Electronic Supplementary Information for

## Ferroelectric Resistive Switching Behavior in Two-Dimensional

## Materials/BiFeO3 Hetero-Junctions

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## **EXPERIMENTAL SECTION**

**Preparation of BFO on Nb:STO substrate by pulsed laser deposition (PLD).** The BiFeO<sub>3</sub> (BFO) films with thickness of 35 nm were grown on (001) Nb-doped SrTiO<sub>3</sub> (Nb:STO) substrate by pulsed laser deposition (PLD). The target was ablated by a KrF laser at a wavelength of 248 nm, 10Hz repetition rate, and a fluence of 2 J cm<sup>-2</sup>. The chamber was pumped to  $5 \times 10^{-6}$  Torr base pressure for PLD. During PLD for BFO growth, the oxygen pressure was maintained at 5 mTorr. The substrate temperature was 600 °C. The distance between the substrate and the targets was 6 cm.

**Transfer of graphene and MoS<sub>2</sub> onto BFO substrate.** Bilayer and few-layer graphene were directly transferred onto BFO substrates. Optical image and AFM were used to determine the thickness of graphene. Monolayer and fewlayer MoS<sub>2</sub> were first transferred onto silicon oxide (300 nm oxide layer) and the thickness of MoS<sub>2</sub> was determined by optical microscopy, AFM and Raman spectroscopy. Then, MoS<sub>2</sub> was transferred onto BFO substrates by wet transfer method described before.

Scanning probe microscope measurements. AFM topography, Kelvin probe microscopy (KPFM) and conductive AFM measurements were conducted on Bruker Dimension ICON-PT with Co/Cr tips. For KPFM measurements, a DC voltage of 0.9 V and liftheight of 20 nm were applied. For the piezoresponse image and local domain swithcing, a AC voltage of 0.8 V with 19 kHz and  $\pm$  4V were applied to the tip. PFM phase/amplitude hysteresis curves were measured after the application of a dc voltage.



Figure S1. X-ray diffraction pattern of BFO on NSTO substrate.



Figure S2. Out-of-plane (top) and in-plane (down) piezoforce microscopy images of BFO film on NSTO substrate.



Figure S3. Phase (a) and amplitude (b) hysteresis of BFO/NSTO.



Figure S4. (a) AFM topography, (b) surface potential mapping, (c) phase image and (d) amplitude image of graphene on BFO with/without ±4 V poling.

Figure S4a shows the AFM image of another trilayer graphene on top of BFO. The thickness is  $\sim 1 \text{ nm. } \pm 4 \text{ V}$  bias was applied to the AFM tip to pole the BFO, and then the surface potential and pieroresponse of BFO were measured by Kelvin probe microscopy by Piezoresponse force microscopy. As presented in Figure S4b, the contact potential difference (CPD) clearly correlates with the patterned domain structure. The potential difference between adjacent domains was 200 mV. The CPD contrast is due to the variation of carrier density distribution between the adjacent ferroelectric domains with opposite polarization field. Figure S4c and d presents the piezoresponse behavior of BFO measured by Piezoresponse force microscopy (PFM), where a clear amplitude and phase contrast was observed after writing patterns with alternative +4 and -4 V biases on the tip. These results clearly indicate the ferroelectric nature, which further supported by the butterfly-like amplitude and hysteresis behavior of the phase signal in the local PFM measurement shown in Figure S3. PFM amplitude contrast suggests that the polarization induced by a voltage pulse is not decayed before the image has been acquired.



Figure S5. Hysteresis behavior of trilayer graphene/BFO hetero-junction.



Figure S6. Hysteresis behavior of thick graphite/BFO hetero-junction. The thickness of of thick graphite is about 12 nm.



Figure S7. (a) Topography of few-layer graphene/BFO/NSTO and (b) corresponding current mapping measured by conductive AFM with tip bias of around 0.5 V. (c) The current section profile along the yellow dash line in b.



Figure S8. (a) Phase and (b) amplitude hysteresis behavior of bilayer MoS<sub>2</sub>/BFO hetero-junction. (c) *I-V* curves of bilayer MoS<sub>2</sub>/BFO hetero-junction for upward and downward polarization in a linear scale. (d) The reading voltage dependence of the resistance ON/OFF ratio.



Figure S9. Phase and amplitude hysteresis behavior of thick  $MoS_2/BFO$  hetero-junction. The thickness of of  $MoS_2$  is about 5-layer (xx nm).



Figure S10. (a,b) *I-V* curves of fewlayer MoS<sub>2</sub>/BFO hetero-junction for upward and downward polarization in a linear scale and log scale. (c) The reading voltage dependence of the resistance ON/OFF ratio. The thickness of of thick MoS<sub>2</sub> is about 5-layer.



Figure S11. (a) Phase and (b) amplitude hysteresis behavior of thick  $MoS_2/BFO$  hetero-junction The thickness of of thick  $MoS_2$  is about 20 nm. (c) I-V curves of  $MoS_2/BFO$  hetero-junction for upward and downward polarization in a linear scale. (d) The reading voltage dependence of the resistance ON/OFF

ratio.



Figure S12. (a) P-V loop of BFO film. (b) I-V curves of NSTO/BFO/Pt measured by Keithley 2400. (c) I-V curves of NSTO/BFO/Pt measured by conductive AFM.



Figure S13. (a) AFM topography of few-layer  $MoS_2$  on BFO substrate. The thickness of  $MoS_2$  is about 4 nm. (b) Potential mapping of BFO/MoS<sub>2</sub> upon  $\pm$  5 V poling process. (c) Section profiles of potential on BFO (red line) and  $MoS_2$  (blue line). The potential difference of  $MoS_2$  upon  $\pm$  5 V poling process is about 100 mV.



Figure S14. (a) AFM topography of few-layer  $MoS_2$  on BFO substrate. The thickness of  $MoS_2$  is about 20 nm. (b) Potential mapping of BFO/MoS<sub>2</sub> upon  $\pm$  5 V poling process. (c) Section profiles of potential on BFO (red line) and  $MoS_2$  (blue line). The potential difference of  $MoS_2$  upon  $\pm$  5 V poling process is about 15 mV. The potential resolution is about 10 mV.



Figure S15. (a, b) Schematics of energy band diagrams of graphene/BFO/Nb:STO modulated by polarization orientations. (c, d) Charge transport mechanism in high resistance (HRS) and low resistance states (LRS) of MoS<sub>2</sub>/BFO/NSTO.