

Supplementary Information

Effects of the Heterointerface on the Growth Characteristics of a Brownmillerite SrFeO_{2.5} Thin Film Grown on SrRuO₃ and SrTiO₃ Perovskites

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S1. Multi-domain structure of BM-SFO thin film

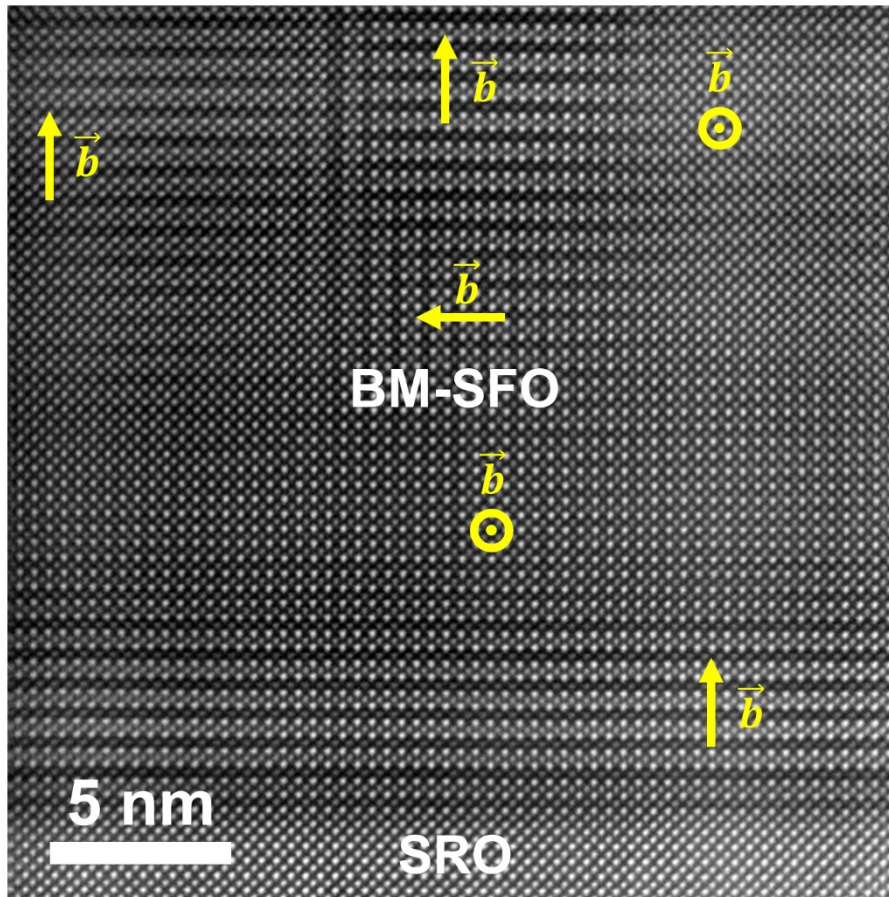


Figure S1. Cross-sectional HAADF-STEM image showing a multi-domain structure of BM-SFO thin film grown on SRO/STO(001). Homogeneous region showing the stacking of FeO_6 octahedra and FeO_4 tetrahedra along the b -axis is observed right above the SFO/SRO heterointerface, as also shown in Fig. 3a. BM-SFO domains with three orthogonal orientations, on the other hand, are observed over the homogeneous region. This indicates the following growth mechanisms; single crystalline BM-SFO thin film is grown along b -axis on the whole surface of SRO/STO(001) substrate, then BM-SFO multi-domains form with three different growth orientations of $[100]_{\text{pc}}$, $[010]_{\text{pc}}$, and $[001]_{\text{pc}}$ to relax the strain from the lattice mismatch with the substrate. The preferential growth direction of the BM-SFO thin film in the multi-domain region was found to be along the b -axis. The direction of the b -axis of the BM-SFO phase is identified with yellow arrows in the domains.

S2. Nonuniform resistive switching behavior of Au/BM-SFO/SRO/STO device

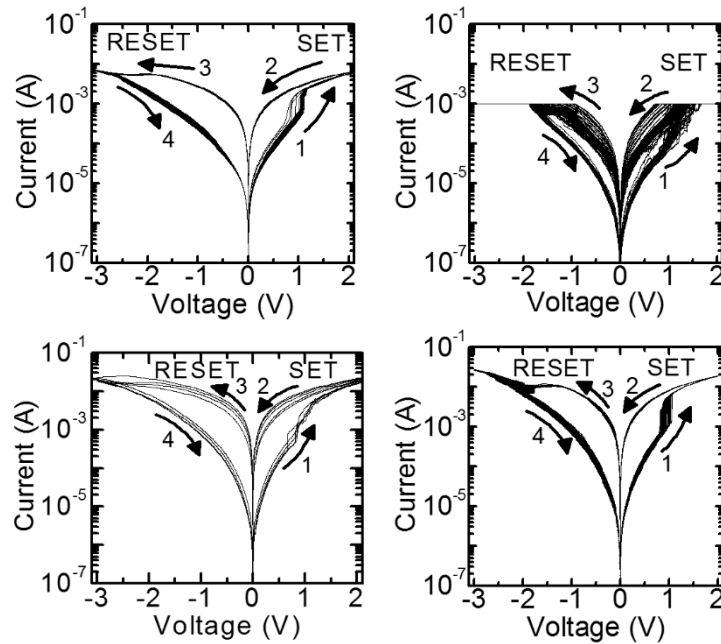


Figure S2. I-V hysteresis loops in four different Au/BM-SFO/SRO resistive switching devices.

Structural inhomogeneity such as multi-domain structure formed within BM-SFO thin film might cause unreliable resistive switching behaviour of the device. BM-SFO/SRO/STO(001) system was applied to the resistive switching device with Au and SRO as top (TE) and bottom electrodes (BE), respectively. Figure S2 shows four I-V curves during resistive switching of four different Au(TE)/BM-SFO/SRO(BE) devices with multi-domain structure in BM-SFO film. These four I-V hysteresis display completely different resistive switching behaviour, such as SET and RESET voltages, and resistances in high and low resistance states, representing poor device to device uniformity. Nonuniform resistive switching behaviour during repeated cycles was also observed even in a single device. Such a nonuniform switching behaviour might be associated with multi-domain structures in the BM-SFO film which hinder the motion of oxygen vacancies in the film, and thus the formation of conducting filaments between both electrodes.^{1,2} From these results, we may conclude that controlling and understanding the structural homogeneity of a switching layer during crystal growth have significant implications in realizing the uniform and reliable resistive switching behaviour.

S3. Other types of heterointerface between the BM-SFO thin film and the STO substrate

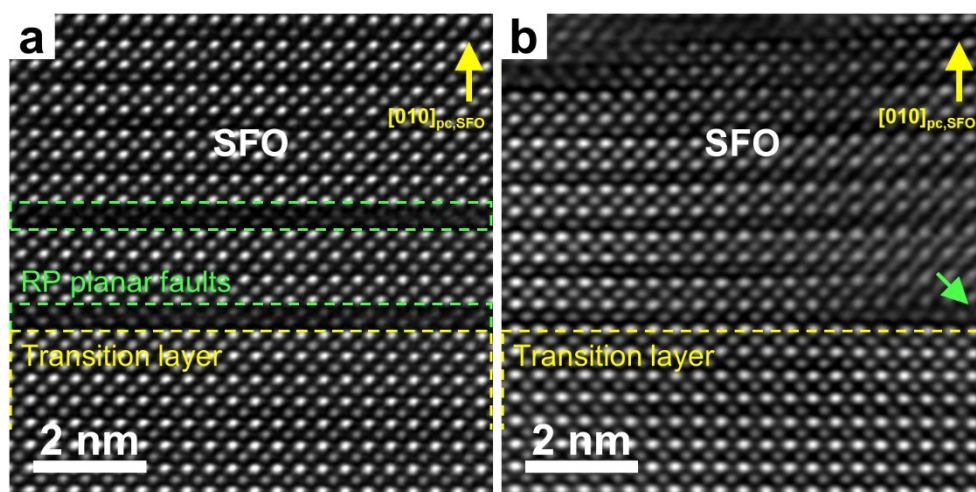


Figure S3. Interfacial structures between BM-SFO and the STO substrate. **(a)** Double RP planar defects formed above the transition layer at the heterointerface. **(b)** No RP planar defects at the heterointerface. A planar defect began to appear at the position marked with a green arrow. The heterointerface was mainly composed of a transition layer and an RP planar defect (Fig. 3c), but other types of interface were also present, as shown in (a) and (b).

S4. Variation in the thickness of the *perovskite-like* SFO layer

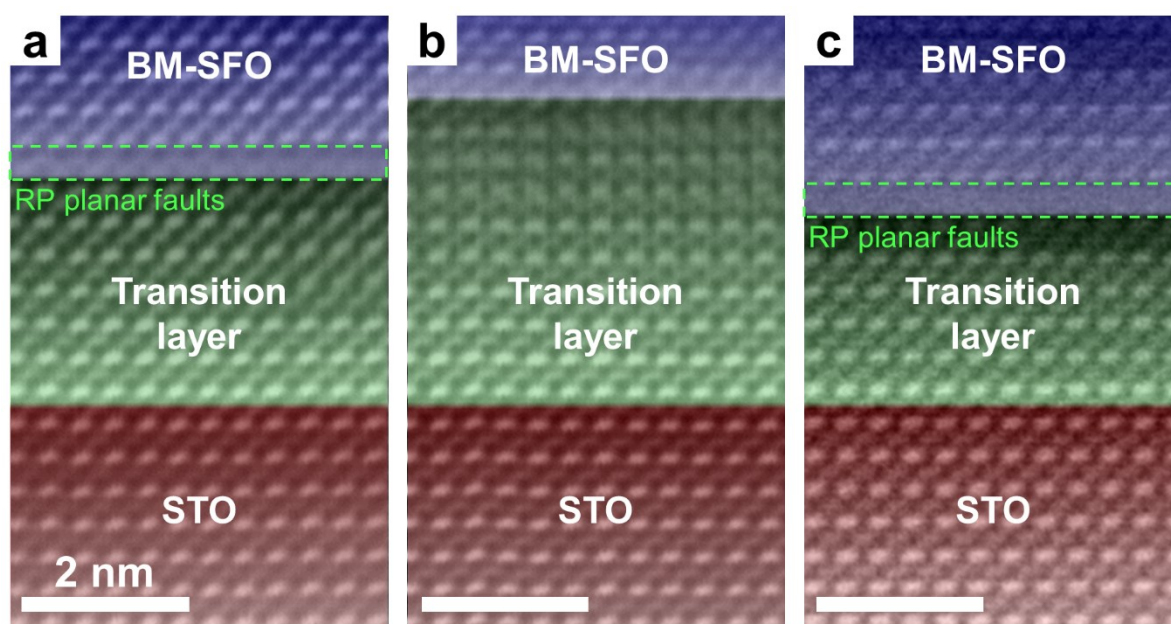


Figure S4. Thickness variation of the *perovskite-like* SFO layer. (a–c) HAADF-STEM images of the BM-SFO/STO(001) heterointerface at three different locations. The regions corresponding to the STO substrate, transition layer, and BM-SFO thin film are coloured in red, green, and blue, respectively. These regions were verified by a series of EELS measurements across the heterointerface; the same procedures were performed in Fig. 4. The thickness of the *perovskite-like* SFO layer varied slightly with location, ranging from 1–5 nm.

S5. Oxygen concentration across the thin film/transition layer interface

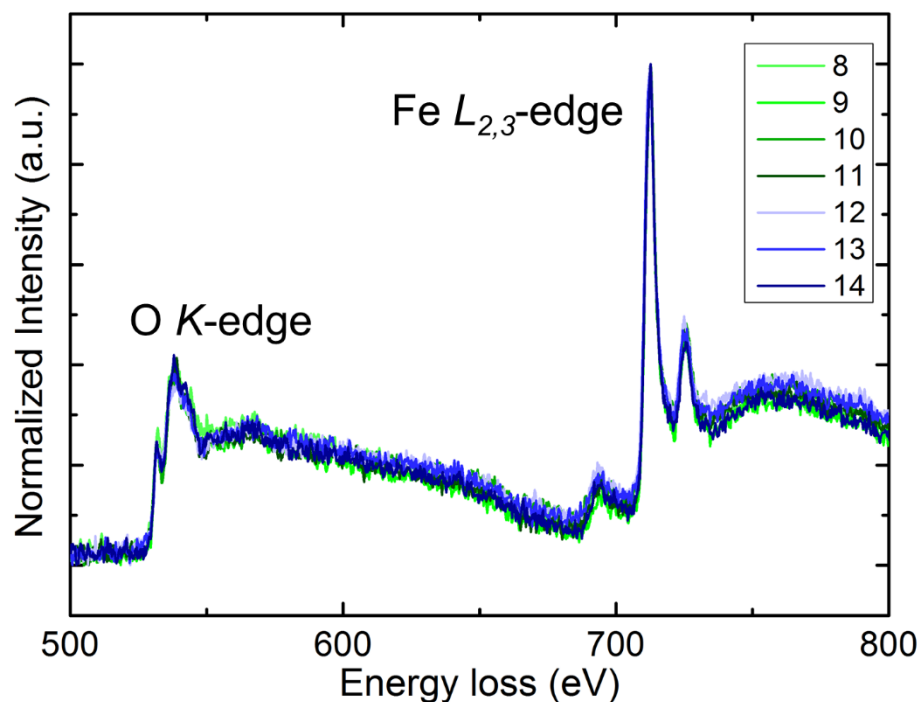


Figure S5. A series of ELNES acquired across the interface between the transition layer and the BM-SFO thin film of the BM-SFO/STO(001) specimen. For the comparison of oxygen concentration, the spectra are normalized by the maximum intensity of Fe L_{3} -edge peaks and overlapped each other. The graph clearly shows that the intensities of the O K -edge peaks and their backgrounds are almost same, which indicates that the oxygen concentration almost remain constant across the interface. This further confirms that the transition layer exhibits the $\text{SrFeO}_{2.5}$ phase and thus the Fe valence state of $3+$. Each spectrum is labelled in the same manner as Fig. 4 (8–11: transition layer, 12–14: BM-SFO thin film).

S6. Discussion on the EELS spectra in SrFeO₃ and SrFeO_{2.5}

The cubic structure in the transition layer may originate from the SrFeO₃ phase having an oxygen stoichiometry of 3. If so, the valence state of Fe would be 4+, which exhibit different Fe *L*-edge from that of BM-SFO phase having the Fe valence state of 3+. The valence state of SrFeO_{3-x} can be investigated by ELNES and X-ray absorption near edge structure that exhibit different features, *i.e.* chemical shift or fine structure shape, depending on the valence state of the element in the material. Q. Liu *et al.* reported that the peak position in the Fe *L*_{2,3}-edge of SrFeO_{2.5} is 1–2 eV lower than that of SrFeO₃.³ Additionally, M. Haruta *et al.* and J.-S. Kang *et al.* reported that SrFeO_{2.5} and SrFeO₃ exhibit different O *K*-edge shapes.^{4,5} These results clearly illustrate differences in the near-edge structures depending on the valence state of Fe and oxygen stoichiometry of the compound. However, this is not the case in our EELS results as shown in Fig. 4, which suggests the same valence state and oxygen stoichiometry between the transition layer and the BM-SFO thin film.

References

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