Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2023

Supplementary Material for

Modulating the resistive switching stability of HfO_2-based RRAM through Gd doping engineering: DFT+U

Dong-lan Zhang,[a] Jiong Wang,*[a] Qing Wu,[b] Yong Du[a]

[a] *State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China*

[b] *Information and Network Center, Central South University, Changsha, Hunan, 410083, China*

**E-mail*: wangjionga@csu.edu.cn

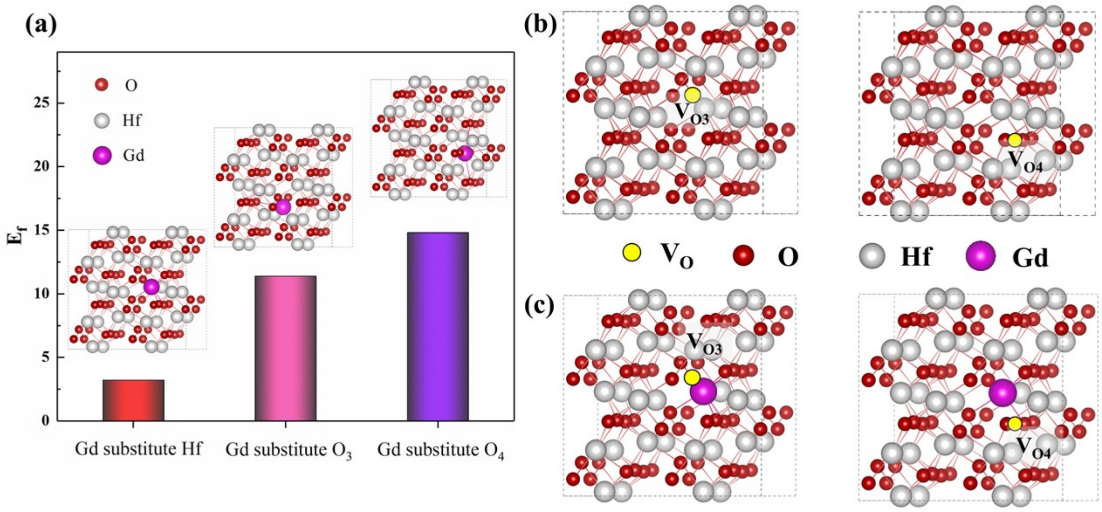

Fig. S1 (a) The doping formation energy of Gd-doped HfO_2 system and the configurations of HfO_2 with single V_O (b) before and (c) after Gd doping.

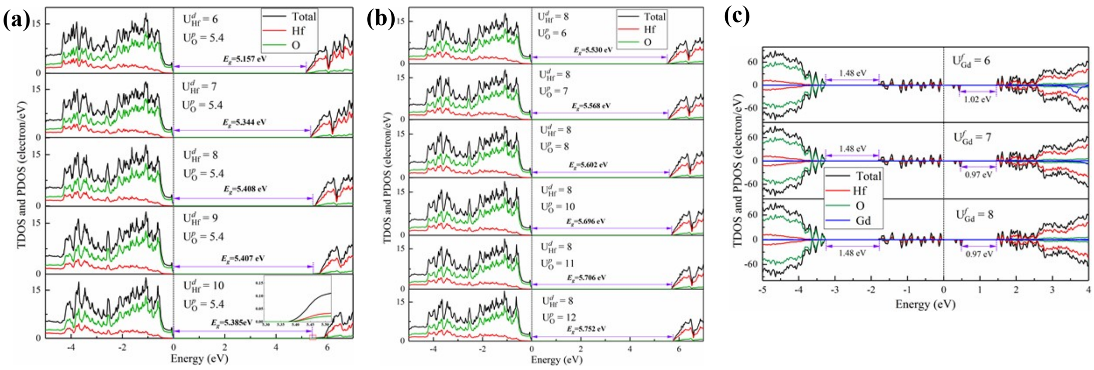

Fig. S2 The density of states calculated with (a) different U^d and a fixed U^p = 5.4 eV, (b) different U^p and a fixed U^d = 8 eV and (c) different U^f and a fixed U^d = 8 eV, a fixed U^p = 10 eV.

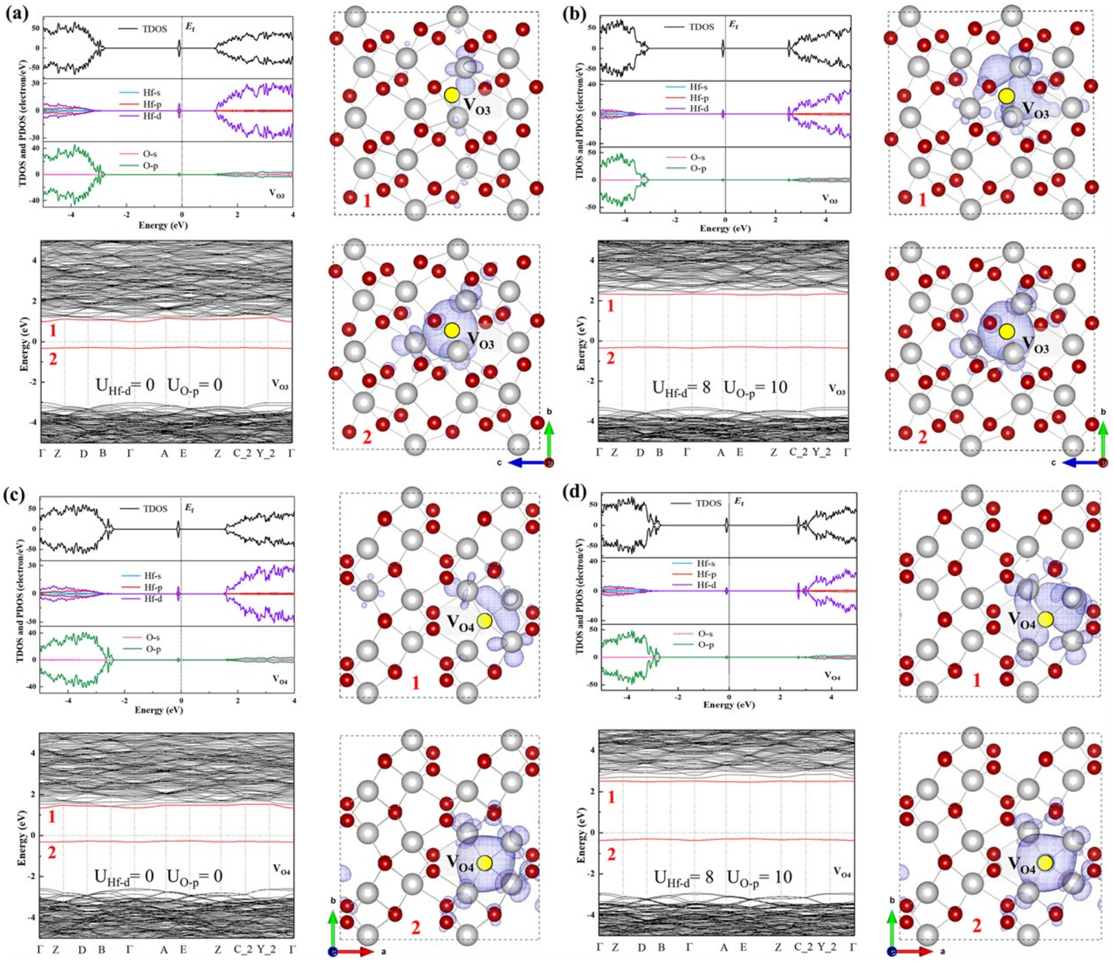

Fig. S3 The electronic structures of *m*-HfO_2 containing (a) and (b) single V_{O3} and (c) and (d) single V_{O4} before and after the applying U^d and U^p value.

To further analyse the changes in the characteristics of the chemical bonding before and after Gd doping, we have analyzed the electron localization function (ELF) distributions, as shown in Fig. S4 below. The ELF value is between 0 and 1, with the upper limit value ELF=1 meaning complete electron localization, the lower limit value ELF=0 meaning complete electron delocalization or no electron, and the middle value ELF=1/2 meaning the electron-gas-like pair probability. It can be seen from Fig. S4 that compared with perfect HfO_2 (Figs. (a) and (d)), when the system contains V_O (Figs. (b) and (e)), there will be obvious electron localization around the V_O, and when Gd is doped (Figs. (c) and (f)), the electrons are not only localized around the V_O, but also around the dopant Gd. There is an obvious charge interaction between Gd and its surrounding O atoms, with the Hf-O bond replaced by a Gd-O bond. The charge state of Gd and the surrounding O atoms also changes significantly compared to that before Gd doping, which will inevitably cause distortion of the local geometry, as shown in Fig. 4 in the manuscript. These results further indicate that Gd doping can cause local distortion of the geometrical configuration, strengthen the charge interaction between atoms, and improve the conductivity of the system.

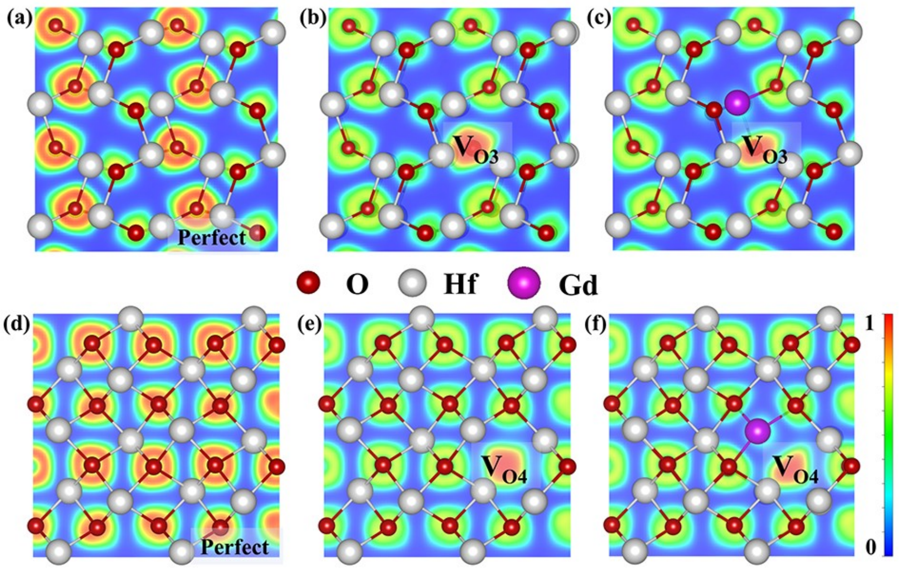

Fig. S4 Electron localization function (ELF) distributions of (a) and (d) perfect *m*-HfO_2, (b) *m*-HfO_2 containing single V_{O3}, (c) Gd-doped *m*-HfO_2 containing single V_{O3}, (e) *m*-HfO_2 containing single V_{O4}, and (f) Gd-doped *m*-HfO_2 containing single V_{O4}.

Table S1 Comparative analysis of the characterization for different metal-doped RRAM devices

Systems	Method	Generation of V_O	Randomicity of V_O formation	Migration barrier of V_O	Coulombic interaction	Stability of device
Gd-doped HfO_2	GGA[1]	↑	↓	—	↑	↑
Gd-doped HfO_2	GGA+U[2]	↑	—	—	↑	—
Gd-doped HfO_2	Exp.[3]	—	↓	↓	—	↑
Gd-doped Ta_2O_{5-x}	Exp.[4]	↓	—	↑	—	↑
Mg-doped HfO_x	Exp. and GGA-1/2[5]	↑	—	↑	—	↑
This work	GGA+U	↑	↓	↑	↑	↑

Meaning of symbols:

Vo represents oxygen vacancy; "↑" represents promotion (enhancement); "↓" represents suppression (reduction); "—"represents not clearly mentioned.

References

1 L. Wang, H. Tu, Y. Xiong, W. Xiao, J. Du, J. Wang and G. Huang, *J. Appl. Phys.*, 2014, **116**, 123505.

2 W. Zhang and Z. F. Hou, *J. Appl. Phys.*, 2014, **115**, 124104.

3 H. Zhang, L. Liu, B. Gao, Y. Qiu, X. Liu, J. Lu, R. Han, J. Kang and B. Yu, *Appl. Phys. Lett.*, 2011, **98**, 042105.

4 K. Shi, H. Xu, Z. Wang, X. Zhao, W. Liu, J. Ma and Y. Liu, *Appl. Phys. Lett.*, 2017, **111**, 223505.

5 L.-H. Li, K.-H. Xue, L.-Q. Zou, J.-H. Yuan, H. Sun and X. Miao, *Appl. Phys. Lett.*, 2021, **119**, 153505.