Appendix A

Supplementary Information

Silicon-Integrated Lead-Free $BaTiO_3$-Based Film Capacitors with Excellent Energy Storage Performance and Highly Stable Irradiation Resistance

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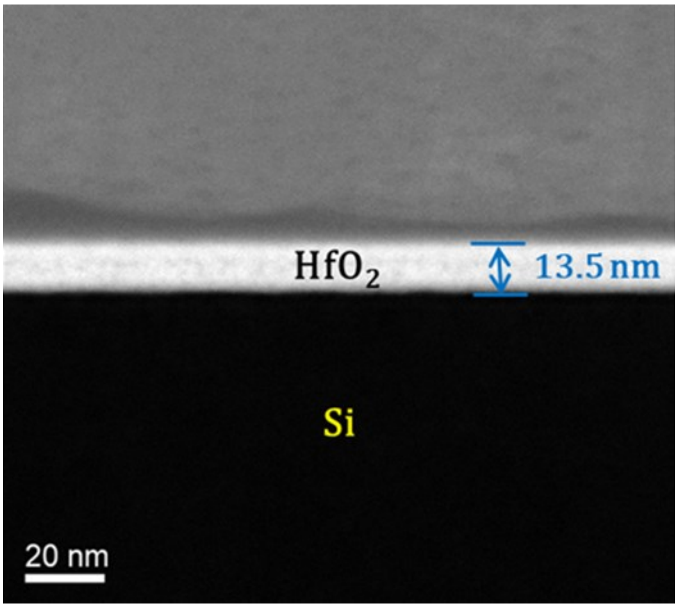

Fig. S1 A low-magnification dark field STEM image of an HfO_2 buffer layer deposited on Si substrate by atomic layer deposition technique.

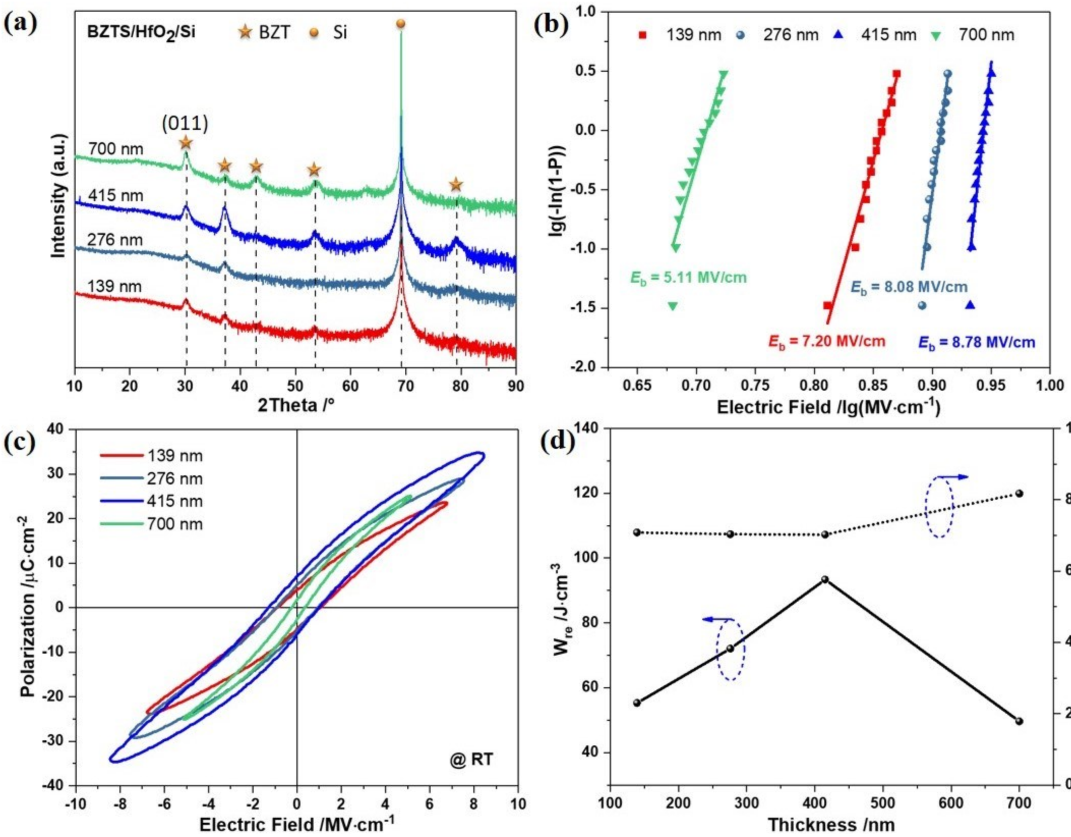

Fig. S2 (a) Typical XRD *θ-2θ* scans of the BZTS/HfO_2 thin films with different thicknesses deposited on Si substrate. (b) The Wei-bull distribution and the fitting lines of E_b for the BZTS/HfO_2 thin films with different thicknesses. (c) *P-E* hysteresis loops of the BZTS/HfO_2 thin films with different thicknesses. (d) W_{re} and η of the BZTS/HfO_2 thin films at room temperature depending on film thickness.

Fig. S2a shows the XRD *θ*-2*θ* scans of the BZTS/HfO_2 thin films deposited on Si substrate with thicknesses of 139, 276, 415 and 700 nm. The results show that the BZTS/HfO_2 thin films of different thicknesses grown on the Si substrate also show perovskite-phase polycrystalline films. It can be seen from the Fig S2a that the diffraction intensity of the BZTS/HfO_2 films increases with increasing thickness, except for the BZTS/HfO_2 films with a thickness of 700 nm. At the same time, we also noticed that the sample with a thickness of 700 nm had a stronger (011) peak, which may be due to its stronger orientation. According to Eq. (1), E_b and P_{max} - P_r are the key parameters determining the W_{re} of dielectric capacitors. The fitting Wei-bull distribution of E_b of the BZTS/HfO_2 thin films with different thicknesses at RT are shown in Fig. S2b. It can be seen that the E_b of the BZTS/HfO_2 thin films first increases and then decreases as the thickness increases. The nonmonotonic variation of E_b with film thickness may be attributed to the following reasons: First, we obtained the highest E_b value (about 8.78 MV/cm) in films with optimized thicknesses of ~415 nm. E_b decreases in thicker films because of the size effect [$E_b \propto 1/\sqrt{thickness}$].[1] Secondly, when the film thickness exceeds a certain level, the contribution of the thinner HfO_2 buffer layer to the breakdown resistance of the film is relatively weak, which may lead to the decrease of E_b. Finally, it may be attributed to the fact that when the film exceeds a certain thickness, its crystalline quality deteriorates as the thickness increases and defects in the film increase, resulting in a decrease in E_b. Fig. S2c shows the *P-E* loops of the BZTS/HfO_2 thin films with different thickness. The energy storage parameters of the BZTS/HfO_2 thin films obtained by *P-E* loops integral calculation are summarized in Table S1. It can be seen that both P_{max} and P_r increase first and then decrease with the increase of film thickness, and P_{max} - P_r reaches the maximum value when the thickness is about 415 nm. Fig. S2d shows the change of W_{re} and η of the BZTS/HfO_2 thin films with the thickness. The results show that the change of W_{re} with thickness of the BZTS/HfO_2 thin films is consistent with that of E_b and P_{max} - P_r. The ultrahigh W_{re} of 93.37 J/cm^3 with η of 70.22% at RT when the film thickness is about 415 nm is mainly due to its higher E_b and P_{max} - P_r.

Table S1

Energy storage parameters of BZTS/HfO_2 thin films with different thickness grown on Si substrate at room temperature

Thickness /nm	E_b /MV·cm^{-1}	P_{max} /μC·cm^{-2}	P_r /μC·cm^{-2}	W_{re} /J·cm^{-3}	η /%
139	7.20	23.65	4.01	55.32	70.83
276	8.08	28.89	5.14	72.08	70.33
415	8.78	34.78	7.07	93.37	70.22
700	5.11	24.96	1.81	49.67	81.73

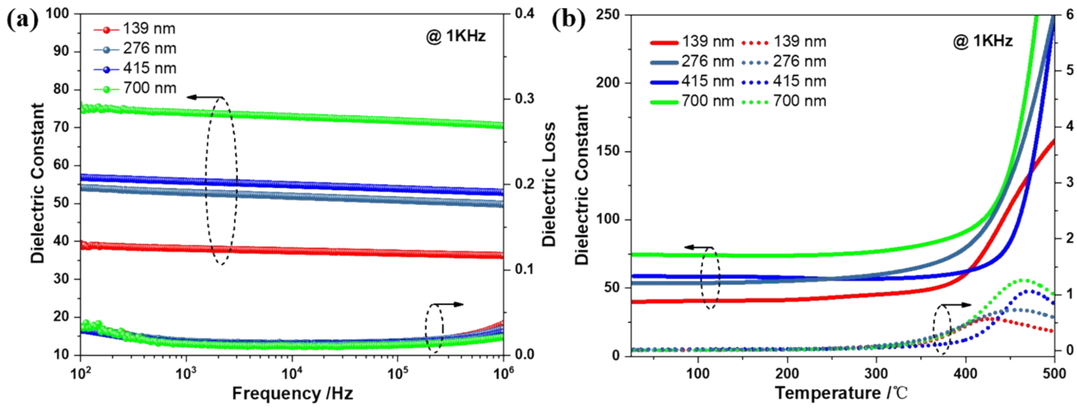

Fig. S3 (a) Frequency dependence of ε_r and tanδ for the BZTS/HfO_2 thin films with different thicknesses at room temperature. (b) Temperature dependence of ε_r and tanδ for the BZTS/HfO_2 thin films with different thicknesses at 1 KHz.

Fig. S3a shows the frequency dependence of ε_r and tanδ for the BZTS/HfO_2 thin films with different thicknesses at RT. The results show that the ε_r of the BZTS/HfO_2 thin films with different thickness decreases monotonously with the increase of frequency. This is mainly due to the polarization relaxation. The ε_r of the BZTS/HfO_2 thin films gradually increases with the increase of the film thickness, which is mainly due to the influence of the interface layer with low dielectric constant on the BZTS/HfO_2 thin films gradually weakens with the increase of the film thickness. In addition, it can be observed from Fig. S3a that the tanδ gradually decreases as the thickness of the BZTS/HfO_2 thin films. Fig. S3b shows the temperature dependence of ε_r and tanδ for the BZTS/HfO_2 thin films of different thicknesses. The results show that the BZTS/HfO_2 thin films with thickness of 415 nm has the best thermal stability.

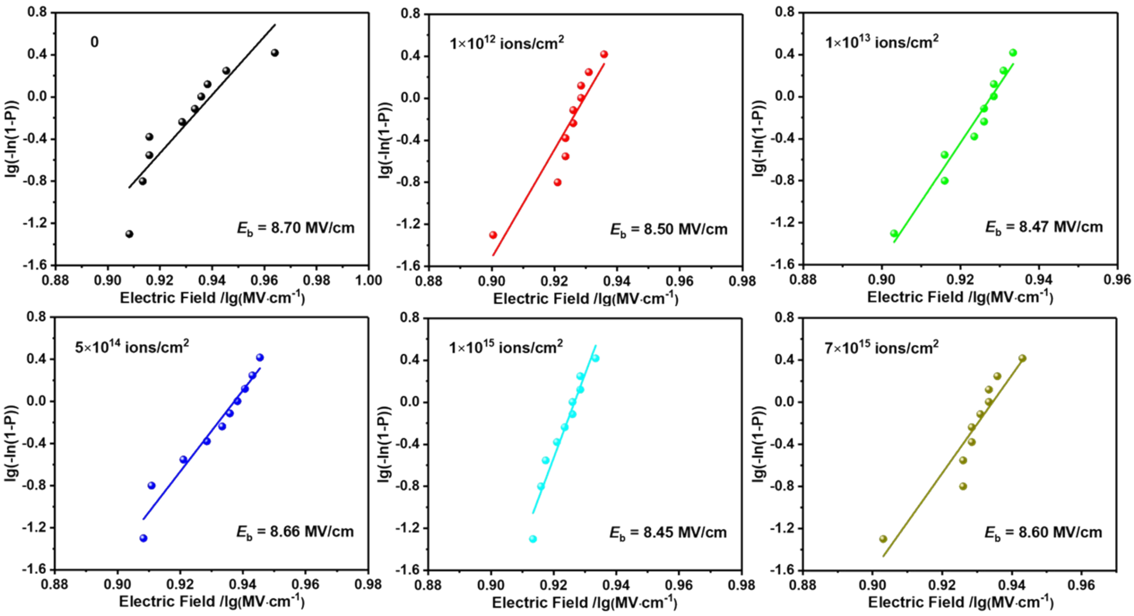

Fig. S4 After He^{+} irradiation with different doses, the Wei-bull distribution and the fitting lines of E_b for the $BZTS/HfO_2$ thin film capacitors.

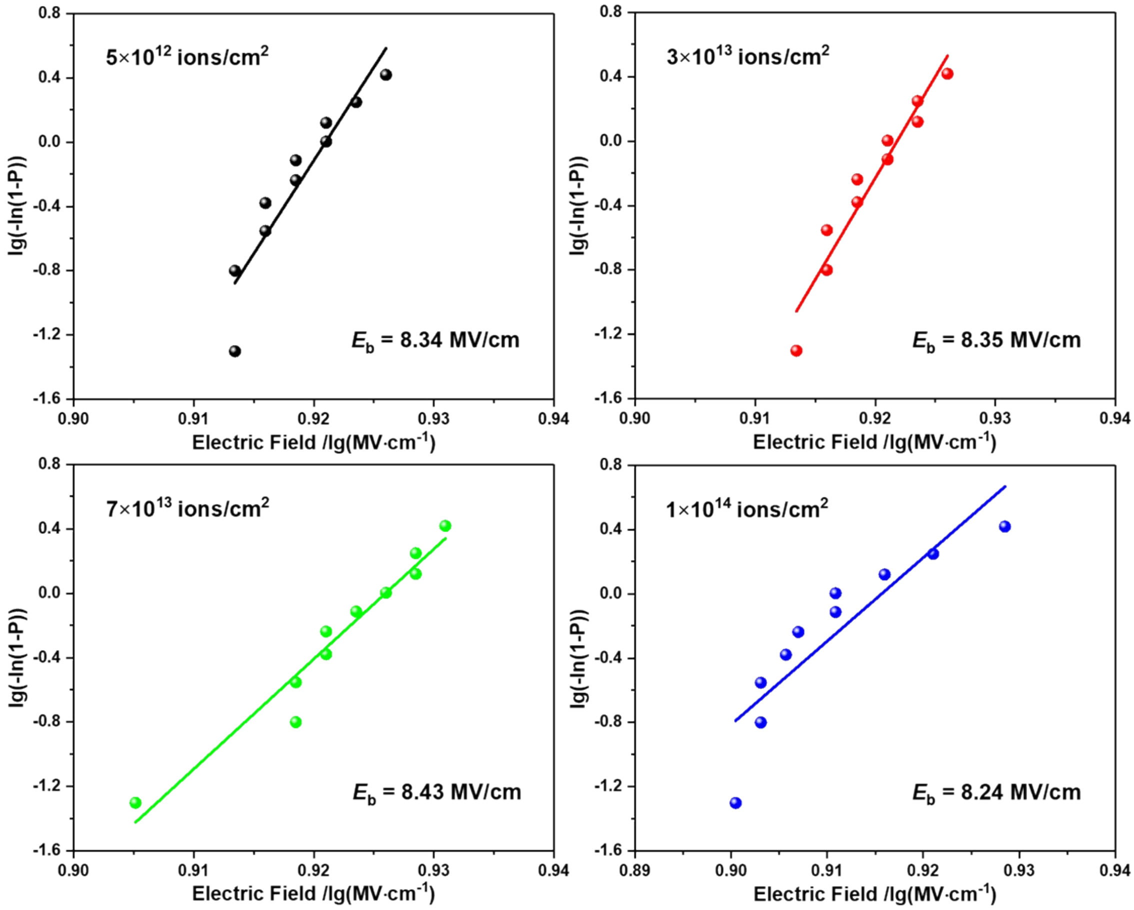

Fig. S5 After neutron irradiation with different doses, the Wei-bull distribution and the fitting lines of E_b for the BZTS/HfO_2 thin film capacitors.

References

1 C. Neusel, G. A. Schneider, J. Mech. Phys. Solids., 2014, **63,** 201-213.