Supplementary materials

Impact of interfacial effects on ferroelectric resistance switching of $Au/BiFeO_3/Nb:SrTiO_3(100)$ Schottky junctions

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S1 Possible conduction mechanisms

I-V curves of $Au/BiFeO_3/Nd:SrTiO_3(001)$ (Au/BFO/NSTO) structure were fitted and possible conduction mechanisms were examined. For BFO films and other similar ferroelectric perovskite oxides, possible conduction mechanisms were presented in literatures, including of Ohmic conduction, the space-charge-limited current (SCLC), the Poole-Frenkel (PF) emission, the Schottky emission and Fowler-Nordheim (FN) tunneling.[1-3]

If leakage current is dominated by SCLC, where current arises when excess space charges are injected into the conduction band, the leakage current density can be expressed as[4]

$$J_{SCLC} = \frac{9\mu\xi_0\xi_r}{8d}E^2, \tag{1}$$

Where J and E are current density and electric field, μ is the mobility of charge carriers, ξ_0 is the permittivity of free space, ξ_r is the relative dielectric constant, and d is the film thickness.

If leakage current is dominated by PF emission, which arises from field-assisted thermal ionization of trapped carriers into the conduction band of the film, the leakage current density can be expressed as[5]

$$J_{PF} = AE\exp(-\frac{E_I - \sqrt{q^3E/\pi\xi_0\xi_r}}{k_BT}), \tag{2}$$

where A is a constant, E_I is the trap ionization energy, q is the electronic charge, and k_B is the Boltzmann constant.

For Schottky emission, which arises from different Fermi levels between a metal and an insulator or semiconductor, the current density is[6]

$$J_S = BT^2\exp(-\frac{\phi_S - \sqrt{q^3E/4\pi\xi_0\xi_r}}{k_BT}), \tag{3}$$

where B is a constant, T is the temperature, and ϕ_S is the Schottky barrier height.

When injection of charge carriers from electrodes takes place by tunneling through an interfacial energy barrier, which is described by the FN tunneling, the leakage current density can be expressed as[7]

$$J_{FN} = CE^2\exp(\frac{-D\phi_i^{3/2}}{E}), \tag{4}$$

where C and D are constant, and ϕ_i is the interfacial barrier height.

S2 The leakage current fitting of Au/$BiFeO_3$/Nd:$SrTiO_3$(001) structure

Based on Eq. (1)-(4) above, J-E characteristics of SCLC, PF emission, Schottky emission and FN tunneling can be represented by linear relation of J-E^2, ln(J/E)-$E^{1/2}$, ln(J)-$E^{1/2}$ and ln(J/E^2)-

(1/E), respectively. By plotting the leakage data (I-V curve) in various manners as a function of voltage or electric field, we can gain insight into the conduction mechanism. Alternatively, the method of Ln(I)-Ln(V) plots[8] is applied.

Figure S1 shows the linear plots of I-V curves of Au/BFO/NSTO junction. Firstly, we use the method of Ln(I)-Ln(V) plots[8] to fit the processes 1-4 in Figure S1, which is shown in Figures S2a-d. The slope n can be obtained for each fitting, which is neither 1 for Ohmic conduction, nor 2 for SCLC mechanism. Thus, the Ohmic conduction and SCLC mechanisms can be ruled out. For a cross check of the SCLC mechanism, it is also fitted by J-E^2 plots, as is shown in Figures S3a-d. They show exponential trends rather than linear relation.

If the leakage current is PF emission, a linear relation between ln(J/E) vs $E^{1/2}$ with a slope of $\frac{\sqrt{q^3/\pi\xi_0\xi_r}}{k_B T}$ should be obtained. As shown in Figure S4a-d, these plots often show regions with straight fits. To identify whether PF emission is the dominated leakage mechanism, it is necessary to extract the dielectric constant from the slopes of these plots. As reported by Iakovlev *et al.*, the dielectric constant of BFO is 6.25, estimated from a refractive index of n=2.5.[9] From the PF emission fits, dielectric constants significantly deviate from 6.25 are obtained (0.88, 0.94, 16.95 (33.52), 13.06 for processes 1, 2, 3, 4, respectively).

Similar analyses of Schottky emission are presented in Figure S5a-d. Dielectric constants of 0.17, 0.18, 2.18 (4.59), 1.67 are obtained for processes 1, 2, 3, 4, respectively. Since the value obtained from Schottky emission fits significantly deviate from the expected value 6.25 of the dielectric constant for BFO.

In summary, the fitting of ln(J/E^2)-(1/E) shown in Figure 2c and 2d in the main text is the best one comparing to others, and the related FN tunneling is the dominated conduction mechanism in Au/BFO/NSTO structure.

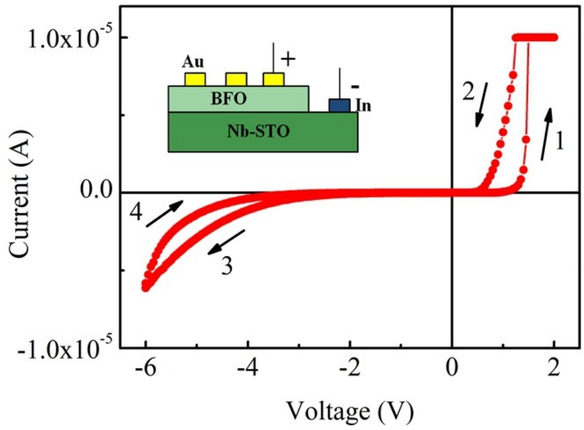

Figure S1 Linear plot of I-V curves of Au/BFO/NSTO junction. The arrows indicate the sweep direction of the applied voltage. The panel of inset schematically indicates the electrode configuration.

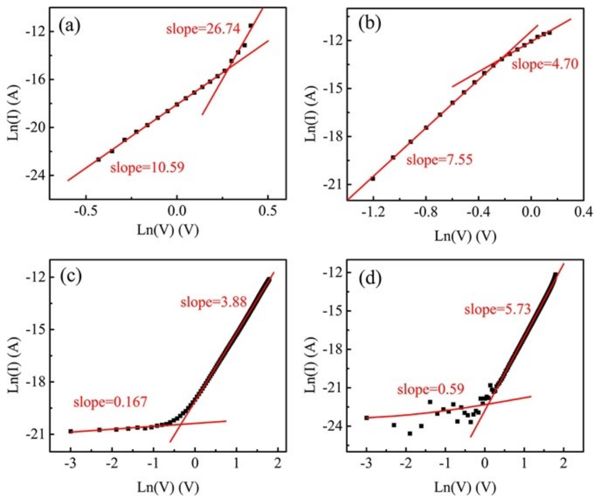

Figure S2a-d The red solid lines are Ln(I)-Ln(V) plots for processes 1-4 of the I-V curves shown in Figure S1, respectively. The slopes n of Ln(I)-Ln(V) plots are also shown.

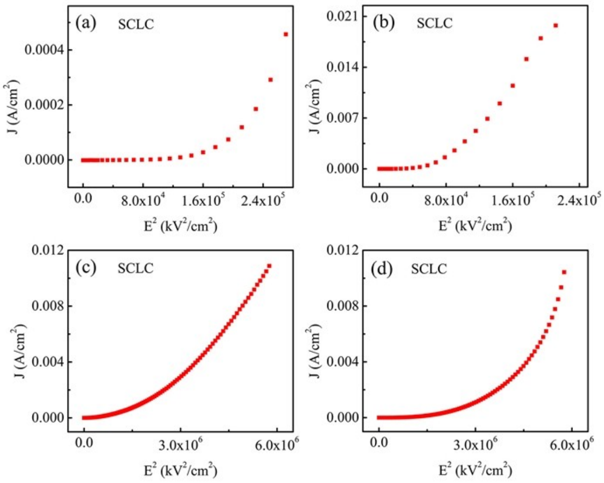

Figure S3a-d J-E^2 plots for processes 1-4 of the I-V curves shown in Figure 1S, respectively.

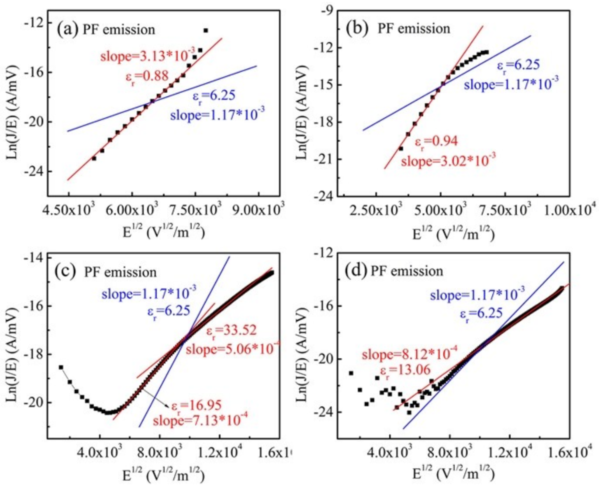

Figure S4a-d Ln(J/E)-E$^{1/2}$ plots for processes 1-4 of the I-V curves shown in Figure S1, respectively. The red lines are the linear fits. The slope of the fits and calculated values of relative dielectric constant ε_r are also shown. The blue lines are linear fits expected for PF emission mechanism when ε_r=6.25 for BFO film.

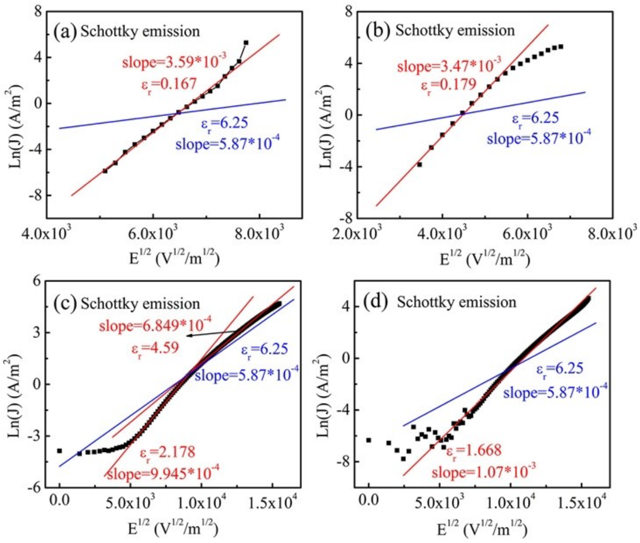

Figure S5a-d Ln(J)-$E^{1/2}$ plots for processes 1-4 of the I-V curves shown in Figure 1S, respectively. The red lines are the linear fits. The slope of the fits and calculated values of ε_r are also shown. The blue lines are linear fits expected for PF emission mechanism when ε_r=6.25 for BFO film.

S3 The comparison of I-V curves for Au/BFO/NSTO and Au/BFO/SRO/STO structures.

Figure S6a and b are the I-V curve for Au/BFO/NSTO and Au/BFO(15nm)/SRO(50nm)/STO structures as a comparison. It indicates that no obvious rectifying diode behavior and no obvious RS behavior is observed in the Au/BFO/SRO structure.

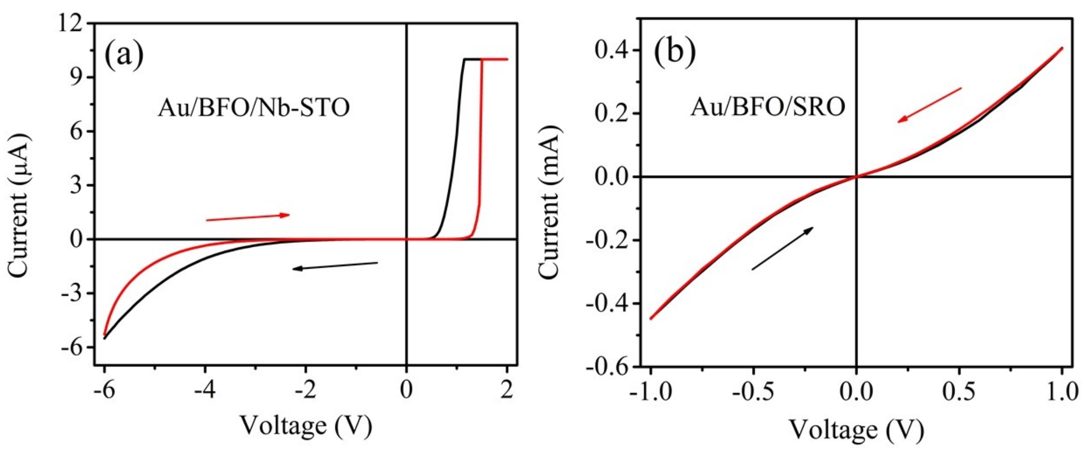

Figure S6 Linear plot of I-V curves of (a) Au/BFO/NSTO junction and Au/BFO/SRO junction. The arrows indicate the sweep direction of the applied voltage.

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