Science Bulletin 67 (2022) 1018–1021

Contents lists available at ScienceDirect

Science Bulletin

journal homepage: www.elsevier.com/locate/scib

www.scibull.com

Perspective

Halide perovskite single crystals for resistive switching

Shuaipeng Ge [a,b], Long-Biao Huang [a,*], Caofeng Pan [a,b,c,*]

[a] Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China
[b] CAS Center for Excellence in Nanoscience, Beijing Key Laboratory of Micro-nano Energy and Sensor, Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 101400, China
[c] School of Nanoscience and Technology, University of Chinese Academy of Sciences, Beijing 100049, China

As one of the most promising nonvolatile memory, resistive switching random-access memory (ReRAM) has exhibited great application potential for information storage and artificial synapses in computing and neuromorphic systems, and has shown great advantages including low power consumption, high integration density, simple device structure, and fast switching speed. Because of remarkable optoelectronic properties, halide perovskites as superstar materials have been intensively pursued in the fields of solar cells, light-emitting diodes, transistors, photodetectors and lasers etc. [1–3]. Especially, halide perovskites hold the ion migration and charge trapping effects which have attracted tremendous attention as dielectric layer for ReRAM applications in recent years. The studies of halide perovskites-based ReRAM are motivated by the hysteresis from forward and reverse scans of photovoltaic devices which reveal the feature of resistive switching. After the first report of halide perovskite with resistive switching behavior [4], the superiorities of simple and low-cost, unique current-voltage (*I*-*V*) hysteresis and excellent light-responsive characteristics in halide perovskites-based ReRAM are exploited. Expanded studies present many outstanding results, such as high ON/OFF ratio, robust endurance, long retention time, multilevel data storage, good mechanical flexibility, and light-modulated switching. Meantime, the studies of resistive switching mechanism are also performed, mainly including filamentary-type switching that the filaments are formed by active metal or halide vacancy, and interface-type switching which is dominated by the Schottky barrier between electrode and insulating layer.

Currently, according to the connectivity character of metal-halide (MX$_6$, M = Pb^{2+}, Sn^{2+}, Bi^{3+}, etc.; X = Cl, Br, I) octahedra, halide perovskite family can be classified into four structural dimensionalities including three-dimensional (3D), two-dimensional (2D), one-dimensional (1D) and zero-dimensional (0D) halide perovskites. 3D halide perovskites (AMX$_3$, A = Cs$^+$, CH$_3$NH$_3^+$, etc.) with cubic structure consist of corner-sharing MX$_6$ octahedra, filled A cations in 12-fold coordinated holes. Low-dimensional perovskites (2D, 1D, and 0D) generally own layered, chainlike and isolated MX$_6$ octahedra structure, respectively, and can be deemed as specific cuts or slices of the 3D structure. At the same time, halide perovskite family also could be classified into four main categories from the chemical compositions with organic–inorganic lead halide perovskites, inorganic lead halide perovskites, organic–inorganic lead-free halide perovskites, and inorganic lead-free halide perovskites.

Nowadays, 3D organic–inorganic lead halide perovskites and inorganic lead halide perovskites are more conventional materials for ReRAM. To overcome hygroscopicity of organic cations and high toxicity of lead, inorganic cations and nontoxic element substitution could be effective solutions. ReRAM based on inorganic lead-free halide perovskites, such as CsSnI$_3$-based and Cs$_2$AgBiBr$_6$-based devices have been preliminarily studied [5,6]. On the other hand, low-dimensional halide perovskite structures are more stable than 3D perovskites due to their loose size constraint of A cations. Low-dimensional structures generally possess high intrinsic resistivity original form the isolated nature of octahedral complex which is beneficial for improving device ON/OFF ratio by suppressing OFF current. Therefore, low-dimensional halide perovskites-based ReRAM recently also attract considerable research, such as 0D Cs$_3$Bi$_2$I$_9$-based and quasi-2D (PEA)$_2$Cs$_3$Pb$_4$I$_{13}$-based devices [7,8]. Both of them exhibit stable resistive switching with ultrahigh ON/OFF ratio that can be used to avoid information misreading and enhance the capacity of multilevel storage in ReRAM.

However, most of halide perovskite films for ReRAM are polycrystalline films as dielectric layers for resistive switching, thanks to the simple fabrication process of polycrystalline films by precursor preparation, spin-coating and low-temperature treatment. Polycrystalline halide perovskite films, especially 3D organic–inorganic and inorganic lead halide perovskites with defect-plagued grain boundaries, are usually unstable in ambient conditions resulting in the degradation of device performances. Additionally, great amount of grain boundaries can also generate large leakage current and operating current leading to high power consumption in polycrystalline halide perovskites-based ReRAM. In contrast, monocrystalline halide perovskites without grain boundaries and pinholes, have presented superior intrinsic properties, such as enhanced stability and improved carrier mobilities, and affirmatively offered an ideal platform to investigate the ultimate resistive switching properties. In fact, halide perovskite single crystals have

---

* Corresponding authors.
E-mail addresses: huanglb@szu.edu.cn (L.-B. Huang), cfpan@binn.cas.cn (C. Pan).

https://doi.org/10.1016/j.scib.2022.02.001

been explored extensively for applications in transistors and photodetectors etc., but few about resistive switching studies so far. Here, we summarize and discuss the recent advances of resistive switching of halide perovskite single crystals.

Among of halide perovskite single crystals, 3D organic–inorganic lead halide perovskite single crystals are more prevailing for optoelectronic devices. In the field of ReRAM, 3D $CH_3NH_3PbBr_3$ perovskite single crystal also has been reported for resistive switching as shown in Fig. 1a [9]. The bulk perovskite single crystals were prepared by inverse temperature crystallization method, and further applied to manufacture Ag/single crystal/Ag device. With recurrent voltage sweep, negative differential resistance (NDR) effect known as the decrease of current with increasing voltage, was observed at both voltage polarities. Interestingly, by carrying out the switching measurements at elevated temperatures, the NDR behavior was eliminated and replaced with small hysteresis window of bipolar switching. Notably, quantum dots embedded perovskite single crystals were also synthesized and exhibited enhanced ambient stability and resistive switching performance in $CH_3NH_3PbBr_3$ perovskite single crystal-based device. The resistive switching behavior was dominated by the migration of Ag ion and the formation of Ag filaments. In addition, the resistive switching behaviors of $CH_3NH_3PbBr_3$ perovskite single crystal were also reported by Xing et al. [13] and Ke et al. [14], and exhibited voltage-regulated multi-resistance states and switchable diode-like behavior, attributing to the charge trapping/de-trapping mechanism and trap-controlled space-charge-limited conduction (SCLC) mechanism, respectively.

Except for 3D organic–inorganic lead halide perovskites, the resistive switching of 3D inorganic lead halide perovskite ($CsPbBr_3$) single crystal also has been investigated [10]. The planar Ag/single crystal/Ag device was fabricated by single crystal self-assembled in liquid phase, and presented bipolar resistive switching behavior (Fig. 1b), accompanied with low power of $\sim 3 \times 10^{-8}$ W, ON/OFF ratio up to 10^3, data retention time about 10^3 s and switching endurance over 400 cycles. Studies of light-responsive resistive switching are meaningful for multifunctional memory, herein, the characteristics of light intensities modulated set and reset voltages were obtained in $CsPbBr_3$ single crystal-based device, ascribing to the photogenerated electron-hole pairs induced additional internal electrical field that facilitated the formation of Ag and Br vacancies conductive filaments.

Low power consumption is one of the most essential features of ReRAM. Ren and co-workers [11] reported resistive switching behavior based on exfoliated 2D $(PEA)_2PbBr_4$ (PEA, phenethylammonium) perovskite single crystal layers (Fig. 1c). Extremely low operating currents down to 10 pA were achieved that maybe related to the 2D perovskite structure of anisotropic charge transport with suppressed out-of-plane direction, indicating the potential for low-power ReRAM applications. The perovskite single crystal layers were obtained by exfoliating bulk single crystals which were synthesized by an antisolvent vapor-assisted crystal-

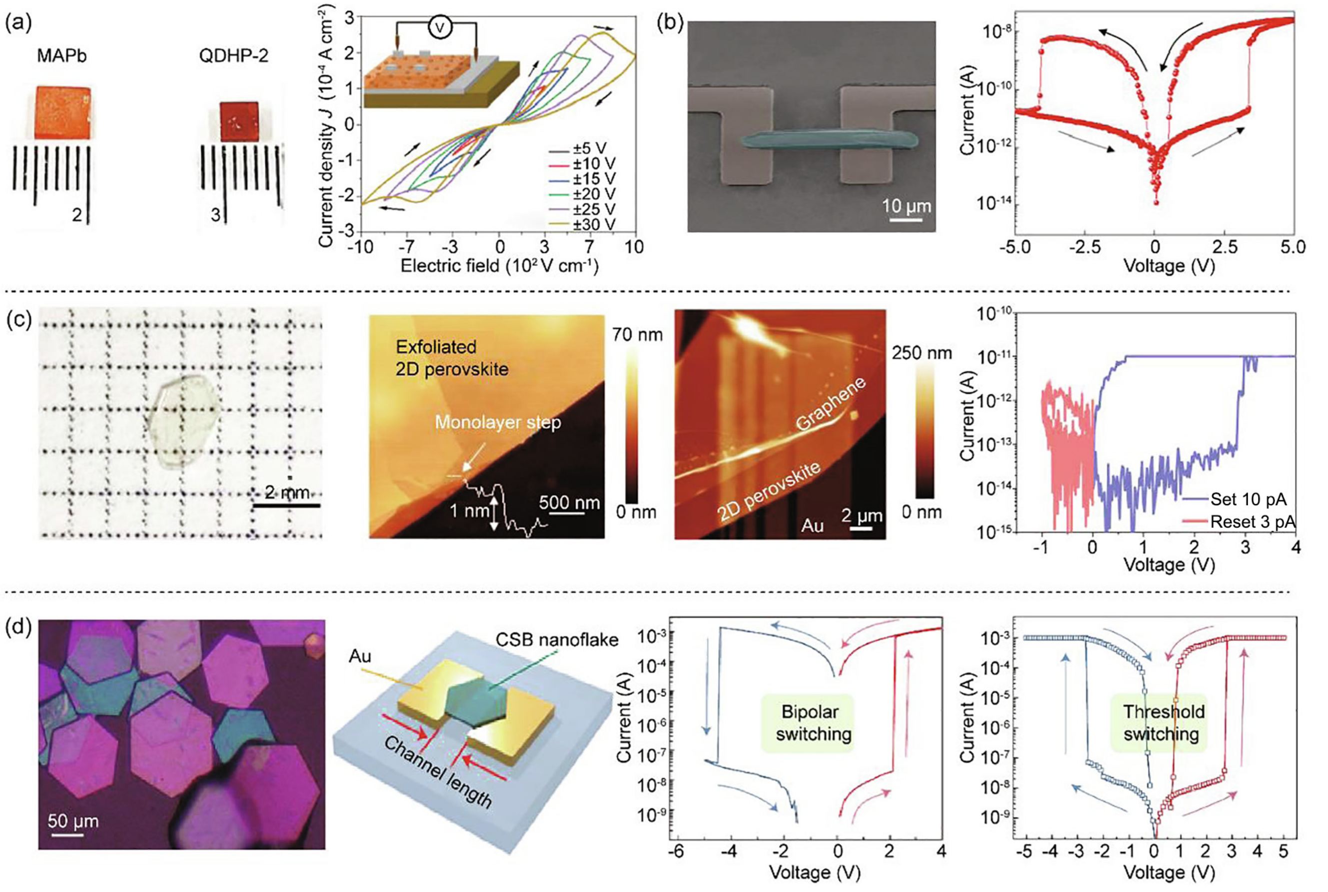


Fig. 1. (Color online) Resistive switching of halide perovskite single crystals. (a) Optical images of pure and quantum dots embedded $CH_3NH_3PbBr_3$ single crystals, and *I-V* curves at various sweep ranges for $CH_3NH_3PbBr_3$ single crystals-based device. Reprinted with permission from Ref. [9], Copyright © 2020 Wiley-VCH. (b) Scanning electronic microscopy image of the $CsPbBr_3$ perovskite single crystal device and typical *I-V* curve in semilogarithmic scale. Reprinted with permission from Ref. [10], Copyright © 2020 American Chemical Society. (c) 2D $(PEA)_2PbBr_4$ perovskite single crystal, atomic force microscopy images of an exfoliated layer and device structure, typical *I-V* curves. Reprinted with permission from Ref. [11], Copyright © 2017 American Chemical Society. (d) Photographs of $Cs_3Sb_2Br_9$ perovskite single crystals and schematic illustration of device, bipolar and threshold switching curves. Reprinted with permission from Ref. [12], Copyright © 2020 Elsevier.

Table 1
Comparison of performance parameters of perovskite single crystals-based resistive switching devices.

Device structure	Set voltage (V)	Operating current (A)	ON/OFF ratio	Retention (s)	Endurance (cycles)	Ref.
Ag/$MAPbBr_3$-PbS QDs/Ag	>10	10^{-5}	>10	3600	100	[9]
Ag/$CsPbBr_3$/Ag	~3.4	~10^{-8}	~10^3	>10^3	400	[10]
graphene/$(PEA)_2PbBr_4$/Au	2.8	10^{-11}	~10	1000	100	[11]
Au/$Cs_3Sb_2Br_9$/Au Nonvolatile	2	<10^{-3}	10^6	2 × 10^4	–	[12]
Au/$Cs_3Sb_2Br_9$/Au Threshold	~2.7	<10^{-3}	>10^3	–	200	[12]
Au/$MAPbBr_3$/Au	~20	<10^{-6}	1.44–8.1	–	320	[13]
Au /$MAPbBr_3$/Au (or Pt)	39/37	10^{-6}	~54	–	–	[14]
Au/$(PEA)_2PbI_4$/Au (or FTO)	4.2	10^{-7}	~10^3	–	–	[15]

lization method. Subsequently, perovskite single crystal layers were incorporated within a graphene/2D perovskite single crystal/Au vertical structure using a polydimethylsiloxane (PDMS) stamp transfer technology. While the sweep voltages were applied at Au electrode and graphene was grounded, the device showed bipolar resistive switching behavior after an electroforming process, with ON/OFF ratio of ~10 and switching endurance up to 100 cycles. By modulating compliance current, multilevel storage was realized with data stability up to 1000 s. The resistive switching mechanism was ascribed to the Br ion and vacancy movement to form filaments. In addition, this device was also performed to mimic biological synapses with the functionalities of short-term potentiation, long-term potentiation and paired pulse facilitation etc. particularly the energy consumption of the single crystal-based device (400 fJ/spike) was very close to that of biological synapses (1–100 fJ/spike). Similarly, 2D $(PEA)_2PbI_4$ perovskite single crystal-based memory device also has been studied in which the resistive switching behavior was related to the I ion filament and charge trapping [15].

In order to solve the problems of instability and toxic lead in organic–inorganic lead halide perovskite-based ReRAM, Han and co-workers [12] reported resistive switching behavior of monocrystalline lead-free all-inorganic $Cs_3Sb_2Br_9$ perovskite nanoflake in 2020 (Fig. 1d). The perovskite single crystal nanoflakes with a diameter of ~100 μm and thickness of ~100 nm, were prepared by inverse temperature crystallization method. A planar structure of Au/$Cs_3Sb_2Br_9$/Au device on SiO_2/quartz substrate was fabricated by direct dripping, crystallization or dry-transfer strategy. Intriguingly, the device presented not only nonvolatile bipolar resistive switching, but also volatile threshold switching by controlling the channel length, that the maximum and minimum channel lengths for bipolar and threshold switching are 5 and 10 μm, respectively. Data retention test of bipolar switching behavior was carried out for 2 × 10^4 s with ON/OFF ratio of approximately 10^6. Threshold switching, meaning the low-resistance state can spontaneously reinstate to high-resistance state during the backward sweep, can be cycled for 200 times with ON/OFF ratio over 10^3 and record-low switching electric field of 2.2×10^5 V m^{-1}. The Br vacancy filaments are responsible to the resistive switching behavior. Similarly, the device was used to imitated short-term Ca^{2+} dynamics of biological synapses, further applied as a reservoir element in neural network-based reservoir computing system to process temporal information exhibiting over 96% recognition accuracy of four letters after successfully training.

Table 1 shows the comparison of performance parameters of single crystals-based resistive switching devices. They show the comparable performance with polycrystalline perovskites-based devices, notably low operating current in most of single crystals-based devices. Although, the recent research results of halide perovskite single crystals have already shown outstanding resistive switching behavior and they exhibit application potential for low power consumption resistive switching due to their stable crystal structure without grain boundaries and pinholes. There are still several foremost challenges for large-scale applications. To the best of our knowledge, only these types of halide perovskite single crystals are investigated for resistive switching. And most of them relied on the Br-based perovskites. Therefore, other halide perovskite single crystals also need to be further exploited, especially low-dimensional lead-free inorganic perovskite single crystals which are with high stability and low toxicity, as well as more studies of resistive switching behavior and mechanism. Halide perovskite single crystals have more excellent photoresponsive properties than polycrystalline perovskites. Light-modulated resistive switching should be paid more attention, further for their multifunctional application in the fields of visual memory, photonic synapses and wireless communication etc. On the other hand, both large size of single crystals and complicated fabrication of device structures in these studies are inapplicable for high density integration. Therefore, based on optimizing device structures, halide perovskite single crystal films, even micro-nano scale film arrays and crossbar arrays for resistive switching may be the next research topic.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

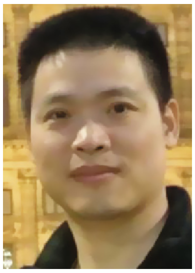
This work was supported by the National Natural Science Foundation of China (51973119, 61804011, 52125205, U20A20166, and 61805015), the Natural Science Foundation of Beijing Municipality (Z180011), the Natural Science Foundation of Guangdong Province (2018A0303130060, 2019A1515011566, and 2019B1515120042), Shenzhen Science and Technology Program (KQTD20170810105439418), and the Fundamental Research Funds for the Central Universities.

References

[1] Younis A, Lin C-H, Guan X, et al. Halide perovskites: a new era of solution-processed electronics. Adv Mater 2021;33:2005000.
[2] Shang Q, Li M, Zhao L, et al. Role of the exciton-polariton in a continuous-wave optically pumped $CsPbBr_3$ perovskite laser. Nano Lett 2020;20:6636–43.
[3] Zhong Y, Liao K, Du W, et al. Large-scale thin $CsPbBr_3$ single-crystal film grown on sapphire via chemical vapor deposition: toward laser array application. ACS Nano 2020;14:15605–15.
[4] Yoo EJ, Lyu M, Yun J-H, et al. Resistive switching behavior in organic-inorganic hybrid $CH_3NH_3PbI_{3-x}Cl_x$ perovskite for resistive random access memory devices. Adv Mater 2015;27:6170–5.
[5] Han JS, Le QV, Choi J, et al. Lead-free all-inorganic cesium tin iodide perovskite for filamentary and interface-type resistive switching toward environment-friendly and temperature-tolerant nonvolatile memories. ACS Appl Mater Interfaces 2019;11:8155–63.
[6] Cheng X-F, Qian W-H, Wang J, et al. Environmentally robust memristor enabled by lead-free double perovskite for high-performance information storage. Small 2019;15:1905731.
[7] Ge S, Guan X, Wang Y, et al. Low-dimensional lead-free inorganic perovskites for resistive switching with ultralow bias. Adv Funct Mater 2020;30:2002110.
[8] Kim H, Choi M-J, Suh JM, et al. Quasi-2D halide perovskites for resistive switching devices with on/off ratios above 10^9. NPG Asia Mater 2020;12:21.

[9] Younis A, Hu L, Sharma P, et al. Enhancing resistive switching performance and ambient stability of hybrid perovskite single crystals via embedding colloidal quantum dots. Adv Funct Mater 2020;30:2002948.
[10] Liu J, Jin J, Yang Z, et al. Extremely low program current memory based on self-assembled all-inorganic perovskite single crystals. ACS Appl Mater Interfaces 2020;12:31776–82.
[11] Tian H, Zhao L, Wang X, et al. Extremely low operating current resistive memory based on exfoliated 2d perovskite single crystals for neuromorphic computing. ACS Nano 2017;11:12247–56.
[12] Mao J-Y, Zheng Z, Xiong Z-Y, et al. Lead-free monocrystalline perovskite resistive switching device for temporal information processing. Nano Energy 2020;71:104616.
[13] Xing J, Zhao C, Zou Y, et al. Modulating the optical and electrical properties of $MAPbBr_3$ single crystals via voltage regulation engineering and application in memristors. Light Sci Appl 2020;9:111.
[14] Ke S, Luo S, Gong J, et al. Electric modulation of conduction in $MAPbBr_3$ single crystals. J Adv Ceram 2021;10:320–7.
[15] Di J, Lin Z, Su J, et al. Two-dimensional $(C_6H_5C_2H_4NH_3)_2PbI_4$ perovskite single crystal resistive switching memory devices. IEEE Electr Device Lett 2021;42:327–30.

Shuaipeng Ge received his Ph.D. degree at Department of Physics, Beihang University in 2020. He currently carries out postdoctoral research work at College of Physics and Optoelectronic Engineering, Shenzhen University, and Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences. His research interest mainly includes synthesis and resistive switching of perovskite materials.



Long-Biao Huang obtained his B.Sc. and M.Sc. degrees from Xi'an Jiaotong University, and then went to Global R&D Center of Dow Chemical as Research Chemist. In 2014, he obtained his Ph.D. degree from Center of Super-Diamond and Advanced Films, City University of Hong Kong. After postdoctoral career in The Hong Kong Polytechnic University under supervision of Prof. Jianhua Hao, he works as associate professor at Shenzhen University. His research interest includes polymer nanomaterials and polymer interface for different applications such as organic electronics, plasmonic, energy harvesting device, and self-powered systems.

Caofeng Pan received his B.S. (2005) and Ph.D. degrees (2010) in Materials Science and Engineering from Tsinghua University. He then joined the group of Prof. Zhong Lin Wang at the Georgia Institute of Technology as a postdoctoral fellow from 2010 to 2013. He is a professor and a group leader at the Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences. His research interest mainly focuses on the fields of piezotronics/piezophototronics for fabricating new electronic and optoelectronic devices, nanopower source, hybrid nanogenerators, and self-powered nanosystems.