Lead-free perovskite MASnBr₃-based memristor for quaternary information storage

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Abstract
Memristors are a new type of circuit element with a resistance that is tunable to discrete levels by a voltage/current and sustainable after removal of power, allowing for low-power computation and multilevel information storage. Many organic-inorganic lead perovskites are reported to demonstrate memristive behavior, but few have been considered for use as a multilevel memory; also, their potential application has been hindered by the toxicity of lead ions. In this article, lead-free perovskite MASnBr₃ was utilized in memristors for quaternary information storage. Indium tin oxide (ITO)/MASnBr₃/Au memristors were fabricated and showed reliable memristive switching with well-separated ON/OFF states of a maxima resistance ratio of 10² to 10³. More importantly, four resistive states can be distinguished and repeatedly written/read/erased with a retention time of 10⁴ seconds and an endurance of 10⁴ pulses. By investigating the current-electrode area relationship, Br distribution in the ON/OFF states by in situ Raman and scanning electron microscopy, and temperature-dependent current decay, the memristive behavior was explicitly attributed to the forming/breaking of conductive filaments caused by the migration of Br⁻ under an electric field. In addition, poly(ethylene terephthalate)-ITO/MASnBr₃/Au devices were found to retain their multiresistance state behavior after being bent for 1000 times, thus demonstrating good device flexibility. Our results will inspire more lead-free perovskite work for multilevel information storage, as well as other memristor-based electronics.

KEYWORDS
MASnBr₃, memristor, perovskite, resistive memory, RRAM
1 | INTRODUCTION

The memristor was firstly postulated by Prof. Chua in 1971 as the fourth fundamental circuit element and was experimentally found in 2008 by Hewlett-Packard Labs. The resistance of a memristor depends on its voltage/current history; thus, such a device can be modulated to discrete levels by a voltage/current, and are sustained after the removal of power. These resistive levels, regarded as 0, 1, 2, 3, ..., can be utilized to store high-density information. Due to their low power consumption, fast switching speed, high durability, long retention time, fine miniaturization, 3D stacking, and compatibility with traditional semiconductor technology, memristors have been recognized as the most promising candidates for the next-generation of solutions for logical and numerical computation, artificial synapses, and artificial neural networks as well as for information storage. These new techniques will have applications in future computers, smartphones, and the net-of-things which produce a massive amount of data every day.

To date, various materials, such as metal oxides, chalcogenides, polymers, and amorphous silicon, have been proposed to construct memristors viable for multilevel information storage. Recently, organic-inorganic hybrid perovskites have arisen as super stars for memristor information storage. Organic-inorganic hybrid perovskites have been proposed to construct memristors viable for multilevel technology, memristors have been recognized as the most promising candidates for the next-generation of solutions for logical and numerical computation, artificial synapses, and artificial neural networks as well as for information storage. These new techniques will have applications in future computers, smartphones, and the net-of-things which produce a massive amount of data every day.

In this work, we demonstrate that a reliable memristor can be achieved using a lead-free hybrid perovskite CH$_3$NH$_3$SnBr$_3$. The indium tin oxide (ITO)/MASnBr$_3$/Au device shows repeatable memristive switching with well-separated ON/OFF states with a resistance ratio range from $10^2$ to $10^3$. More importantly, four resistive states can be distinguished with a retention time of $10^4$ seconds and an endurance of $10^5$ pulses. By investigating the current-electrode area relationship, in situ Raman imaging and element mapping of Br in the ON/OFF states, and temperature-dependent current decay behavior, the observed memristive behavior is explicitly attributed to the formation/rupture of conductive filaments caused by the Br$^-$ migration under an electric field. Flexible poly(ethylene terephthalate)-ITO/MASnBr$_3$/Au devices retain their multilevel memory behavior after being bent by 1000 times, thus demonstrating good device flexibility.

2 | EXPERIMENTAL SECTION

2.1 | Materials

SnBr$_2$ and CH$_3$NH$_3$Br were purchased from Sigma-Aldrich. Toluene and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All these reagents were used as received without further purification.

2.2 | Fabrication of the memory device

SnBr$_2$ (2.785 g, 10 mmol) and NH$_3$CH$_3$Br (1.12 g, 10 mmol) were dissolved in 2 mL of DMF to afford a 5 mol/L solution. The ITO glass and polyethylene terephthalate (PET)/ITO substrates were first cleaned in an ultrasonic bath of detergent, deionized water, acetone for 10 minutes, respectively. Then, the substrate was tried and cleaned in an UV-ozone cleaner for 15 minutes. For the lateral device used for Raman imaging, the substrate was composed of a SiO$_2$-covered Si substrate with gold interdigital electrodes on the surface (channel length: 20 μm). To fabricate flexible device, the prepared MASnBr$_3$ solution was spin-cast on to the PET/ITO substrate at 500 rotations per minute for 60 seconds in a N$_2$ protected glove box. In the first few seconds of the rotation, 5 mL of toluene was uniformly drop onto the substrate. After sping-coating, the obtained film was annealed at 70°C for 30 minutes. Next, Au-electrode array was evaporated onto the film through a covered metal shadow mask by magnetron sputtering deposition. The electrodes are of a thickness of 60 nm and a diameter of 20 μm, respectively. For scanning electron microscopy (SEM), Au interdigital electrodes were deposited onto SiO$_2$/Si substrates with a channel length of 4 μm.

2.3 | Measurement and characterization

SEM images and element mapping were collected using a Hitachi S-4700 scanning electron microscope. X-ray diffraction (XRD) patterns were obtained using a Multiple Crystals X-ray Diffractometer (X’Pert PRO, PANalytical). The photoluminescence spectra were obtained by a Horiba FluoroMax-4. The memristor current-voltage scanning was performed using a semiconductor parameter analyzer (Keithley 4200-SCS), which connect to a cryogenic probe station (LakeShore TTPX). Raman in situ imaging was performed by sampling 22 × 23 pixels distributed in a zone of 44 × 46 μm by a HORIBA NANO Raman system. For the lateral device test, the voltage to onset was 20 V.
3 | RESULTS AND DISCUSSION

3.1 | Synthesis of MASnBr₃ and fabrication of the memory devices

To fabricate a memristor, a pinhole-free, maroon layer of MASnBr₃ with closely packed grains (Figure 1A-C) was obtained by spin-coating a DMF solution of MASnBr₃ (5 mol/L) onto ITO glass (Figure S1), followed by the pooling of a large volume of toluene. Intense diffraction peaks were obtained for the film from XRD at 15.02°, 26.14°, and 30.40° (Figure 1D), which are assigned to the cubic structure of the (100), (110), and (200) planes of the MASnBr₃ perovskite powders, respectively (PDF#00-032-1927). No peaks due to the reactants were detected, suggesting that the film had high phase purity. Most of these peaks belong to the (100) plane and its higher orders with enhanced intensity, strongly indicating that the MASnBr₃ perovskite film may grow along the (100) direction on ITO (Figure 1E). An emission peak at 580 nm appears in the photoluminescence spectrum of the MASnBr₃ film, in agreement with the reference (Figure S2a). Then, an Au-electrode array was deposited onto a MASnBr₃ film covered by a mask by magnetron sputtering. The cross section of the device in Figure 1F shows that the thicknesses of the perovskite layer and Au electrode are 2 μm and 60 nm, respectively.

3.2 | Memristive performance

The ITO/MASnBr₃/Au sandwich device shows repeatable and stable memristive behavior judging from the observation of pinched loops for the current-voltage (I-V) relation under periodic voltage sweeping, conforming to the exact definition of a memristor (Figure S3a). In the view of memory operation, the virginal device always remains in a high-resistance state (HRS or OFF state). A positive sweep was applied to initialize a low-resistance state (LRS, or ON state) for a voltage above 2 V, serving as the forming operation in memory (first cycle in Figure 2A). The device remained in the ON state when the voltage was swept backward, indicating the nonvolatile characteristic. A reverse sweep from 0 to −3.1 V can recover the HRS, serving as the “reset” or “erase” process. In the following sweeps, the set voltages are much smaller (~0.65 V, the second cycle in Figure 2A). A typical memristor was able to repeat the loops by 130-350 (Figure 2B and S3b) times, exhibiting good repeatability.

The operational parameters during these cycles are quite...
uniform, with the set voltage \( V_{\text{set}} \) \( 0.65 \pm 0.15 \) V and reset voltage \( V_{\text{reset}} \) \( -3.1 \pm 0.6 \) V distributed in a narrow range and well separated from each other, allowing reliable write and erase operations with least errors (Figure 2C). Meanwhile, the resistance of the ON (262 ± 20 Ω) and OFF states \( 4 \times 10^3 \) to \( 5.2 \times 10^4 \) Ω are also distinct from each other (Figure 2D). Therefore, an ON/OFF ratio in the range between 10 and \( 10^3 \) was

**FIGURE 2** Memristive behavior of the ITO/MASnBr₃/Au devices. A, Typical I-V characteristics of the initial 2 cycles and, B, 127 consecutive cycles. C, Histogram and Gaussian fitting of the set and reset voltage distribution. D, The histogram and Gaussian fitting of ON/OFF resistance distribution. ITO, indium tin oxide

**FIGURE 3** Multilevel operation of the MASnBr₃-based devices. A, Quaternary mode of memristor under different applied voltages. B, Retention of the four resistive states. C, Endurance characteristics of four resistive states read at \(-0.1\) voltages under the pulse-test mode. D, A pulse mode in waveform setting. F, Four states of MASnBr₃-based memristor were obtained by a pulse train. Read voltage: \(-0.1\) V
achieved (Table S1). Compared to memory devices based on lead halide perovskites including CsPbX₃, CH₃NH₃PbX₃ (X is a halide), our devices are comparable in performance (in Table S1).

### 3.3 Multilevel information storage

More importantly, the ITO/MASnBr₃/Au devices can be utilized for multilevel information storage. In Figure 3A, four loops with different enclosed areas can be achieved by applying periodic voltage sweeps with different magnitudes (0 → \( V_{\text{max}} \) → 0 → \(-V_{\text{max}}\) → 0, \( V_{\text{max}} = 1.1, 1.7, \) and 5 V) to the memristor devices. Using a positive sweep (0 → \( V_{\text{max}} \)), the MASnBr₃-based device was set to the LRS with a different resistance, depending on the value of \( V_{\text{max}} \). These three LRSs, together with the HRS (OFF) state, were retained for more than 10⁴ seconds for the constant reading mode (reading voltage: −0.1 V, Figure 3B). A pulse-mode test suggests that these states can be maintained under stress for more than 10⁴ cycles (Figure 3C). We further assess the multilevel data reading/writing/erasing performance by applying a voltage pulse train (Figure 3D). In this train, a write (+1.1/1.7/1.5 V, width: 0.6 μs), read (−0.1 V, width: 8 μs), and erase (−5.0 V, width: 0.6 μs) operation was repeated applied to the device (Figure 3E). The four resistive states of the devices can be written/read/erased for several cycles, showing good repeatability. The writing and reading time is as short as 0.6 and 8 μs, respectively, subject to the apparatus functionality.

### 4 MECHANISM OF THE MEMRISTIVE SWITCH

It is important to understand the mechanism of the memristive switching for further improving their performance. First, we examined the resistance of the HRS and LRS by varying the top electrode area (Figure S4A,B). The average currents for the LRS and HRS are independent of the electrode area, indicating that the...
memristive switching is related to conductive filament. To trace possible element drift under an electric field, we imaged the Sn-Br concentration distribution in a lateral device under the OFF and ON states (Figure 4A); this device was prepared by spin-coating a thin layer of MASnBr₃ onto a SiO₂ substrate with a pair of Au interdigitated electrodes (see details in Section 2). The Raman spectrum of the CH₃NH₃SnBr₃ film shows a main peak at 169 cm⁻¹ (Figure S5A), which is attributable to the Sn-Br stretching mode. Therefore this peak could represent the Br concentration. The distribution of the Br element was imaged by monitoring the peak intensity at 169 cm⁻¹ in the OFF (Figure 4B) and ON (Figure 4C) states of the lateral memory device. By comparing Figure 4B,C, one can observe that the color in region A of the cathode changes from orange to green, showing that the Br concentration decreases when the device is switched from the OFF to ON state. In contrast, region B on the anode shows a color change from a partially orange to almost fully orange, suggesting a remarkable decrease of Br concentration under the pooling of an electric field. These data clearly show that the concentration of Br decreases near the cathode, but accumulates at the anode. Figure 4D further shows the evolution of the Br concentration near the anode (Figure S5B). The Br near the anode first rises rapidly in the first 500 seconds, then gradually approaches a saturation value, which is consistent with the literature. Finally, supporting evidence is provided from the observation of composition and morphology changes during poling of the lateral device for more than 70 minutes (Movie S1). The distribution of Br and Sn in the OFF/ON state was mapped. It is found that Br was distributed uniformly on the substrate in the OFF state, whereas in the ON state it mainly accumulated on the Au anode (Figure 4E). In contrast, the Sn distribution remained unchanged in both OFF and ON states. This is in good agreement with our previous work as well as that found in other lead-hybrid perovskites.

The above evidence and our previous studies suggested that during the writing process, Br⁻⁻ ions are attracted to the anode and oxidized to Br atoms and stored in the Au film at low anodic potentials. Concurrently, this process creates VₓBr⁻⁻ in the MASnBr₃ film, where the highest VₓBr⁻⁻ concentration occurs near the cathode. Continuous voltage bias for an applied voltage...
of $V > V_{set}$ will cause a drift in $V_{Br-}$ toward the anode, which will eventually lead to the formation of a $V_{Br-}$ rich channel to bridge the electrodes. This channel is conductive due to the doping effect of $V_{Br-}$, and thus switches the device from the HRS to LRS (Figure 4G). Under an applied voltage of $V > V_{Reset}$, the stored $Br$ atoms can relax and diffuse away from the Au electrode and recombine with $V_{Br}$ in the conductive channel slowly. The recovering process can be accelerated at high temperature or by using a negative electric field, leading to conductive channels rupture and retention failure (Figures 4F and S6). Then, the memristor will change from the LRS to HRS. Quantitatively, the $Br^-$ migration was confirmed by measuring the temperature dependence of the current retention failure of our device (Figure S6a). The current in the memristive ON state decayed with different speeds when the working temperature was increased from $312$ to $360$ K (Table S2).

The logarithm of the character retention time ($\ln(t)$) vs inverse of reciprocal temperature time $1/k_B T$ is shown in Figure S6b, where $k_B$ is the Boltzmann constant. The data show a strictly linear relationship, offering an activation energy $E_a$ of 0.57 eV. This value is similar to that expected for the transportation of $\Gamma^-$ in the form of a vacancy ($V_{Br}$) or ion ($\Gamma^-$, 0.08-0.6 eV) but not Sn$^{2+}$, suggesting that the $Br^-$ ion migration cause the memristive switching.

5 | FLEXIBLE MEMRISTOR DEVICE

Finally, we demonstrated that MASnBr$_3$ is suitable for fabricating flexible memory devices on ITO-coated PET (PET-ITO) sheets (Figure 5A). Photoluminescence spectra showed that an emission peak at 580 nm only appeared for the device structure of Au/MASnBr$_3$/PET/ITO, indicating that MASnBr$_3$ was unchanged after coating on PET-ITO film (Figure S2b). Following bending by 1000 times with a radius curvature of 7.84 mm, the four resistive states for the memristive behavior remain intact (Figure 5B-D), demonstrating the compatibility of hybrid perovskites based on MASnBr$_3$ with flexible devices compared with previous reports.

6 | CONCLUSIONS

In this study, lead-free perovskite MASnBr$_3$ was utilized in memristors for quaternary information storage. An ITO/MASnBr$_3$/Au device showed repeatable memristive switching with well-separated ON/OFF states, with a resistance ratio of $10^2$ to $10^3$. More importantly, four resistive states can be distinguished with a retention time of $10^7$ seconds and an endurance of $10^4$ pulses. More states may be possible if one can further increase the total ON/OFF ratio, leaving a sufficiently wider resistance window to accommodate more levels. The memristive behavior is explicitly attributed to the formation/rupture of conductive filaments caused by the migration of $Br^-$ under an electric field. Given that $Br^-$ is the major migration ion, other lead-free halide perovskites might also demonstrate similar memristive behavior. Flexible poly(ethylene terephthalate)-ITO/MASnBr$_3$/Au devices retained their multiresistance state behavior after being bent 1000 times, thus demonstrating good device flexibility. Our results will inspire more lead-free perovskite work for multilevel information storage, as well as other memristor-based electronics.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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**SUPPORTING INFORMATION**

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