loops of I-V curves of proposed RRAM with different O<sub>3</sub> treatments: (a) 0 O<sub>3</sub> Pulse, (b) 10 O<sub>3</sub> Pulses, (c) 20 O<sub>3</sub> Pulses and (d) 40 O<sub>3</sub> Pulses.

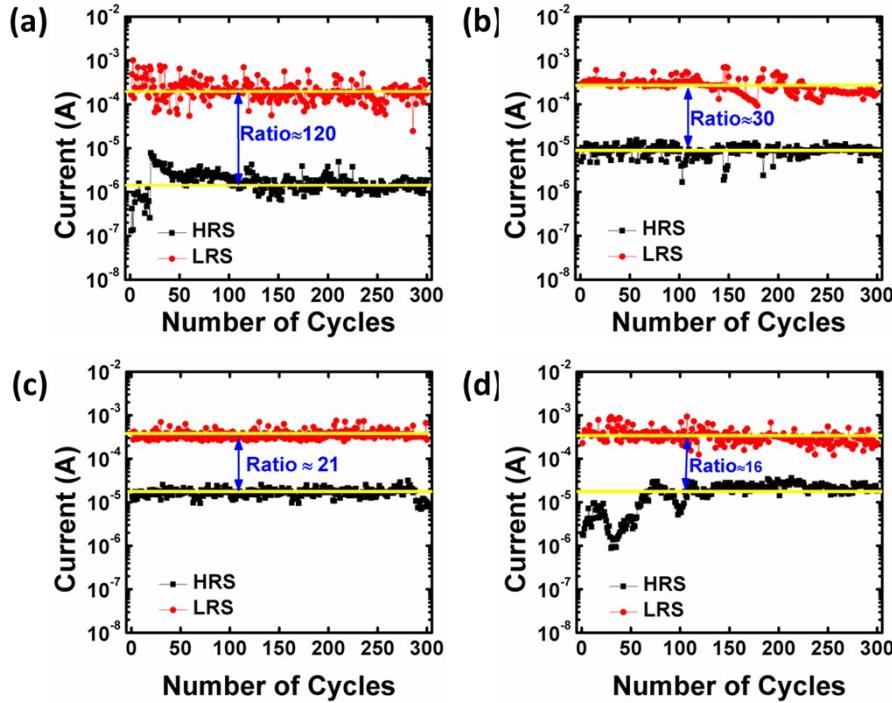


Fig.S4. DC endurance characteristics of proposed RRAM devices with the read voltage of -0.2 V: (a) 0 O<sub>3</sub> Pulse, (b) 10 O<sub>3</sub> Pulses, (c) 20 O<sub>3</sub> Pulses and (d) 40 O<sub>3</sub> Pulses.

Fig. S3 shows 300 loops of I-V curves collected in experiment. All samples are subject to the same test parameters: CC = 1mA, sweep voltage of -2 ~ 0 V/0 V ~ 2 V in Set/Reset process. Fig.S4 presents DC endurance characteristics of 0, 10, 20 and 40 O<sub>3</sub> Pulses, that 300 data are extracted from relevant 300 continuous I-V curves shown in Fig. S3. Obviously, it exhibits best stability and moderate ratio in case of 20 Pulses.

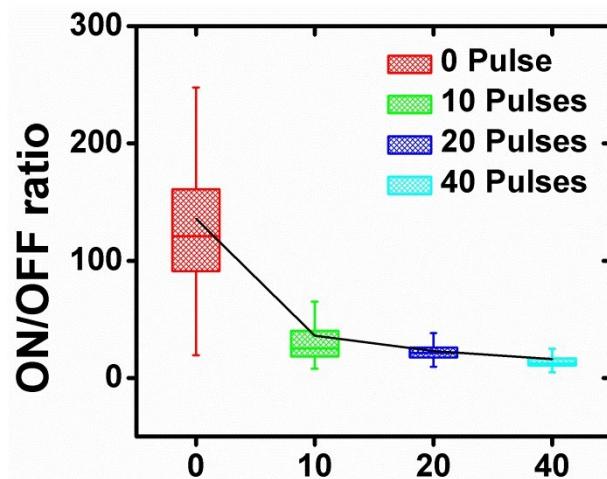


Fig.S5. ON/OFF ratio versus different pulses of O<sub>3</sub> treatment.

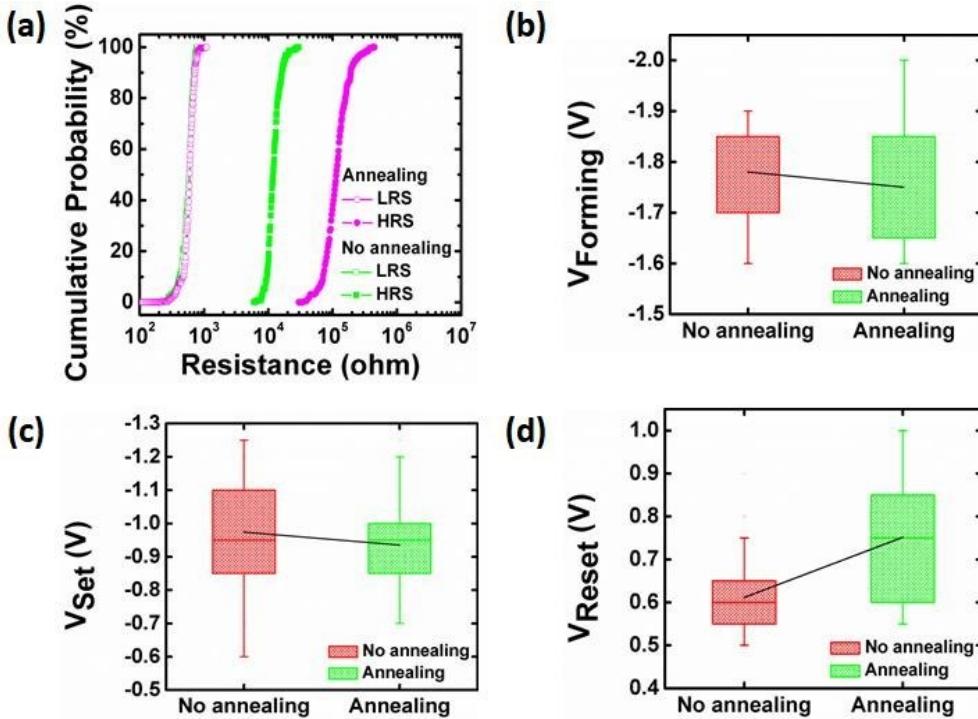


Fig.S6. Comparison of endurance characteristics between cases of annealed and non-annealed: (a) cumulative probability, (b)  $V_{\text{Forming}}$ , (c)  $V_{\text{Set}}$  and (d)  $V_{\text{Reset}}$ .

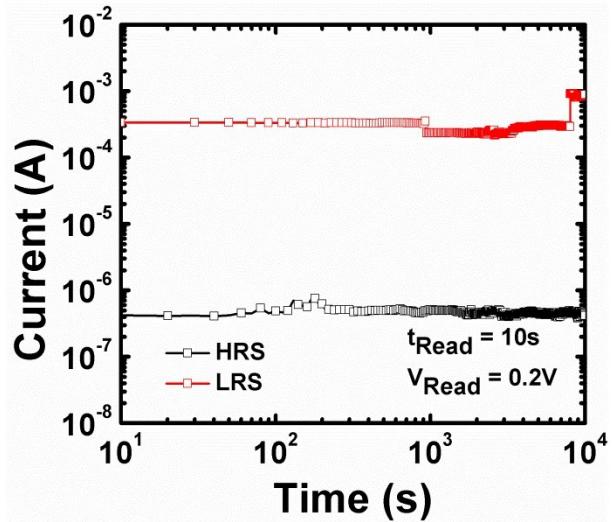


Fig.S7. DC retention of proposed RRAM, with the read voltage of 0.2 V and the interval of 10s.

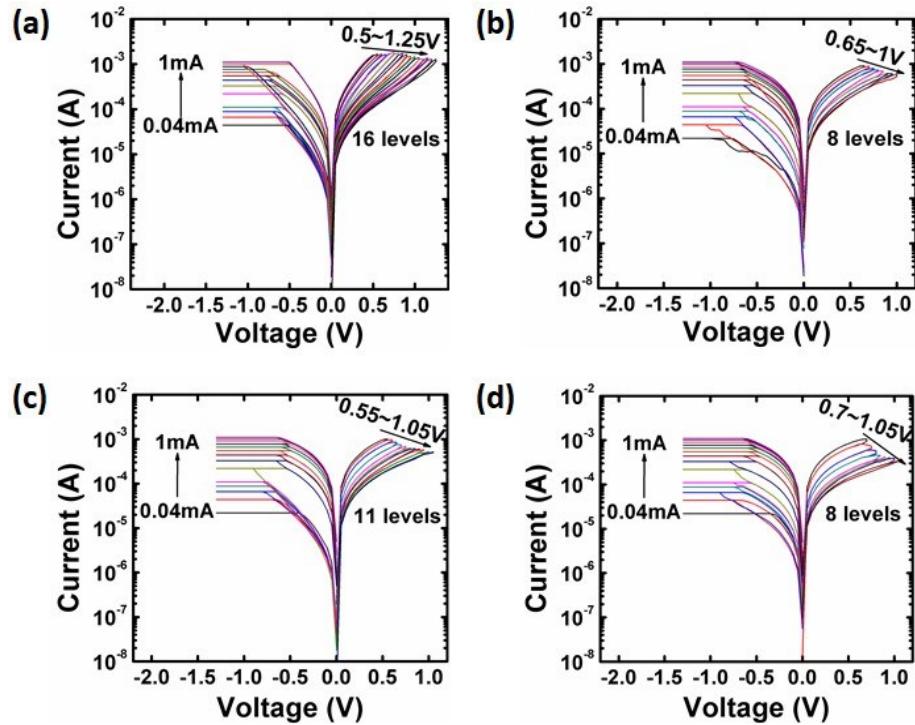


Fig.S8. Analog resistance of proposed RRAM devices in DC mode: (a) 0  $O_3$  Pulse, (b) 10  $O_3$  Pulses, (c) 20  $O_3$  Pulses and (d) 40  $O_3$  Pulses.