**Supplementary Material**

***In situ* study of phase transition in HZO ferroelectric thin films via TEM electron beam irradiation**

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1. Characterization of electron beam-induced Vo in W/HZO/W capacitors inside TEM

Before the electron beam irradiation, an EDX characterization analysis of the element distribution was performed on the W/HZO/W ferroelectric capacitor. As shown in Figure S1(a), the HRTEM image shows clear lattice fringes in the area to be irradiated, indicating good crystallinity. The elements Hf, Zr, O, and W were evenly distributed, with no obvious element diffusion phenomenon. After irradiating this area with an electron beam for 1 hour, as shown in Figure S1 (b), the HRTEM image clearly shows that the phase in the irradiated area changed, and the regularly arranged lattice fringes in the HZO thin film have almost

disappeared, replaced by a disordered amorphous structure. Meanwhile, the EDX characterization results show that all elements have exhibited a certain degree of diffusion caused by electron beam irradiation. The distribution of the number of Hf atoms and O atoms before and after electron beam irradiation along the growth direction of the HZO thin film was analyzed, and the change in the ratio of Hf atoms to O atoms was taken as the ordinate function, resulting in the semi-quantitative analysis results of Vo concentration in Figure S1(c). The intensity ratio of Hf and O in the red line after irradiation was increased than before in the black line within the HZO layer denoted with green color, thus the Vo in the W/HZO/W ferroelectric capacitor was increased after an hour of electron beam irradiation.

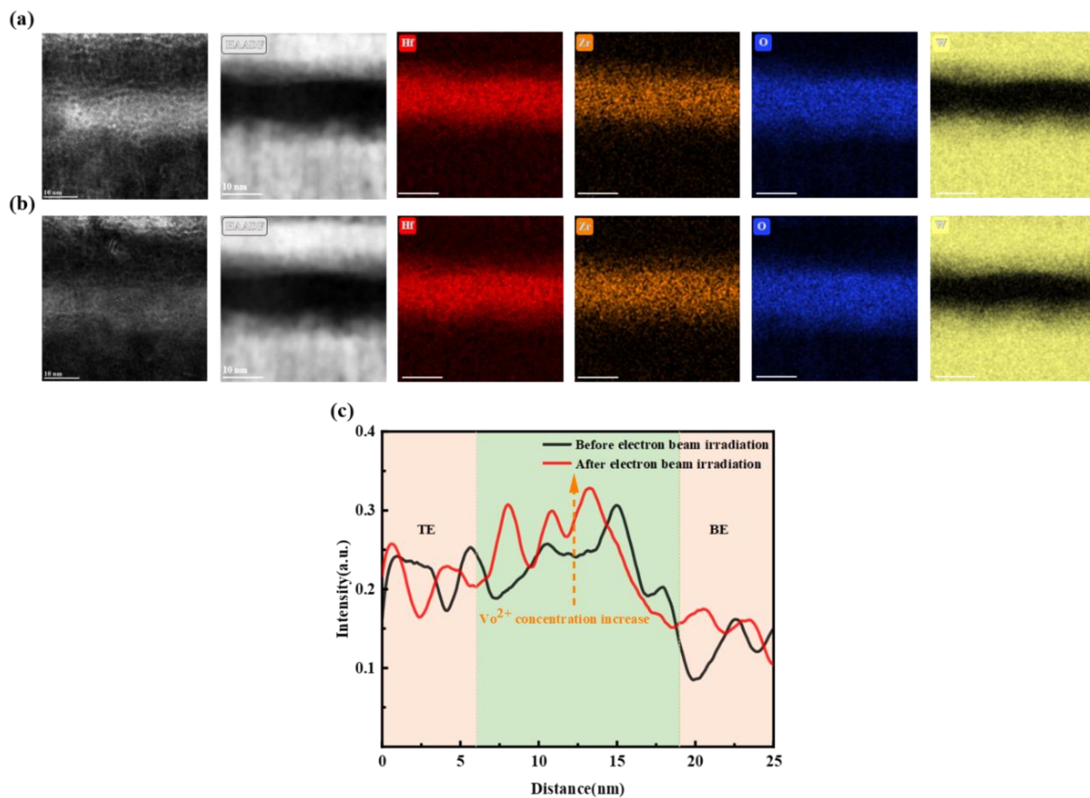


Figure S1. (a) EDX element mapping of the W/HZO/W ferroelectric thin film before electron beam irradiation, (b) EDX element mapping of the W//HZO/W ferroelectric thin

film after electron beam irradiation., (c) Semi-quantitative analysis of Vo concentration before and after electron beam irradiation of the W/HZO/W ferroelectric thin film

2. Ferroelectric phase transition from t-phase to o-phase in HZO thin films by electron beam irradiation

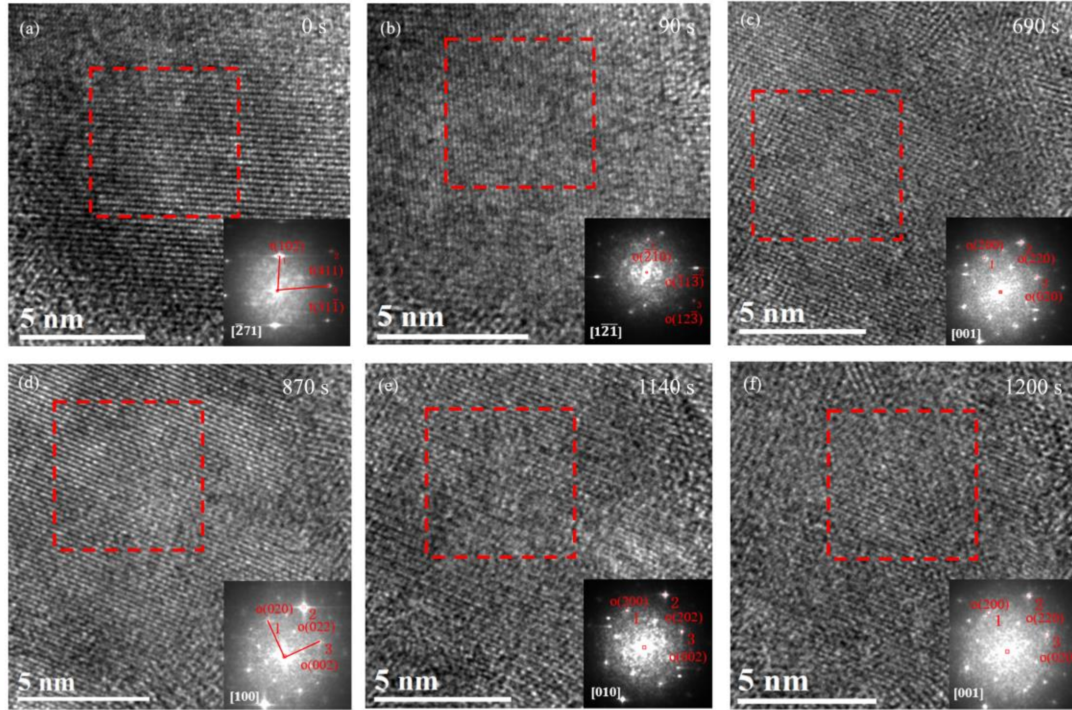


Figure S2. Electron beam irradiation-induced phase transition from t-phase to o-phase and domain flipping in HZO thin film. (a) t-phase before irradiation, (b) phase transition from t-phase to o-phase occurs about 90 s after irradiation, (c) after 690 s of irradiation, the o-phase transforms into a low-index [001] zone axis with in-plane polarization, (d) after 870 s of irradiation, the o-phase transforms into a [100] zone axis with out-of-plane polarization, (e) after 1140 s of irradiation, the o-phase transforms from [100] zone axis to [010] zone axis, (f) after 1200 s of irradiation, the o-phase transforms back into a [001] zone axis with in-plane polarization.

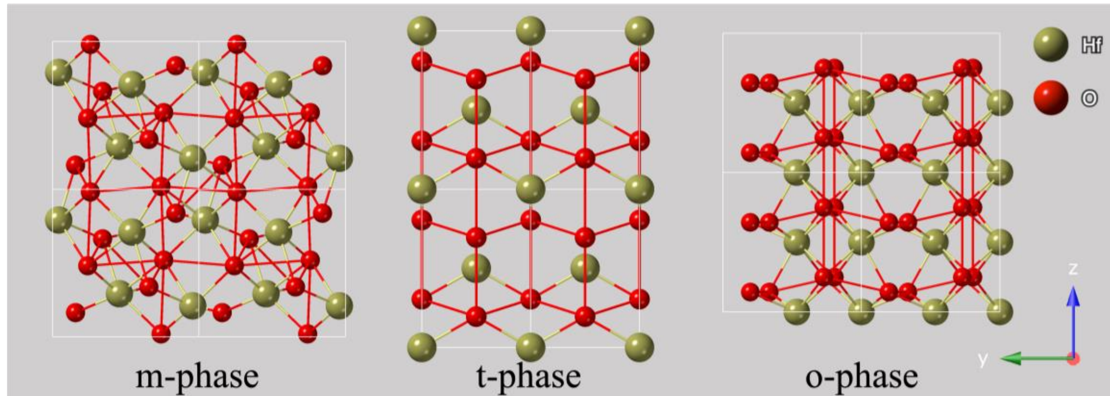


Figure S3. Schematic structure of unit cells of m-, t-, and o-phases $HfO_2$.

Projection area calculation before and after the phase transition from $[1\bar{1}0]$m to [010]o

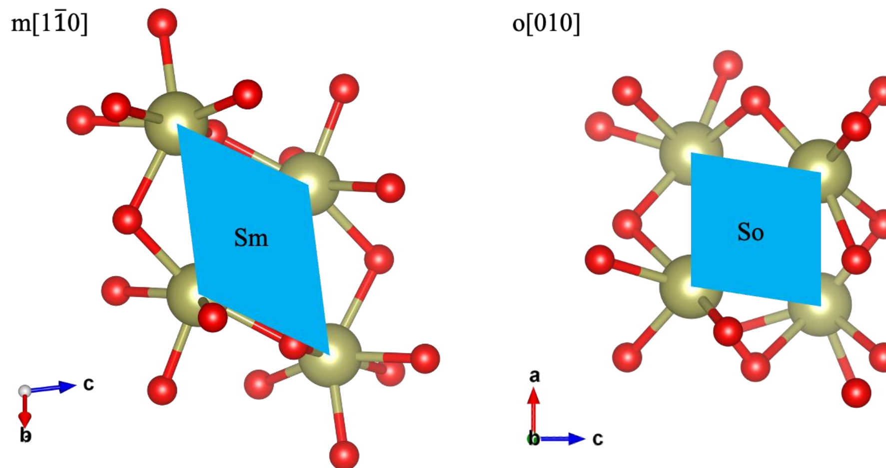


Figure S4. The areas of the unit cell projection planes (Sm for [1-10]m and So for [010]o) were marked in blue color.

3. Crystallinity test of HZO thin films without RTA

Compared to HZO ferroelectric thin films after RTA, the GIXRD results of the HZO films without RTA show only a weak o/t-phase diffraction peak at 2θ=30.5°, as well as diffraction peaks corresponding to the TiN electrode, with no very pronounced diffraction peaks observed. This proves that the phase composition of the HZO films without RTA was almost entirely amorphous.

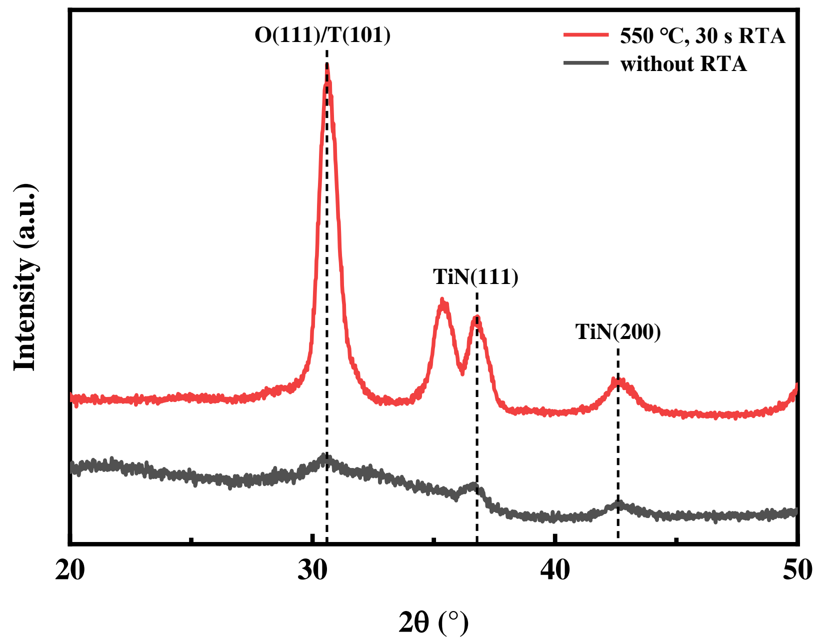


Figure S5. Comparison of GIXRD results of HZO thin films before and after RTA.