Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

10 MA/cm^2 Current Density in Nanoscale Resistive Threshold Switching Selector via Densely Localized Cation Sources

Qi Lin,[a] Jinlong Feng,[a] Junhui Yuan,[a] Long Liu,[a] Jason K. Eshraghian,[b] Hao Tong*[a], Ming Xu*[a], Xingsheng Wang,[a] Xiangshui Miao*[a]

[a] *Wuhan National Laboratory for optoelectronics, School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan, 430074, China.*

E-mail: tonghao@hust.edu.cn; mxu@hust.edu.cn; miaoxs@hust.edu.cn;

[b]*Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, 48109, USA.*

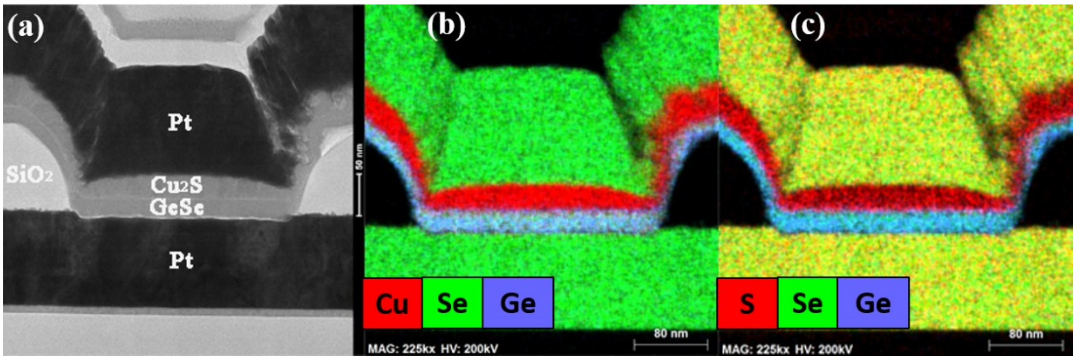

Figure S 1 20 nm GeSe switching layer and 25 nm thick Cu_2S cation layer are successively deposited into 250 nm diameter via hole.

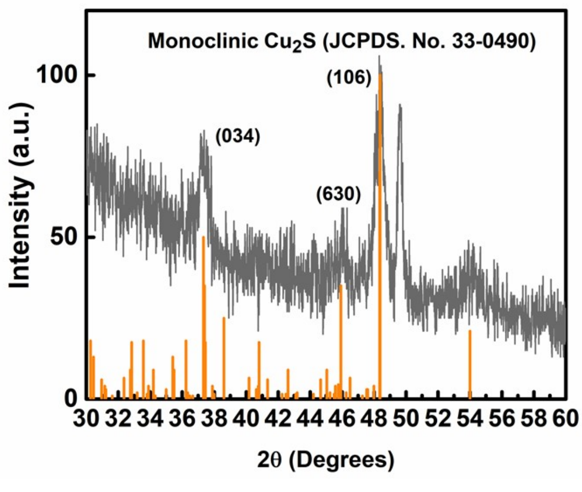

Figure S 2 The XRD pattern of as-deposited Cu_2S shows monoclinic lattice peaks.

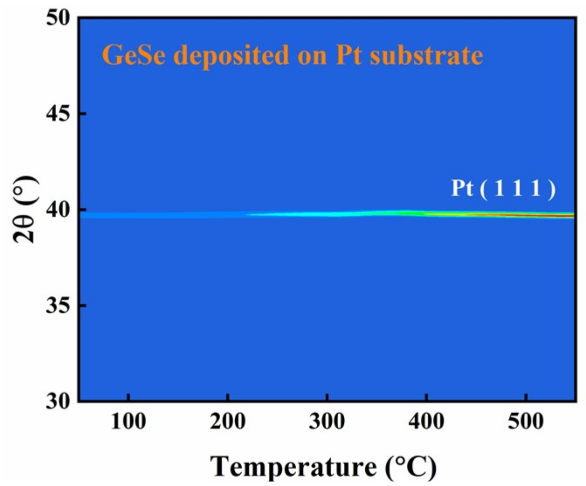

Figure S 3 In situ XRD of GeSe film indicates thermal stability over 550 ℃, compatible to BEOL process.

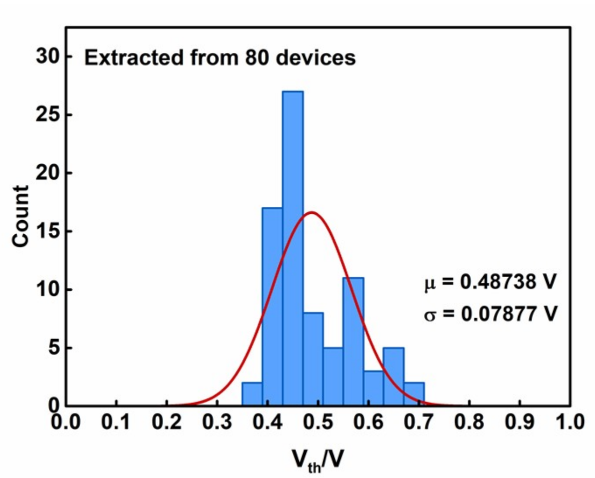

Figure S 4 The distribution of Vth extracted from 80 devices.

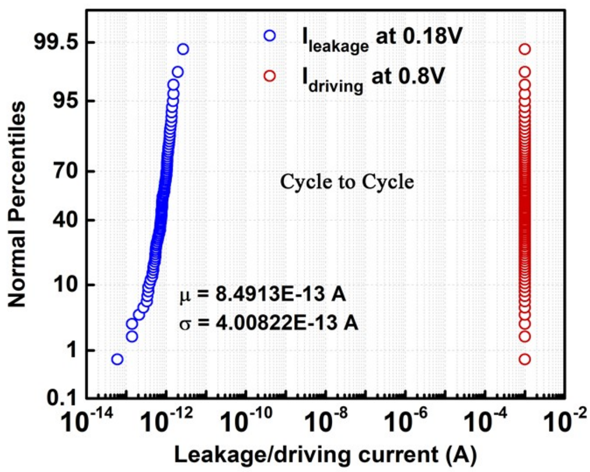

Figure S 5 The cumulative probability plot of HRS and LRS from cycle to cycle shows good leakage blocking and uniform on-state.

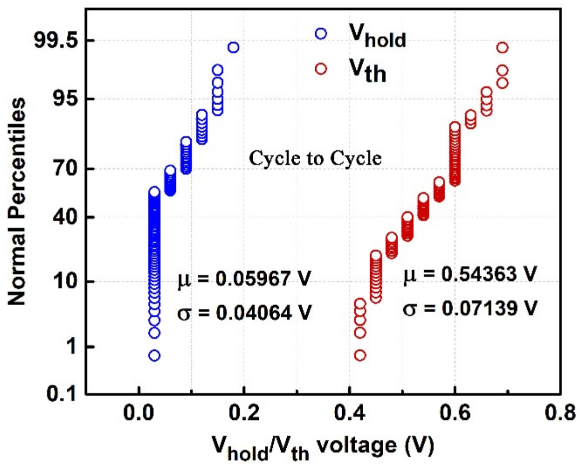

Figure S 6 The cumulative probability plot of V_{hold} and V_{th} from cycle to cycle indicates a large operating window.

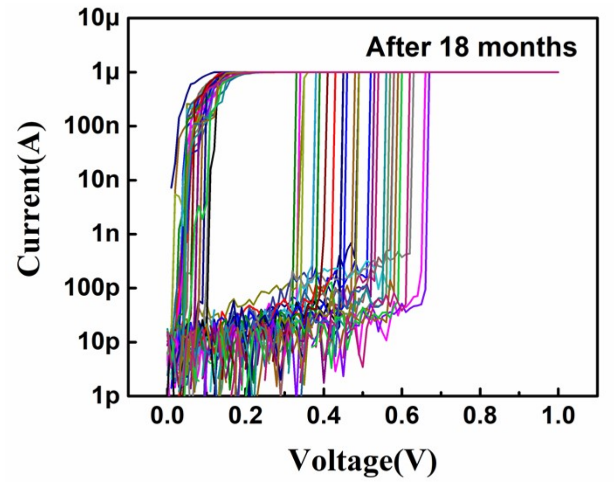

Figure S 7 The reliable switching of selectors after 18 months away from fabrication.

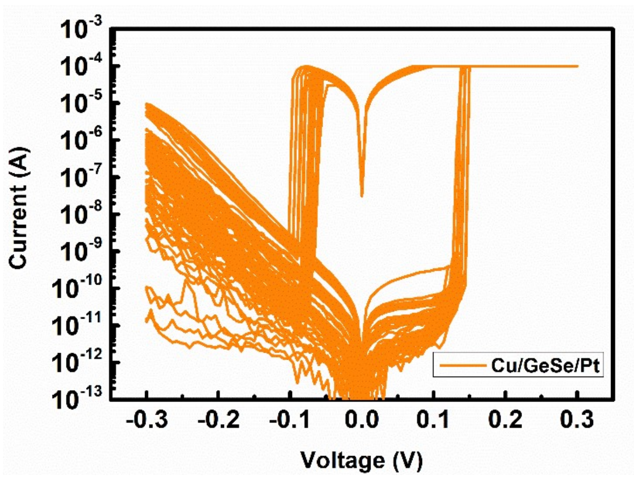

Figure S 8 Repeatable memory switching of Cu/GeSe/Pt devices under 100 μA I_{CC}.

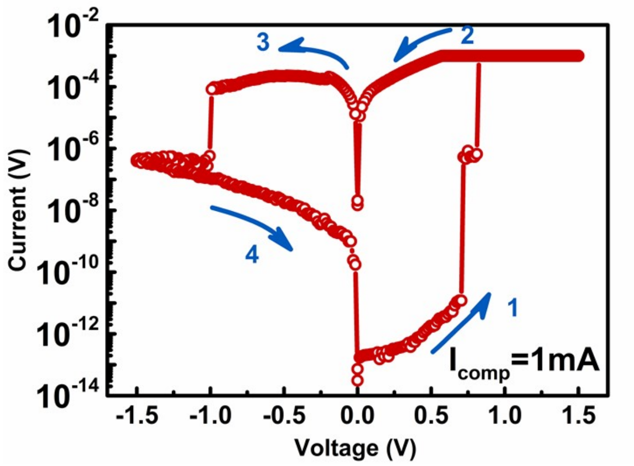

Figure S 9 Memory switching of Pt/CuS/GeSe/Pt devices at 1mA I_{CC}.

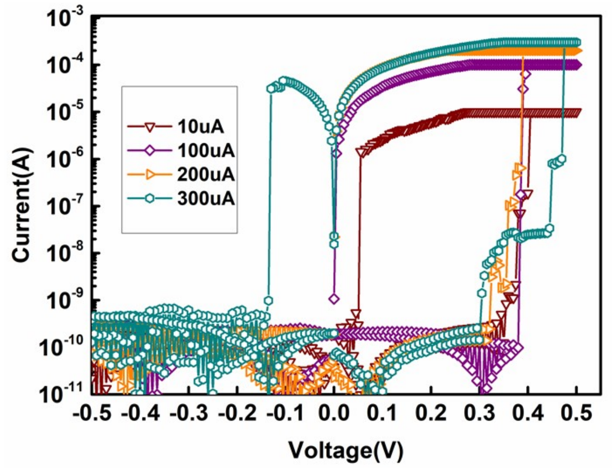

Figure S 10 Ag/GeSe switching behavior. The switching curve transit from TS to MS at 300 μA.

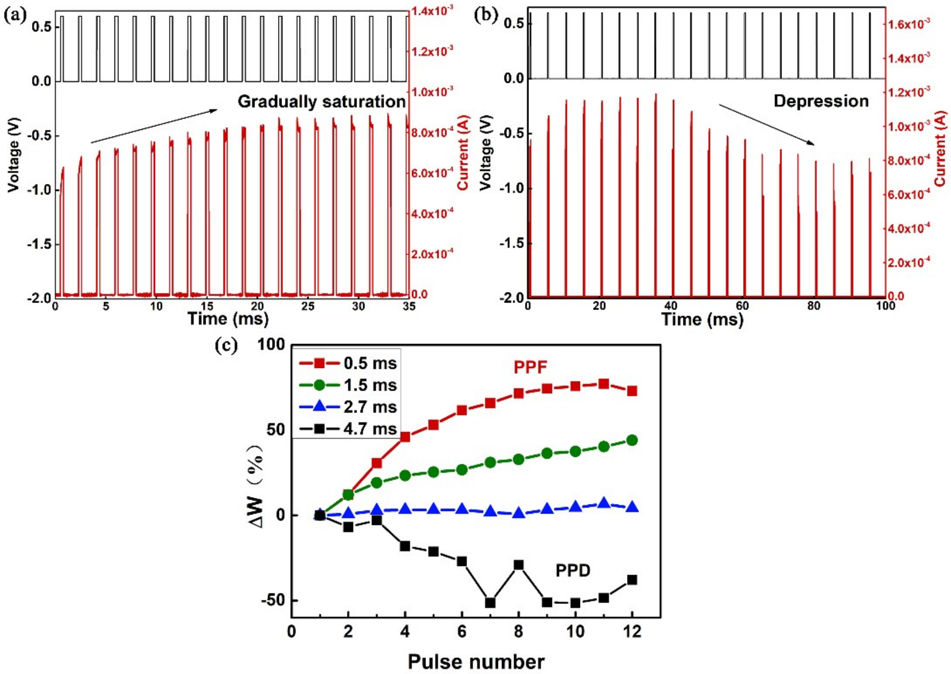

Figure S 11 The paired-pulse facilitation (PPF) and paired-pulse depression (PPD) of devices when swept at different pulse interval

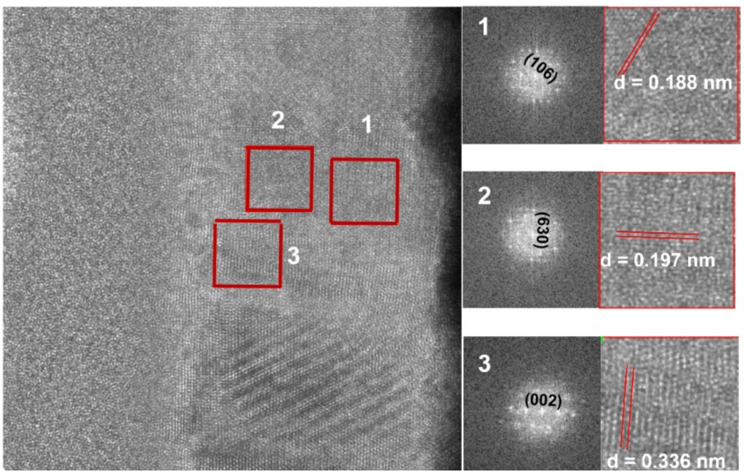

Figure S 12 Smaller grains at the areas surrounding nanocrystal channels.

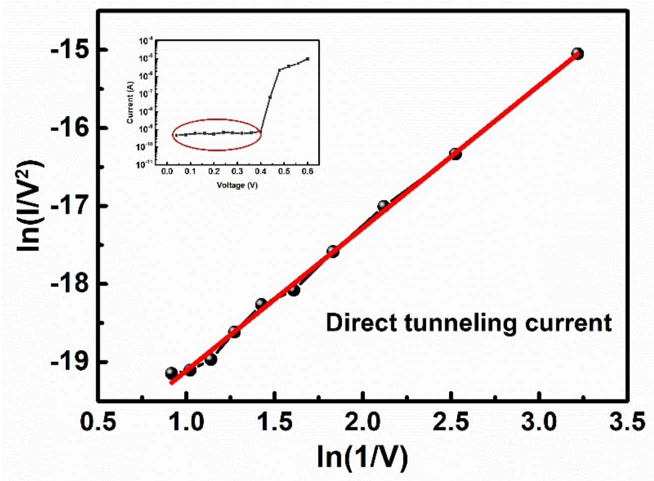

Figure S 13 Off-current fitting of the electrical annealing operations indicates a direct-tunneling conduction.

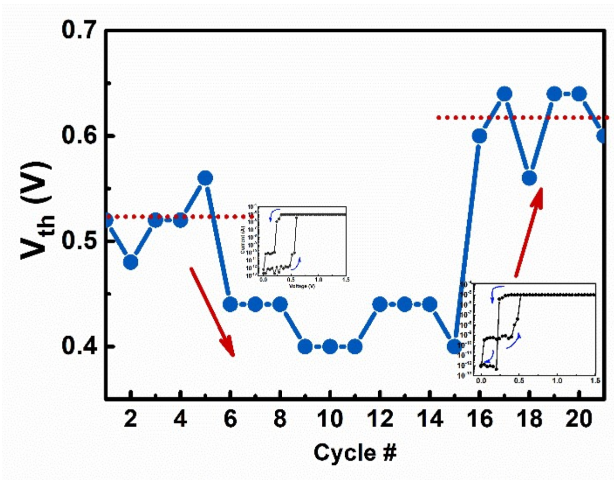

Figure S 14 V_{th} change during the electrical annealing operations, reflecting the barrier change along with filament residual growing and removement.

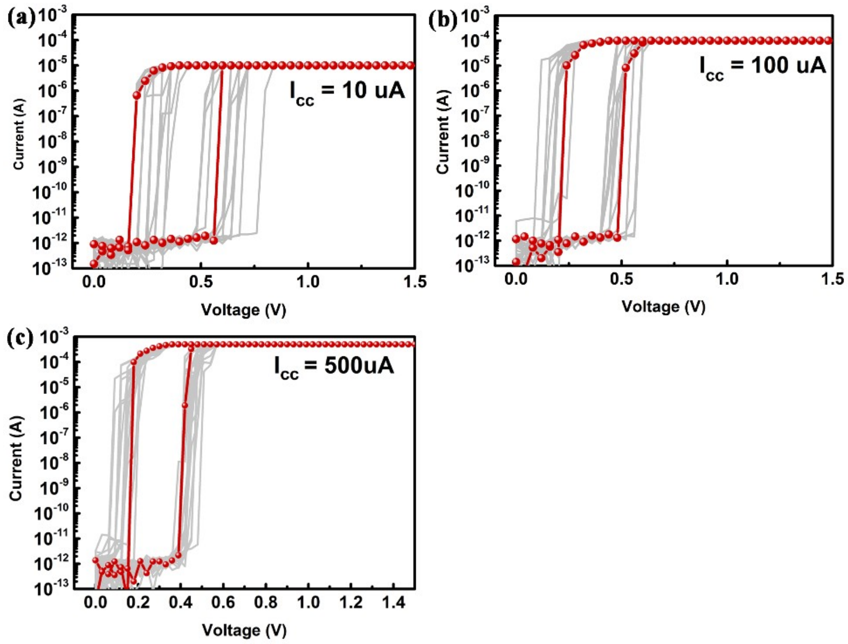

Figure S 15 IV characteristics of selectors at different $I_{cc.}$

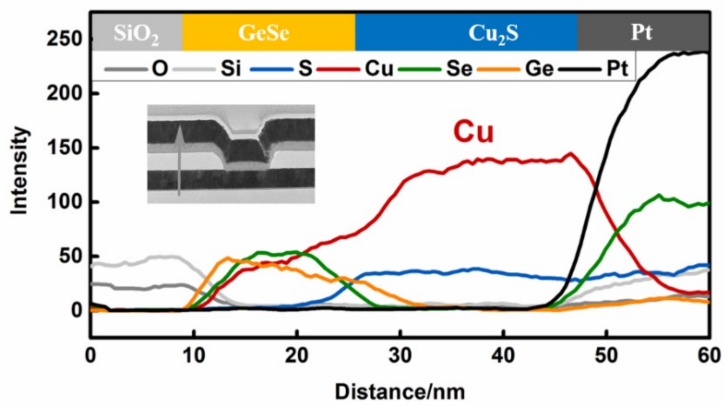

Figure S 16 The EDS line scan of non-via area shows progressively decreased Cu diffusion into GeSe, compared with highly concentrated copper in the middle of GeSe in via area.

Table SI: Thermal simulation parameters

	Pt	**Cu_2S [1-2]**	**GeSe [3]**	**Cu filament at 10 μA I_{CC}**
Electrical conductivity (S/m)	8.9e6	5.4e4	1e-3	2.88e7
Thermal conductivity (W/(m*K))	71.6	2.5	1.8	386.5
Heat capacity (J/(g*K))	0.133	0.63	0.329	0.385
Relative permittivity	1	19.14	15.3	1
Density (g/cm^3)	21.45	6.17	5.52	8.937
Diameter (nm)	100	100	100	0.256 0.768

Supple note for thermal simulation:

1. The model building

The model is built by three equations as attached below. The first one is to solve the electrical conductivity σ of CF by combining the measured IV curve in figure S18 and the real CF shape. The second one is the current continuty equations and the third one is the electromagnetic heating equation. The second and third equatons can be solved by given the electrical conductivity σ. This simulation flow has been described in other CF works [4].

Next we will illustrate the calculation process of σ in detail. First, the CF shape is built according to the relationship of low resistance state (LRS) conductance and atom contact area [5]. Second, the electrical conductivity σ is calculated by combining the measured IV curve and the shape of filament, as described in the following equation (1). Third, to keep the current and voltage consistent with the measured IV curve, a coefficient η is tuned, where η is the ratio of $(R_{Cu2S}+R_{CF})/R_{CF}$. This is because the calculated σ without η is contributed by both of Cu_2S and CF. In detail, the equations are as following:

Equation1:

The electrical conductivity calculation:

$$\sigma = \eta * (I/V) * (L/S)$$

I and V are extracted from the measured IV curve. L is the GeSe thickness and S is the contact area of CF with Cu_2S. η is the ratio of $(R_{Cu2S}+R_{CF})/R_{CF}$.

Equation2:

The current continuity equations:

$$\nabla \cdot \sigma \nabla \psi = 0$$

Equation3:

Electromagnetic heating equations:

$$-\nabla \cdot (k \nabla T) = J \cdot E = \sigma |\nabla \psi|^2$$

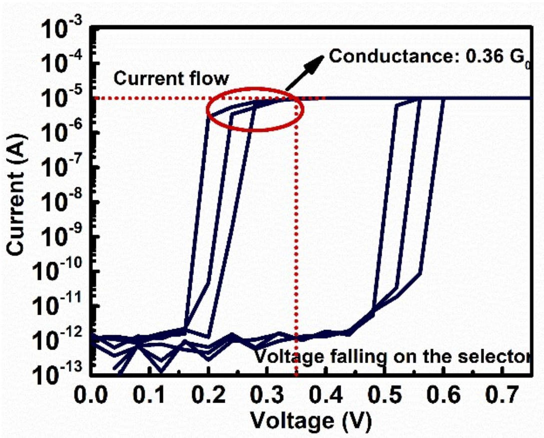

Figure S17 the measured IV curve

2. the boundary conditions

The top electrode (TE) of Pt is connected to a current source of 10 μA, while the bottom electrode (BE) of Pt is connected to the ground. The sidewalls are all set to be electrical isolated. The initial electric potentials of all domains are 0 V.

The temperatures of the upper surface of TE and bottom surface of BE are bounded to 300 k, the room temperature, since they are exposed to the air. The sidewalls are all set to be thermal isolated since they are surrounded by SiO_2. The initial temperatures of all domains are 300 K.

References:

[1] Q. Jiang, H. Yan, J. Khaliq, K. Simpson; M. J. Reece, Enhancement of thermoelectric properties by atomic-scale percolation in digenite Cu_xS, *J. Mater. Chem. A*, **2014**, *2*, 9486

[2] P. Qiu, Y. Zhu, Y. Qin, X. Shi, L. Chen, Electrical and thermal transports of binary copper sulfides CuxS with x from 1.8 to 1.96, *APL Mater.* **2016**, *4*, 104805.

[3] X. Zhang, J. Shen, S. Lin, J. Li, Z. Chen, W. Li, Y. Pei, Thermoelectric properties of GeSe, *J Materiomics* **2016**, *2*, 331-337.

[4] Kim, Sungho, et al. "Physical electro-thermal model of resistive switching in bi-layered resistance-change memory." Scientific reports 3.1 (2013): 1-6.
[5] F. Ducry et al., "Ab-initio modeling of CBRAM cells: From ballistic transport properties to electro-thermal effects", *IEEE International Electron Devices Meeting (IEDM)*, 2017, pp. 4.2.1-4.2.4