Electronic Supplementary Material (ESI) for Nanoscale
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Brownmillerite Thin Film as a Fast Ion Conductor for the High-Performance Resistance Switching Memory

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Keywords: resistive switching memory; brownmillerite thin film; 111 growth orientation; high endurance; uniform switching parameters

Supplementary Information I

Morphological change of the top electrode with the bias voltage and switching mechanism

The formation of filaments during electroforming is frequently associated with other physical changes in the structure of a ReRAM material. These changes include the morphological change of the top electrodes, in some cases creating bubbles, craters, or dendrite-like structures.[1-3] All these changes strongly suggest that localized Joule heating took place. In the proposed device, when an initial bias was applied along the positive direction, the morphology of the top electrode changed, as shown in the field emission scanning electron microscopy (FESEM) image in Figure S1a, but when an initial negative voltage bias was

applied, the top electrode became brighter, and local bubble-like structures were seen, as shown in the FESEM image in Figure S1b. A similar bubble formation of the top electrode was observed by Yang et al. in their Pt/TiO_2/Pt device, and they attributed this physical change in the top electrode to the O_2 gas eruption and Joule heating.[1] These morphological changes suggest that strong Joule heating occurs while applying a negative voltage. The reason for the abnormal electroforming behavior of this specific stacked material (i.e., electroforming occurs in the negative bias region whereas the set occurs in the positive bias region) can be found in the asymmetric current-voltage (I-V) curve of the pristine sample shown in Figure S1c. The current at -3 V was ~1.5 times higher than that at +3 V, which might have been induced by the asymmetric Schottky barrier at the Au/BM-SFO and BM-SFO/SRO interfaces. Therefore, the Joule heating effect could have been higher when the negative bias was applied, and there could have been greater chances of achieving electroforming under this condition. The deformation of the top electrode was quite notable, as can be seen in the embedded video clip. During the I-V sweep into the negative bias direction, the electrode started to shine abruptly within only several seconds when a sufficiently high voltage was applied, reflecting a very abrupt change in the Au electrode morphology. The shining is due to the diffuse scattering of light. Such effect can also be understood from the very fast oxygen transport across the BM-SFO film. When a high-enough negative bias was applied, the oxygen atoms adsorbed on and within the Au electrode from the atmosphere drifted towards the BE interface and piled up there because the underlying SRO/STO are much less efficient in transporting oxygen atoms. Then oxygen gas bubbles were formed at that interface, and the entire structure started to be damaged by the bubble formation and even by the delamination, as can be seen in Figure S1b. Therefore, the electroforming voltage and time duration must be carefully controlled so as not to induce too much deformation of the structure. In contrast, when the positive bias was applied, the oxygen ions within the SRO/STO substrate had to be dragged towards the Au TE, which must have been considerably less active compared with the opposite bias case. The lower Joule heating under this condition also lowers the chance of oxygen migration across the entire electrode area. It must be noted that this may not be the case once the device is electroformed and local current flows afterwards, which ensures fluent oxygen exchange between the BM-SFO and SRO layers during normal ReRAM operation.

The reason for the formation of an intermediate RS immediately after the electroforming (see Figure 3a in the main text) is not clearly understood. The slight structural deformation/distortion of the lattice by the excessive oxygen incorporation, however, may adversely interfere with the electrical conduction at this state. After the application of the

normal set voltage (into the positive bias direction), such structural defect can be cured, and the normal RSs set in, and a stable RS can be achieved afterwards. The CF-based switching mechanism can be further backed up by the electrode area dependency of the resistance shown in the section below.

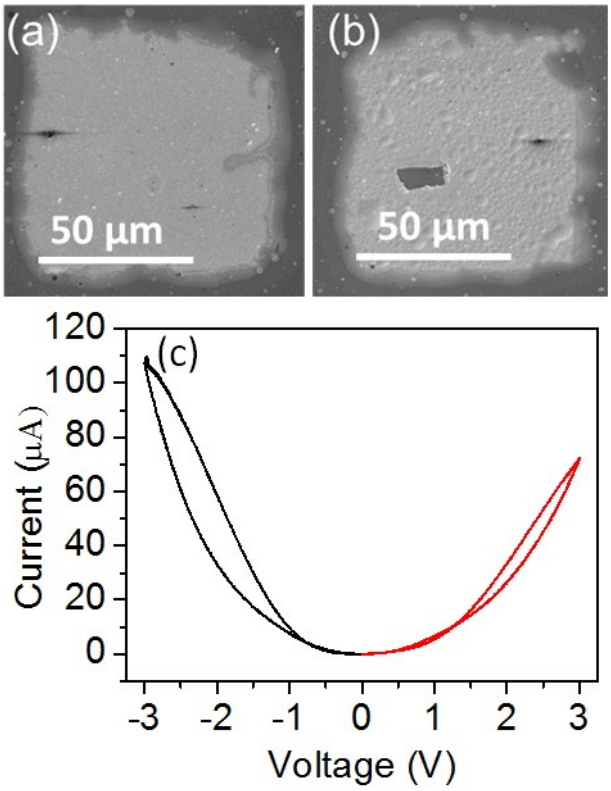

Figure S1. FESEM image of the top Au electrode for the (a) positive bias and (b) negative bias. (c) Current-voltage plot (linear scale) of the pristine sample at 3 V, measured before electroforming.

Supplementary Information II

Cell area dependence of the low resistance state (LRS) and high resistance state (HRS)

The area dependence of each RS can provide a clue to the underlying resistive switching mechanism. Figure S2 shows the resistances of the LRS and HRS for cells with different cell areas. As the cell area increased, the LRS resistance remained approximately constant while the HRS resistance depended much on the area. For the cells with 150X150 μm^2 areas, the switching behavior practically disappeared, possibly due to the high leakage current. The resistance-cell area relationship is an indirect approach used to demonstrate the switching

mechanism.[4] The weak dependence of the LRS resistance on the cell area suggests that the Au/BM-SFO/SRO switching mechanism was the filamentary conducting path model.[10] The area-dependent current of the HRS implies that the leakage current flowed uniformly across the entire area of the memory cell.

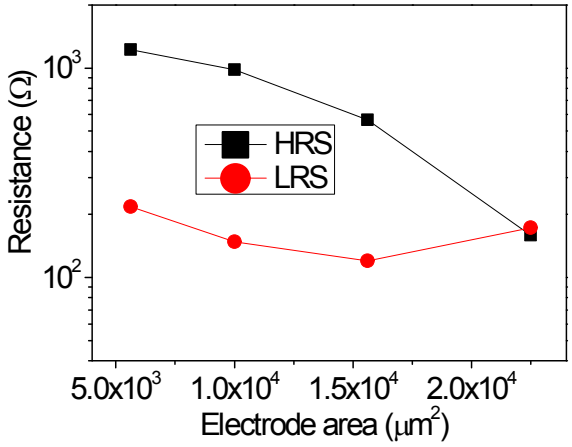

Figure S2. Cell area dependence of the LRS and HRS after the set and reset steps.

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