Appendix A

Supplementary Information

Silicon-Integrated Lead-Free BaTiO$_3$-Based Film Capacitors with Excellent Energy Storage Performance and Highly Stable Irradiation Resistance

Fan Zhao,\textsuperscript{ab} Yilin Wu,\textsuperscript{ab} Yanzhu Dai,\textsuperscript{ab} Guangliang Hu,\textsuperscript{ab} Ming Liu,\textsuperscript{*ab} Runlong Gao,\textsuperscript{cd} Linyue Liu,\textsuperscript{*c} Xin Liu,\textsuperscript{c} Yonghong Cheng,\textsuperscript{*c} Tian-Yi Hu,\textsuperscript{b} Chunrui Ma,\textsuperscript{b} Dengwei Hu,\textsuperscript{f} Xiaoping Ouyang\textsuperscript{e} and Chun-Lin Jia\textsuperscript{abg}

\textsuperscript{a}School of Microelectronics, Xi’an Jiaotong University, Xi’an 710049, China
\textsuperscript{b}State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an 710049, China
\textsuperscript{c}State Key Laboratory of Intense Pulsed Radiation Simulation and Effect, Northwest Institute of Nuclear Technology, Xi’an 710024, China
\textsuperscript{d}School of Nuclear Science and Technology, Xi’an Jiaotong University, Xi’an 710049, China
\textsuperscript{e}State Key Laboratory of Electrical Insulation and Power Equipment, School of Electrical Engineering, Xi’an Jiaotong University, Xi’an 710049, China
\textsuperscript{f}Faculty of Chemistry and Chemical Engineering, Engineering Research Center of Advanced Ferroelectric Functional Materials, Key Laboratory of Phytochemistry of Shaanxi Province, Baoji University of Arts and Sciences, 1 Hi-Tech Avenue, Baoji, Shaanxi, 721013 P. R. China
\textsuperscript{g}Ernst Ruska Centre for Microscopy and Spectroscopy with Electrons, Forschungszentrum Jülich, D-52425 Jülich, Germany

* Email address: m.liu@xjtu.edu.cn; 13619269436@163.com; cyh@xjtu.edu.cn
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 $\theta$-$2\theta$ 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 $\eta$ of the BZTS/HfO$_2$ thin films at room temperature depending on film thickness.

Fig. S2a shows the XRD $\theta$-$2\theta$ 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 $P_{max} - P_f$ 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 [$E_b \propto 1/\sqrt{\text{thickness}}$].\(^1\) 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 $P_{\text{max}}$ and $P_r$ increase first and then decrease with the increase of film thickness, and $P_{\text{max}} - P_r$ reaches the maximum value when the thickness is about 415 nm. Fig. S2d shows the change of $W_{\text{re}}$ and $\eta$ of the BZTS/HfO$_2$ thin films with the thickness. The results show that the change of $W_{\text{re}}$ with thickness of the BZTS/HfO$_2$ thin films is consistent with that of $E_b$ and $P_{\text{max}} - P_r$. The ultrahigh $W_{\text{re}}$ of 93.37 J/cm$^3$ with $\eta$ of 70.22% at RT when the film thickness is about 415 nm is mainly due to its higher $E_b$ and $P_{\text{max}} - P_r$.

**Table S1**

Energy storage parameters of BZTS/HfO$_2$ thin films with different thickness grown on Si substrate at room temperature

<table>
<thead>
<tr>
<th>Thickness /nm</th>
<th>$E_b$/MV·cm$^{-1}$</th>
<th>$P_{\text{max}}$/μC·cm$^{-2}$</th>
<th>$P_r$/μC·cm$^{-2}$</th>
<th>$W_{\text{re}}$/J·cm$^{-3}$</th>
<th>$\eta$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>139</td>
<td>7.20</td>
<td>23.65</td>
<td>4.01</td>
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<td>70.83</td>
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<tr>
<td>276</td>
<td>8.08</td>
<td>28.89</td>
<td>5.14</td>
<td>72.08</td>
<td>70.33</td>
</tr>
<tr>
<td>415</td>
<td>8.78</td>
<td>34.78</td>
<td>7.07</td>
<td>93.37</td>
<td>70.22</td>
</tr>
<tr>
<td>700</td>
<td>5.11</td>
<td>24.96</td>
<td>1.81</td>
<td>49.67</td>
<td>81.73</td>
</tr>
</tbody>
</table>
Fig. S3 (a) Frequency dependence of $\varepsilon_r$ and $\tan\delta$ for the BZTS/HfO$_2$ thin films with different thicknesses at room temperature. (b) Temperature dependence of $\varepsilon_r$ and $\tan\delta$ for the BZTS/HfO$_2$ thin films with different thicknesses at 1 KHz.

Fig. S3a shows the frequency dependence of $\varepsilon_r$ and $\tan\delta$ for the BZTS/HfO$_2$ thin films with different thicknesses at RT. The results show that the $\varepsilon_r$ 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 $\varepsilon_r$ 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 $\tan\delta$ gradually decreases as the thickness of the BZTS/HfO$_2$ thin films. Fig. S3b shows the temperature dependence of $\varepsilon_r$ and $\tan\delta$ 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