Conductive metallic filaments dominate in hybrid perovskite-based memory devices

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ABSTRACT Organic–inorganic hybrid perovskites (OHPs) are well-known as light-absorbing materials in solar cells and have recently attracted considerable attention for the applications in resistive switching memory. Previous studies have shown that ions can migrate to form a conductive channel in perovskites under an external voltage. However, the exact resistance mechanism for Ag or halogens which dominate the resistive behavior is still controversial. Here, we demonstrate a resistive switching memory device based on Ag/FA_{0.83}MA_{0.17}Pb(I_{0.82}Br_{0.18})₃/fluorine doped tin oxide (FTO). The migration of Ag cations and halide anions is demonstrated by energy dispersive X-ray spectroscopy (EDS) after the SET process (positive voltage on Ag). By comparing the *I*–*V* behavior of the Au-based devices, it is clear that the conductive channel formed by Ag is the main factor of the switching characteristics for Ag-based devices. Meanwhile, by controlling the appropriate SET voltage, two kinds of resistance characteristics of the analog switch and threshold switch can be realized in the Ag-based device. As a result, it may be possible to implement both data storage and neuro-morphic computing in a single device.

Keywords: Ag filament, perovskite memory, analog switch, threshold switch, resistance mechanism

INTRODUCTION

Organic-inorganic hybrid perovskite (OHP) materials possess a high absorption coefficient and mobility [1,2], low trap-state density [3,4], small exciton binding energy [5] and a long carrier diffusion [3]. Several OHP-based devices, including photovoltaics [6], light-emitting diodes [7], photodetectors [8], and triboelectric nanogenerators [9], with high performance have recently been assembled.

Many studies suggest that I[–] and Br[–] can mobilize and induce electric fields because of their low migration activation energies [10,11] and shallow defects. When an external voltage is applied to the OHP films with a bi-directional scan, a hysteresis characteristic makes OHPs become promising materials for applications in memory devices [12,13].

The first resistive random access memory (ReRAM) device based on OHPs was reported by Yoo *et al.* [14] in 2015. These OHPs show excellent resistive switching behaviors in terms of high endurance, retention time, and ON/OFF ratios. The structural flexibility and low temperature processing make OHPs a promising candidate for manufacturing wearable devices [15]. In addition, ReRAM devices can be used not only in data storage but also in the field of artificial synapses [16,17]. However, high efficiency resistive memories were rarely reported, and the ionic mobility and atomic diffusion coefficient that form the conductive channel in memory devices still need additional exploration.

The general formula for OHPs is ABX₃, where A is a monovalent cation such as methyl-ammonium (MA), formamidinium (FA), or cesium; B is a divalent metal cation such as lead or tin; and X is a halide anion. The crystal structure supplies the lattice with sufficient room to accommodate different cations and anions. Therefore, OHP materials are not limited to the common CH₃NH₃-PbI₃ form to crystallize. It has been reported that the stability and efficiency can be improved by incorporating FA⁺ with MA⁺ at the A site, along with a mixture of Cl, Br, and I halide anions at the X site [18,19]. It is apparent that the composition in the A and/or X sites alters the device functionality by tuning its crystal structure or film

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morphology. Several studies have shown that composition engineering of OHPs can alter the light/field-induced ionic migration [11,13]. For example, incorporating MA^+ into FAPbI_3 weakens the Gibbs free energy due to lattice contraction and an increasing cation disorder [20]. In addition, the mixing FA^+ and MA^+ at the A site can enhance the thermal stability [18]. This characteristic can form conductive pathways that are induced by the electric field. While there are several reports related to high efficiency of solar cells based on $\text{FA}_x\text{MA}_{1-x}\text{PbX}_3$ [21–23], there are few reports regarding its resistance behavior and its application in memory devices.

In this work, we studied $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.82}\text{Br}_{0.18})_3$ thin films with a low roughness in a memory device in which Ag and fluorine doped tin oxide (FTO) were the upper and lower electrodes, respectively. Furthermore, we analyzed changes in the Ag, I, and Pb contents before and after exposure to electric fields using the energy dispersive X-ray spectroscopy (EDS), and a clear Ag migration was observed. Furthermore, by comparing the I - V characteristics of the Au-based device, it is clear that the conductive channel formed by Ag is the main factor causing the switching behavior of Ag-based devices. Meanwhile, by controlling the appropriate SET voltage, two kinds of resistance characteristics of analog switches and threshold switches can be realized in Ag-based devices.

EXPERIMENTAL SECTION

Materials

PbI_2 (98.0%) and PbBr_2 (98.0%) (TCI), formamidinium iodide (FAI 99.5%) and methyl-ammonium bromide (MABr 99.5%) (Xi'an Polymer Light Technology Corp), acetone (99.5%, Beijing Shiji), ethanol (99.7%), and isopropanol alcohol (IPA 99.7% Sinopharm Chemical Reagent Co., Ltd) were used as received. Dimethylformamide (DMF, 99.8%), dimethylsulfoxide (DMSO, 99.9%), and chlorobenzene (99.8%) were purchased from Sigma Aldrich and used without further purification.

Perovskite precursor solution preparation

$\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.82}\text{Br}_{0.18})_3$ was prepared with an anhydrous mixture of DMF and DMSO (volume ratio of 4:1) containing FAI (1.0 mol L^{-1}), PbI_2 (1.1 mol L^{-1}), MABr (0.2 mol L^{-1}), and PbBr_2 (0.22 mol L^{-1}) by stirring at 50°C for 1 h. It should be noted that the added volume of Pb^{2+} and I^- ions was designed much more than their stoichiometric ratio of (A:B:X = 1:1:3) for perovskite (ABX_3 , A = FA^+/MA^+ , B = Pb^{2+} , X = Cl^-/Br^-) and the excess

amount of Pb^{2+} and I^- is 0.12 and 0.24 mol L^{-1} , respectively.

Resistive switching memory device fabrication

Firstly, FTO glasses were sequentially washed with deionized water, ethanol, acetone, and isopropanol. Secondly, the washed FTO glasses were treated with UV-ozone for 30 min. Then, the remaining film preparation was carried out in a glove box filled with dry air. Afterwards, 30 μL of the perovskite precursor solution was dropped on the FTO substrates followed by a two-stage spin coating process. The first spin coating stage was at 1,000 rpm for 10 s with a 1 s acceleration. The second spin coating stage was at 6,000 rpm for 20 s with a 6 s acceleration in which 150 μL of chlorobenzene was dropped on the spinning substrate at 5 s prior to the end of the program to speed up the crystallization. Then, the substrates were annealed at 100°C for 50 min for good crystallization. Finally, 250 nm Ag/Au electrodes were thermally evaporated under a high vacuum using a mask with the holes of 200 μm in diameter.

Characterization

Scanning electron microscopy (SEM) and EDS were performed with a FEI FEG450. The atomic force microscopy (AFM) images were captured using a Bruker Dimension Icon FastScan system. The crystal structure of the $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.82}\text{Br}_{0.18})_3$ films was examined in the θ - 2θ mode with X-ray diffraction (XRD, Bruker D8 ADVANCE) using Cu K α radiation ($\lambda = 0.1542 \text{ nm}$). The electrical properties of the devices were characterized using a Keithley 4200 semiconductor analyzer under ambient and dark conditions. Steady-state photoluminescence (PL) was analyzed by Edinburgh LP 920 Laser Flash spectrometer with an excitation at 404 nm. Time-resolved photoluminescence (TRPL) was obtained by using the time-correlated single photon counter technology. Excitation of the sample was achieved with a pulse laser (PIXEA-CU-1, AUREA, France) of 406 nm wavelength, 0.5 MHz repetition rate and $\sim 35 \text{ ps}$ pulse width. The excitation laser beam focuses on the sample through a 100 $\times$ air objective lens (NA=0.95, Olympus PLFLN 100X) with the spot radius of 0.624 μm ($1/e^2$ of the maximum intensity measured with an EMCCD camera, DU-897U-CS0-#BV, Andor, UK).

RESULTS AND DISCUSSION

Fig. 1a presents a schematic illustration of the memory device in the Ag/ $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.82}\text{Br}_{0.18})_3$ /FTO configuration. Considering the cross-section view in Fig. 1b, a

Figure 1 The device structure and film properties. (a) Illustration of the Ag/FA_{0.83}MA_{0.17}Pb(I_{0.82}Br_{0.18})₃/FTO device structure. (b) Cross-sectional SEM image of the device and the corresponding thickness. (c) Cubic crystal structure of the perovskite. (d) AFM image of the perovskite film (RMS = 38.2 nm). (e) SEM image of the surface morphology. (f) XRD spectra of perovskite film of FA_{0.83}MA_{0.17}Pb(I_{0.82}Br_{0.18})₃, precursors including FAI, MABr, PbI₂ and PbBr₂, and the substrate of FTO. (g) TRPL decay curves of perovskite films with PbI₂ (black circle) and without PbI₂ (red triangle) on glass/FTO substrate, excited with pulsed excitation (406 nm, 500 kHz repetition rate, 1 μW). (h) PL measurement of the FA_{0.83}MA_{0.17}Pb(I_{0.82}Br_{0.18})₃ films with PbI₂ (black line) and without PbI₂ (red line) on glass/FTO substrate.

FA_{0.83}MA_{0.17}Pb(I_{0.82}Br_{0.18})₃ thin film with 726 nm thickness was deposited onto an FTO electrode (thickness of 220 nm) on a glass substrate using a one-step solution method. A 250 nm-thick Ag layer was used as the top electrode, which was connected to an electric-switching source, and was deposited using mask-assisted thermal evaporation. Fig. 1c illustrates a simple crystal structure of the perovskite where FA⁺ and MA⁺ occupy the A sites and coordinate with the PbX₆ octahedra, and the I⁻ and Br⁻ are located at the X sites. The surface roughness is as low as 38.2 nm as measured by AFM and shown in Fig. 1d. Therefore, the FA_{0.83}MA_{0.17}Pb(I_{0.82}Br_{0.18})₃ layer would exhibit a low recombination rate. The grain boundaries, where the migrated ions induced by light/electric fields can easily recombine, are reduced with the large particle size along with a smooth surface [24,25]. From the top-view surface morphology of the FA_{0.83}MA_{0.17}Pb(I_{0.82}Br_{0.18})₃ layer measured *via* SEM in Fig. 1e, the film is composed of crystalline particles. The particle size ranges from 120 to 476 nm, which is larger than

those in other studies with similar elemental compositions [24]. Additionally, a large number of brightly parasitic particles (~140 nm) are distributed on the surface and grain boundaries of perovskite grains uniformly. The XRD pattern shows (Fig. 1f) that the diffraction peaks at 14.2°, 19.9°, 24.4°, 28.4°, 31.8°, 34.9°, 40.6°, 43.2°, 50.3°, 52.5°, 54.6° and 60.7° are assigned to the cubic α perovskite crystal phase with high crystallinity. Meanwhile, a diffraction pattern of PbI₂ at 12.7° is observed [24,26–29]. These results demonstrate the formation of PbI₂ which is similar to the results reported by others [27,30]. Additionally, the crystal phases of PbBr₂, FAI, and MABr are hardly detected except for some distinctive SnO₂ peaks (26.5°, 33.8°, 37.8°, 51.7°, 61.7°, 65.7°), which are from the FTO substrate. The TRPL decay kinetics (Fig. 1g) on a semilog plot is measured in FA_{0.83}MA_{0.17}Pb(I_{0.82}Br_{0.18})₃ perovskite. The fast decay component, τ_1 , might come from bimolecular recombination [31]. The long decay component, τ_2 , could be attributed to recombination of free carriers in the ra-

diative channel [1]. The τ_1 and τ_2 of the sample with PbI_2 are longer than that without PbI_2 . Meanwhile, the PL measurement gives a corresponding result in Fig. 1h, and the excitation intensity in the film with PbI_2 is enhanced compared with the film without PbI_2 . This demonstrates that a moderate amount of PbI_2 has a positive effect due to effective passivation of surface/grain boundary defects.

Fig. 2a presents the analog switching characteristic of the $\text{Ag}/\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.82}\text{Br}_{0.18})_3/\text{FTO}$ device with a voltage below 0.5 V. A DC voltage was applied on the Ag top electrode while the bottom FTO electrode was grounded. A compliance current of 1 mA was set to prevent thermal-induced breakdown. When six consecutive positive voltage sweeps of $0 \rightarrow +0.5 \rightarrow 0$ V were applied to the device, the current amplitude gradually increased after each sweep. By contrast, when six consecutive negative voltage sweeps of $0 \rightarrow -0.5 \rightarrow 0$ V were applied to the device, the current amplitude gradually decreased after each sweep. Fig. 2b shows the direct changes in the conductance with continuous voltage sweeps.

To more clearly demonstrate the induced current change from consecutive voltage sweeps, current responses with continuously applied pulses were measured and shown in Fig. 2c and d. Twenty sequential positive and negative pulses ($+0.6$ V/ -0.5 V at 2 ms) were applied

to the Ag electrodes, and the current either increased or decreased as the number of pulses increased. These results illustrate that the conductance is also gradually potentiated or depressed by successive pulses.

Interestingly, when the SET voltage was raised to $+0.8$ V, the device exhibited threshold switching characteristics without a forming process, as shown in Fig. 2e. As a positive voltage sweep was applied from 0 to $+0.8$ V, the device was switched from a high resistance state (HRS) to a low resistance state (LRS) at $+0.65$ V. Then, the device returned to the HRS in a voltage sweep from 0 to -1.5 V. Fig. 2f demonstrates the endurance test for 40 cycles, and the HRS/LRS ratio of the perovskite memory cell is greater than 10. It should be noted that all of the above electrical tests were performed under dark conditions.

As mentioned above, when the SET voltage was 0.5 V, several sweeps were needed to reach the LRS. However, when the voltage increased to 0.8 V, only one stimulus was sufficient to reach LRS. In other words, increasing the bias amplitude reduces the number of required stimuli, and the device requires only one stimulus to transit from HRS to LRS. Thus, an appropriate bias voltage could achieve the transition from an analog switch to a threshold switch.

Based on the device structure and composition, a

Figure 2 The analog switching (a–d) and threshold switching (e, f) characteristics for the $\text{Ag}/\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.82}\text{Br}_{0.18})_3/\text{FTO}$. (a) I - V characteristics of the device during six consecutive positive ($0 \rightarrow +0.5 \rightarrow 0$ V) and negative ($0 \rightarrow -0.5 \rightarrow 0$ V) sweeps. (b) Changes of the device conductance during consecutive sweeps. (c) Current responses with time based on the positive pulses ($+0.6$ V at 2 ms). (d) Current responses with time based on the negative pulses (-0.5 V at 2 ms). (e) I - V characteristics of the device from four series sweeps ($0 \rightarrow +0.8 \rightarrow 0 \rightarrow -1.5 \rightarrow 0$ V). (f) Endurance performance read at 0.05 V.

proposed mechanism for the resistive switching behavior may be derived from two primary reasons. Firstly, the I - V switching behavior under electric fields could arise from the nature of this OHP material including the ionic migration and charge trapping/detrapping effects related with defect states inside the perovskite films [32]. In our work, as mentioned above, the defect sites derived from the surface or grain particles of the OHPs have been passivated by the excess of crystalline PbI_2 during the fabrication process. Therefore it is necessary to pay more attention to the ionic migration which has been widely reported due to its lower activation energy [13,33]. Ionic migration is assumed to be one of the possible reasons for the switching behavior in these memory devices. The accumulation of ions resulting from ionic migration induced by external electric fields could explain the variations in the current intensities. Based on the $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.82}\text{Br}_{0.18})_3$ material, the migration candidates include MA^+ , FA^+ , I^- , and Br^- ions. Many researchers have suggested that the migration of I^- ions is dominant due to the lowest activation energy [34,35] and high diffusion coefficient [10]. Secondly, the Ag electrode can easily diffuse to form a metal filament, especially after the setting process [36]. Therefore, the Ag conductive filament is assumed to be the other alternative candidate reason to the switching behavior in the memory device.

To further verify the hypotheses, the switching behavior was first studied using the measurement device, which has another architecture ($\text{Au}/\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.82}\text{Br}_{0.18})_3/\text{FTO}$), as demonstrated in Fig. 3a, where the top Ag electrode is replaced with Au. In the I - V curves from Fig. 3b and c, subjected to positive voltage ($0 \rightarrow 1.5 \rightarrow 0$ V) sweeps with five cycles, the device presents a variety of variable I - V hysteresis loops with increasing voltage sweep cycles, where the current intensity in each cycle at the same potential gradually decreases. From these results, the electrical characteristics based on the $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.82}\text{Br}_{0.18})_3$ arise from ions migration and accumulation. After applying an external electric field, the I^- ions transfer towards the opposite electric direction [37]. In the case of high-energy stimulated situation with a strong voltage, a small amount of Br^- ions accompanied with some MA^+ and FA^+ could also actively migrate and move along the positive and negative directions of the electric field, respectively [38]. Then, a built-in field, which is opposite to the external electric field, is generated due to the migrating charge accumulation. This field can dramatically decrease the effective potential that is applied to the measured device. Therefore, the current intensity is significantly weakened compared with the

first and second voltage circles shown in Fig. 3b. When increasing the voltage-scan circles or extending the electric-field excitation time, the enhanced charge accumulation leads to an increased built-in electric field. Consequently, the current intensity gradually decreases as the effective potential decreases along with the increasing voltage scan circles. This is further verified by the negative voltage scan circles shown in Fig. 3c. A more intuitive schematic of the above phenomena is demonstrated in Fig. 3d.

In addition, SEM accompanied with EDS was used to characterize the ionic migration under electric fields and the formation of an Ag metal filament in the fabricated memory devices. Fig. 4a and c show the EDS profiles of the cross-sectional elemental distribution before and after applying a positive voltage stress to the Ag electrode, and Fig. 4b shows the corresponding cross-sectional SEM image of the device. For the EDS profile (Fig. 4a) without applying a voltage stress, the content of I is consistent with that of Pb, which gradually decreases towards the electrode. This means that I atoms are stable within the perovskite before the applied voltage. The Ag, as an active metal, can be easily oxidized into Ag^+ after exposure to ambient air and react with the halide ions in the perovskite [37]. After applying a positive voltage stress onto the Ag electrode, Fig. 4c shows the I is increasingly concentrated at the upper perovskite layer and supports

Figure 3 (a) Illustration of the structure and characterization schematics of the $\text{Au}/\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.82}\text{Br}_{0.18})_3/\text{FTO}$ device. (b) I - V characteristics of the device during six consecutive positive ($0 \rightarrow +1.5 \rightarrow 0$ V) sweeps. (c) I - V characteristics of the device during six consecutive negative ($0 \rightarrow -2.5 \rightarrow 0$ V) sweeps. (d) The formation process of the built-in electric field under the action of an external electric field.

Figure 4 EDS analysis of the Ag/FA_{0.83}MA_{0.17}Pb(I_{0.82}Br_{0.18})₃/FTO device and the formation of the Ag conductive filament. (a) EDS profiles of the cross-sectional element distribution before applying a positive voltage to the Ag electrode. (b) The cross-sectional SEM image corresponding to the EDS profiles. (c) EDS profiles of the cross-sectional element distribution after applying a positive voltage on the Ag electrode. (d) The formation process of the Ag conductive filament with a positive voltage on the Ag electrode.

that the Γ^- ions migrate towards the opposite direction of the electric field [10].

For the Ag element, the atomic content significantly increased towards the cathode and decreased dramatically at the interface between the Ag electrode and the perovskite layer. This means that atomic Ag migration occurred under an applied electric field. As a result, the resistance decreased due to a formed Ag filament that bridged both electrodes. Fig. 4d exhibits the formation process of the conductive filament with a positive voltage on the Ag electrode. Meanwhile, it has been previously explained that the Ag migration can be ascribed to thermal driven diffusion and bipolar electrode effects [39,40]. Under a voltage stress, the current passes throughout the entire resistance switching layer and heats some regions, which provides a thermal channel for Ag migration towards the cathode with the aid of the bipolar electrodes. At the same time, oxidation reactions occur in the interface between the Ag electrode and the perovskite layer [41,42]. After oxidation, the Ag^+ migrates through the perovskite layer and is again reduced into atomic Ag with the electrons from the cathode. This explains why the Ag content at the interface region decreased dramatically after the voltage was applied.

However, in the Ag-based device, it is still unclear whether the intrinsic properties of the OHPs or the Ag dominate regarding the switching behavior. It is noteworthy that the electrical characteristics of the Ag-based device in Fig. 2a are different from that of the Au-based device in Fig. 3b and c.

Firstly, the conductance of the Ag-based device gradually grew with a repeated forward scan voltage, while the conductance of the Au-based device gradually reduced. Secondly, in the same scan interval (0 to +0.5 V), the current intensity of the Ag-based device was larger than that for the Au-based device.

As the previous analysis, ionic migration and the resulting built-in potential field contribute to the I - V switching characteristics in the Au-based device. The Ag^+ ions dominate the resistive switching properties of the Ag-based device, since Ag is easily oxidized by an electric field and migrates in the field direction. When a positive bias was applied to the Ag electrode, Ag atoms could be dissolved to Ag^+ ions, which subsequently diffused towards the bottom FTO electrode and were reduced to atomic Ag, in the switching layer. Thus, the Ag atoms gradually piled-up between the Ag and FTO electrodes and Ag conducting filaments were grown from the reduced Ag atoms, leading to a narrowed electrode separation. Therefore, when a periodic positive voltage was applied to the Ag electrode, the gap between the top and the bottom electrodes decreased and the lateral width of the conducting filaments increased, which resulted in the increasing current (Fig. 2c). By contrast, with a successive negative bias, the Ag conducting filaments gradually decreased due to the Ag oxidation, which led to the decreasing current (Fig. 2d).

In Fig. 2a–d, when the SET voltage was 0.5 V, the device conductance continuously changed with the cyclic stimuli. This change was related to both the amount of stimulations and the stimulus frequency [43,44]. Next, frequency-dependent tests (Fig. 5a) illustrate spike-rate-dependent plasticity (SRDP) [16,45], one of the basic characteristics of synaptic plasticity. To investigate the influence of the spiking rate, we used pairs of consecutive pulses separated by different intervals, where each stimulation cycle was one pulse (0.5 V at 1 ms). Fig. 5a demonstrates the relationship between the weight change (ΔW) and the pulse interval with successive pulses. The weight change is given by $\Delta W = (G_n - G_1)/G_1$, where ΔG is the change in conductance between two pulses, and G_1 and G_n are the initial and n -th pulse conductance, respectively.

When the stimulation interval was short (10 μs), the

Figure 5 The short-term plasticity of the synapse and stability of the Ag/FA_{0.83}MA_{0.17}Pb(I_{0.82}Br_{0.18})₃/FTO device. (a) The change in the conductance (weight) percentage given by different pulse intervals. When the pulse interval increases from 10 μ s to 100 ms, the weight change reduces with the rise of pulse number and finally reverses. (b) Retention behaviors of the device. (c) I - V characteristics of the device over 3 days. (d) The fluctuation in HRS and LRS corresponding to (c).

weight change increased significantly with an increase in the number of pulses, which was similar to the paired-pulse facilitation (PPF) [46] in bio-synapses. As the stimulation interval increased, the increase in the weight change became less pronounced. In fact, the weight change began to decrease as the stimulation interval increased to 100 ms, which was similar to the paired-pulse depression (PPD) in bio-synapses [46].

In bio-synapses, stimulation from the pre-synapses triggers the release of calcium ions. Their concentration affects the release of neurotransmitters, which amplifies the ability of synapses to transmit signals. However, the concentration of calcium ions gradually returns to its initial value over time. When the interval between two stimulations is less than the time when the concentration of calcium ions returns to the initial state, the response of the post-synapses is stronger than the previous one, which is called PPF. Similarly, if the interval between the two stimulations is more than the time, the calcium ions channels are partially inactivated before the second stimulation comes. In this case, the calcium ions concentration is lower than the previous value, and therefore the response of the post-synapses is weaker than the previous one, which is called PPD [47]. The above experimental results demonstrate that the memory device shows a functionality that is analogous to artificial

synapses. Thus, when a pulse train with varying intervals is applied, the memory device exhibits different bio-synaptic characteristics (PPF and PPD), which is consistent with the current research on PPF and PPD memristor artificial synapses [48,49].

The above observations may be due to the accumulation of Ag⁺ in the perovskite films, which leads to the gradual growth of Ag conductive filaments between the two electrodes during the short intervals of continuous stimulations. When a pulse train with long intervals is applied, the facilitation turns into depression, because the strength of the applied electric field is weakened with longer pulse intervals and the spontaneous diffusion effects of the Ag atoms are dominant [48]. By observing the dependence of the weight change and stimulation frequency, we were able to simulate the synaptic short-term plasticity from PPF to PPD.

When the SET voltage was 0.8 V, the device exhibited a threshold switching characteristic, as given in Fig. 2e, under a DC voltage bias sweep. To verify the stability of the HRS and LRS, the retention of each state was measured at a reading voltage of 0.05 V for 5.2×10^3 s, as shown in Fig. 5b. In this case, the memory device exhibited good non-volatile characteristics. We further characterized the electrical properties to demonstrate the stability in Fig. 5c and d. The inverse hysteresis window of the curve ($0 \rightarrow -1.5 \rightarrow 0$ V) tested on the fourth day became smaller, while both the HRS and the LRS became larger. A window of 10 times (HRS/LRS) indicated the stability of the device.

CONCLUSION

We demonstrated a device that exhibits resistive behaviors based on the material structure Ag/FA_{0.83}MA_{0.17}Pb(I_{0.82}Br_{0.18})₃/FTO. The conductive Ag filaments play a decisive role in the resistive behavior. By controlling the appropriate SET voltage, two kinds of resistance characteristics of an analog switch and threshold switch can be realized. When the SET voltage is low, the analog switching characteristics can be realized through the successive growth and contraction of the conductive Ag filaments. The device conductance continuously changes with consecutive voltage pulses and mimics the short-term plasticity of the synapses (PPF and PPD), which can be useful in the future neuromorphic computing devices. When the SET voltage is high, we realized the threshold switching characteristics through the formation and fracturing of the Ag conductive filaments. The conductance was abrupt with the applied voltage and had a suitable switch window and hold time. Thus, the pro-

posed device can be a promising candidate for non-volatile memory applications.

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Author contributions Huang Y and Zhao Z, Wang C and Wu H designed the experiment. Huang Y prepared the perovskite precursor solution, characterized the SEM, AFM, XRD, EDS of all the films and electrical features of all devices. Fan H prepared the perovskite films and participated in the characterizations. Huang Y, Wang C and Zhao Z prepared the manuscript. Bian J, Yang Y and Wu H helped revise the manuscript. The final version of the manuscript was approved by all authors.

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电导金属细丝主导的杂化钙钛矿基存储器

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摘要 有机-无机杂化钙钛矿(OHPs)作为太阳能电池中的光吸收材料备受重视, 并且在电阻开关(RS)存储器的应用中引起了广泛关注. 以前的研究表明, 在外电场作用下钙钛矿中的离子能够发生迁移并形成导电通道. 然而, 主导其阻变行为的是Ag还是卤素仍然存在争议. 本文中, 我们研究了一种基于Ag/FA_{0.83}MA_{0.17}Pb(I_{0.82}Br_{0.18})₃/FTO(掺杂的氧化锡)的电阻开关存储器. 在开启过程(在Ag电极端施加正向扫描电压)完成后, 我们通过EDS(能量色散X射线谱)发现了银离子和卤素离子的迁移. 并通过对比基于Au电极器件的电流-电压特征曲线, 发现由Ag形成的导电通道是影响Ag基器件开关特性的主要因素. 同时, 通过控制合适大小的开启电压, 基于Ag电极的电阻开关器件实现了模拟开关和阈值开关两种不同的阻变开关特性. 因此, 在未来有可能在单个器件中同时实现数据存储和神经形态计算两种功能.