Supporting information

Highly Stable Performance of Flexible $Hf_{0.6}Zr_{0.4}O_2$ Ferroelectric Thin Films under Multi-Service Conditions

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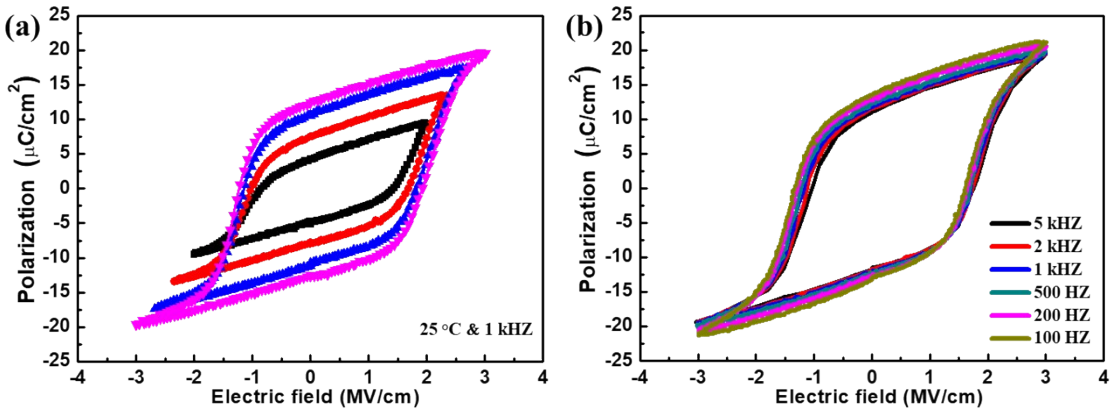

Figure S1. (a) *P-E* hysteresis loops of flexible HZO film measured at 1kHz. (b) Frequency dependence of *P-E* loops at room temperature.

Figure S1(a) shows the *P-E* hysteresis loops with applied electric field up to 3 MV/cm at 1 kHz. It is worth noting that the saturated polarization (P_{sat}) and the remnant polarization (P_r) are about 22 and 12.5 $\mu C/cm^2$ at an applied electric field of 3 MV / cm, respectively, which is comparable to the HfO_2-based films on rigid substrates[1]. Figure S1(b) depicts the *P-E* hysteresis loops for the flexible HZO film at frequencies ranging from 100 Hz to 5 kHz. The weak dependence of polarization behavior on frequency can be observed, which is reflected by the decrease of $2P_r$ from 26.7 to 23$\mu C/cm^2$. This behavior suggests little contribution from leakage current, nonlinear dielectric effects, and fast switching of the domain[2,3].

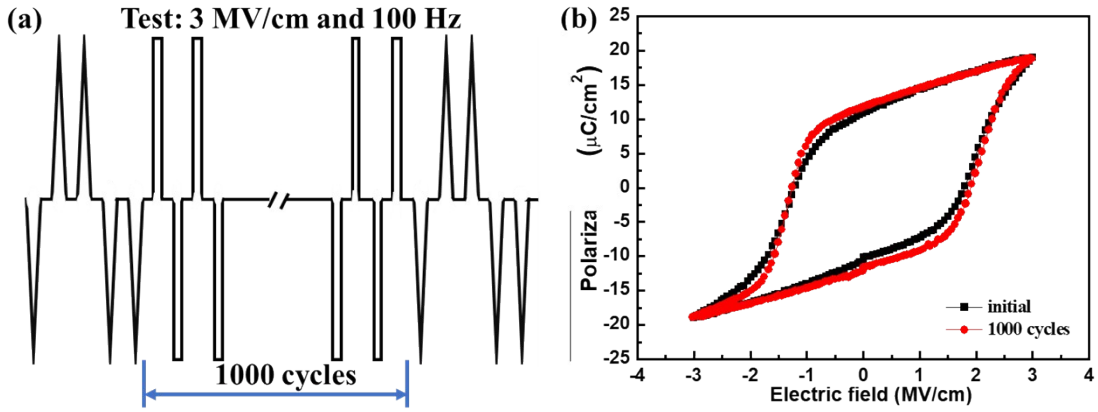

Figure S2. (a) Test sequences used for measuring *P*–*E* hysteresis loops under bipolar cycling. (b) *P*−*E* hysteresis loops of the flexible HZO film before and after the application of the bipolar switching cycles.

The pulse sequence applied during the test is shown in Figure S2 (a), whereas a wake-up behavior is observed for the flexible HZO ferroelectric film in Figure S2(b). Compared with the initial state, an expanding of the polarization and coercive field can be observed, and the $2P_r$ value and $2E_c$ are increased by 11% and 7%, respectively. What's more, after applying a circulating electric field, the hysteresis loop is more symmetrical than before. There are many theoretical explanations for this phenomenon in the current reports, such as the redistribution of oxygen vacancies, the de-pinning of domains, and the transformation of non-ferroelectric phase into ferroelectric phase in the film during the process of electric field circulation[4,5].

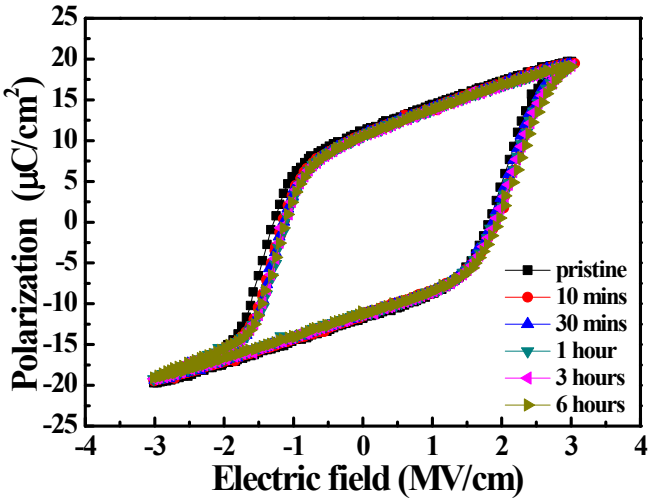

Figure R3. The change of hysteresis loops of flexible HZO film with humidification time.

Figure R3 shows the effect of humidification time on the ferroelectric properties of flexible $Hf_{0.6}Zr_{0.4}O_2$ thin films. When the relative humidity is 80%, the ferroelectric properties of the film do not exhibit noticeable change with the increase of humidification time.

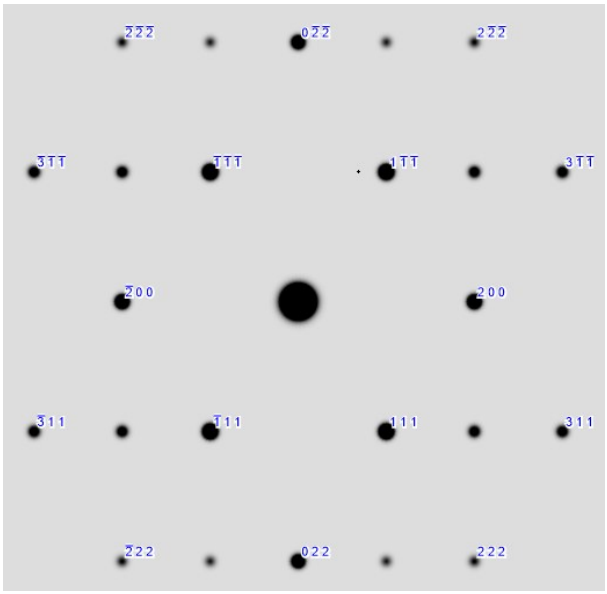

Figure S4. Simulated diffraction pattern of orthorhombic HZO with space group $Pbc2_1$, corresponding to $[0\bar{1}1]$ zone axes

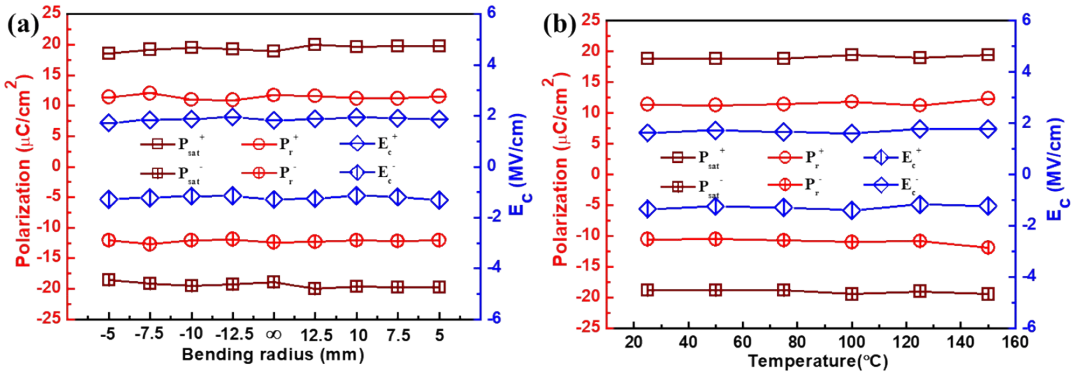

Figure S5. (a) Variations of P_{sat}, P_r, and E_c of flexible HZO films under stress and electric field conditions and (b) under temperature and electric field conditions.

Figure S5(a) shows the change in P_{sat}, P_r and E_c values of the flexible HZO film as a function of bending radius. The unbent flexible HZO ferroelectric thin film shows a P_s of about 20 μC/cm^2, a $2P_r$ of about 25 μC/cm^2, and a E_c of about 1.5 MV/cm. Compared with the values measured under various bending conditions, it can be found that the changes of these three parameters are negligible, revealing that the robust properties of the flexible HZO films against to mechanical stress. Figure S5(b) provides the variation of the P_s, P_r and E_c as a function of temperature. Based on the ferroelectric properties of the initial flexible HZO ferroelectric thin film (P_s~19 μC/cm^2, $2P_r$~23 μC/cm^2, E_c~1.5 MV/cm), the changes of P_s, P_r and E_c values are slight, indicating stable ferroelectric properties of the film under high temperature and electric field conditions.

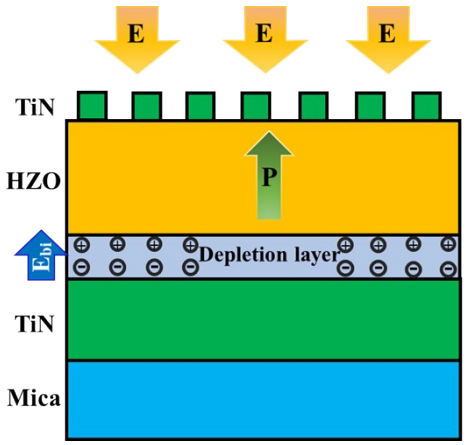

Figure S6. Schematic of built-in electric field in the HZO film

Figure S6 shows the schematic of built-in electric field in HZO film, and the polarization is represented by P, the built-in electric field is E_{bi}, and the applied electric field is E.

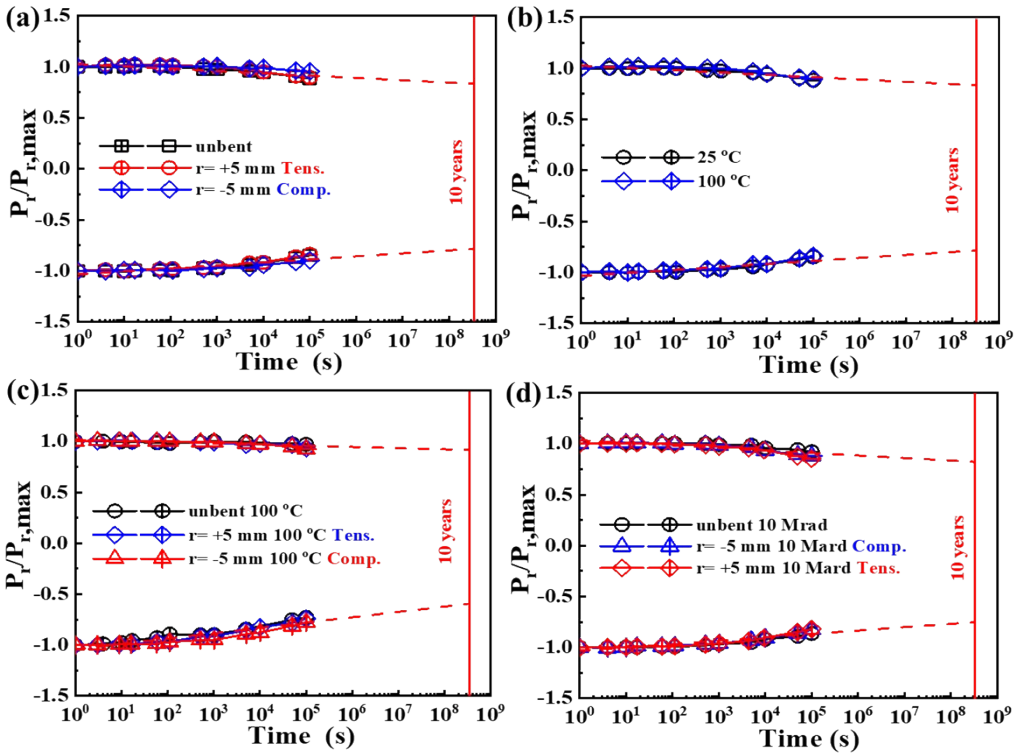

Figure S7. Retention (>10 years)

Firstly, the extrapolated failure retention times of more than 10 years were fitted and extended, as shown in Figure R7.

Secondly, the retention time transforming from high temperature to an arbitrary temperature is given by, $t_2 = t_1^{m^*}$, $m^* = exp[\frac{E_a}{K}(\frac{1}{T_2} - \frac{1}{T_1})]$, t_2 is time at a desired

temperature, t_1 is the time tested at high temperature, T_1 is the high temperature where retention is measured, T_2 is the desired temperature we want to transform. From Fig. 2, T_1 is 100°C, t_1 is 10^5 s. Assume our target temperature is 69°C (T_2), according the above expression, t_2 is about 10 years. This method provides a rough assessment of retention time for long periods of time as experimentally it is difficult to continue measurement for such a long period.

In general, both methods can prove that our retention time can reach more than 10 years.

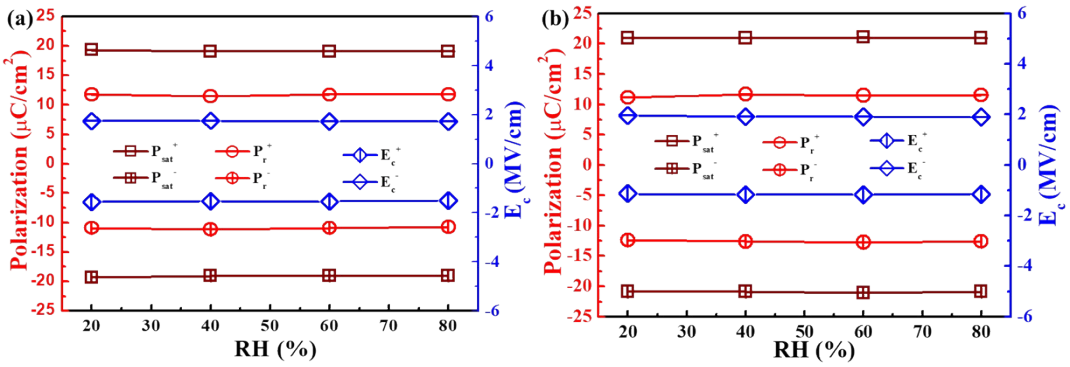

Figure S8. variations of P_{sat}, P_r, and E_c of the P-E hysteresis loops of the flexible HZO films (a) under humidity and electric field conditions, (d) under humidity, high temperature and electric field conditions.

Reference

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