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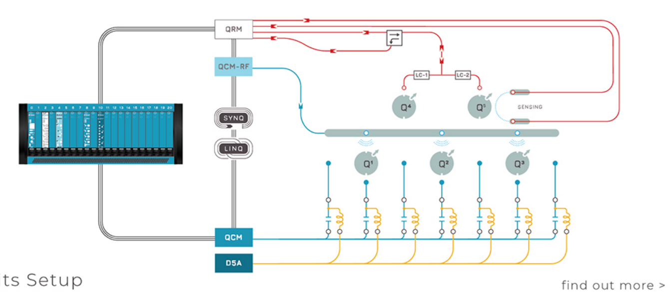

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ABSTRACT

A special wake-up effect from antiferroelectric-like to ferroelectric (AFE-FE) characteristics in $Hf_xZr_{1-x}O_2$ thin films has been discussed intensively in terms of endurance performance enhancement. However, its physical origin and general impact on endurance remain unclear. In this work, the influence of various process parameters on the AFE-FE wake-up effect as well as on endurance performance and the material changes during AFE-FE wake-up are systematically studied. It is found that various parameters induce the AFE-FE wake-up effect and enhance endurance performance in the same way with enhancing tetragonal phase formation in $Hf_xZr_{1-x}O_2$ films, and the cycles of wake-up are universally associated with those of total endurance. In addition, via synchrotron-based grazing incidence x-ray diffraction, a tetragonal-orthorhombic-monoclinic phase transition is observed during AFE-FE wake-up. On the basis of these results, a correlation among crystalline composition, the AFE-FE wake-up effect, and the endurance performance of $Hf_xZr_{1-x}O_2$ thin films is established. This provides a clear guideline to a viable solution for the high endurance of $Hf_xZr_{1-x}O_2$ FE memory devices via crystal phase engineering.

HfO_2-based ferroelectric (FE) thin films have attracted great interest since their discovery in 2011.[1] They are generally considered to have originated from a metastable orthorhombic (O) $Pca2_1$ phase.[2–4] This phase may be formed during the transition from the tetragonal (T) to monoclinic (M) phase in rapid thermal annealing (RTA).[5,6] Various dopants with suitable concentration have been reported to induce this phase in HfO_2 films, including Si, Al, Ge, Sc, Zr, N, and Y.[7–12] Among them, Zr-doped HfO_2 films have attracted much attention, because the FE phase can be formed with a wide range of Zr concentrations.[13,14] In addition, with higher concentrations of some dopants than that for FE phase formation, including Si, Al, and Zr, antiferroelectric (AFE)-like properties are also observed with the T-phase.[11,14,15] Comparing to conventional FE/AFE materials, HfO_2-based FE/AFE films have the advantages of full compatibility with state-of-the-art complementary metal oxide semiconductor (CMOS) technology, high scalability, and environmentally friendly composition. These make them promising in the application of non-volatile memory (NVM) devices.[16–18]

For application of memory devices, the endurance performance of FE films is one of the major concerns, as it determines the reliability of devices. During the polarization switching cycling, HfO_2-based FE films show an increase followed by a decrease in remnant polarization (P_r), namely, wake-up and fatigue effects, which significantly affect endurance performance.[19] In addition, breakdown also limits the endurance cycles.[20] In order to achieve high endurance performance, these effects should be physically understood and technically engineered. Particularly, a special wake-up phenomenon, observed in mostly studied $Hf_xZr_{1-x}O_2$ films, has recently attracted intensive attention. AFE-like properties appear in the pristine state, and it transforms into FE properties after certain polarization switching cycles.[8,19,21–27] We call this AFE-FE wake-up in this work. It has been reported to appear with the scaling down of $Hf_xZr_{1-x}O_2$ films or with decreasing oxidant dose time in the atomic layer deposition (ALD) of the films.[25,26] More interestingly, it seems that this wake-up effect has an impact on the endurance performance of $Hf_xZr_{1-x}O_2$ films. In the above-mentioned studies, higher endurance can be obtained with AFE-FE wake-up by reducing the ozone dosing time during ALD.[26] Also, by engineering film thickness down to 4 nm with a strong AFE-FE wake-up effect, an endurance performance of 10^{10}, projecting to 10^{14}, can be achieved in contrast to 10^7 in the absence of this effect.[25] As for the physical understanding of this special wake-up, defects redistribution, including oxygen vacancies (V_O), is a common explanation without experimental evidence.[22,24] In addition, M–O or T–O phase transition,[22,24] as well as the depolarization field caused by the T-phase,[26] has also been speculated as the origin of AFE-FE wake-up. Experimentally, Lomenzo *et al.* tried grazing incidence x-ray diffraction (GIXRD) investigation and reported that no phase transition occurs in $Hf_{0.3}Z_{0.7}O_2$.[27] So, they considered defects redistribution as the physical origin rather than phase transition. Chen *et al.* reported O_{Pbca}–O_{Pbc21} phase transition occurred in the wake-up process through a cross-sectional transmission electron microscope (TEM).[19] Although many studies have been carried out on controlling and understanding of AFE-FE wake-up, controlling by different process conditions was individual, and the physical understanding was short of consistent view and macroscopic evidence. Several key questions still remain unclear, including the followings: Is there an intrinsic factor inducing AFE-FE wake-up effect beyond various process conditions? What does really occur during AFE-FE wake-up physically? Is there a direct correlation between AFE-FE wake-up and endurance performance? It is critical to address these questions for materials science knowledge of HfO_2-based ferroelectric films as well as for a general guideline toward high endurance of FE-based memory devices.

In our recent work, we found that AFE-FE evolution also occurs in typical AFE $Hf_xZr_{1-x}O_2$ (x = 0.2) films with higher Zr concentration and even in pure ZrO_2 thin films, which is quite similar to AFE-FE wake-up in typical FE $Hf_{0.5}Zr_{0.5}O_2$ films.[28] By engineering AFE-FE evolution in AFE films, we achieved $>10^{12}$ endurance under full polarization switching conditions. This finding correlated with the AFE-FE wake-up effect with typical AFE properties of $Hf_xZr_{1-x}O_2$ films. Because the difference between AFE and FE $Hf_xZr_{1-x}O_2$ films physically lies in the crystalline phase, it is possible that AFE-FE wake-up and its impact on endurance are associated with phase composition. Therefore, in this work, we systematically investigate the influence of different process factors on AFE-FE wake-up and endurance, as well as the material changes during AFE-FE wake-up from a viewpoint of phase composition in the $Hf_xZr_{1-x}O_2$ films. This is done to establish a correlation among phase composition, AFE-FE wake-up, and endurance performance. In addition, we obtained macroscopic experimental evidence of T–O–M phase transition during the cycling process through grazing incidence x-ray diffraction (GIXRD) testing and specially designed samples. On this basis, we develop a general guideline for phase engineering toward achieving higher endurance performance in AFE/FE $Hf_xZr_{1-x}O_2$ films.

Typical $Hf_xZr_{1-x}O_2$ metal-insulator-metal (MIM) capacitors with x = 0–0.5 were fabricated and characterized. Figure 1(a) shows the process flow of $Hf_xZr_{1-x}O_2$ capacitors. First, highly doped p-Si wafers were cleaned by the RCA process, followed by 30 nm TiN films deposition by reactive magnetron sputtering at room temperature. The sputter power was 250 W, and the atmosphere is Ar:N_2=50:4 sccm. Then 6–30 nm $Hf_xZr_{1-x}O_2$ films were deposited by ALD at 250 °C with the precursors TEMAHf and TEMAZr. The deposition rates for HfO_2 and ZrO_2 were 0.09 and 0.07 nm/cycle, respectively. The hafnia concentration x was controlled by the deposition sequence of the HfO_2 and ZrO_2 layer. Then, 30 nm TiN was sputtered and patterned through photo-lithography and liftoff process, followed by 30 nm W. The size of the top electrodes was $40 \times 40\ \mu m^2$, and the distance between the electrodes was 40 μm. Finally, post-metallization annealing (PMA) was carried out at 550–750 °C for 30 s in flowing N_2 ambient. The film thickness was characterized by an ellipsometer and a transmission electron microscope (TEM). Figure 1(b) shows the cross-sectional TEM images of 15 nm $Hf_{0.5}Zr_{0.5}O_2$ and $Hf_{0.2}Zr_{0.8}O_2$ capacitors. Polarization–field (P–E) and current–field (I–E) characterization were carried out by a semiconductor parameter analyzer (Keithley 4200A-SCS) under 10 kHz, and endurance tests were conducted under 500 kHz with a 4 MV/cm field.

In addition, in order to precisely measure the crystalline structure during the polarization switching cycle, two sets of samples in a pristine state, with wake-up cycling and with fatigue cycling, were prepared on Ge and TiN substrates with relatively thick $Hf_xZr_{1-x}O_2$ films. The Ge substrate was continually cleaned with acetone, isopropanol,

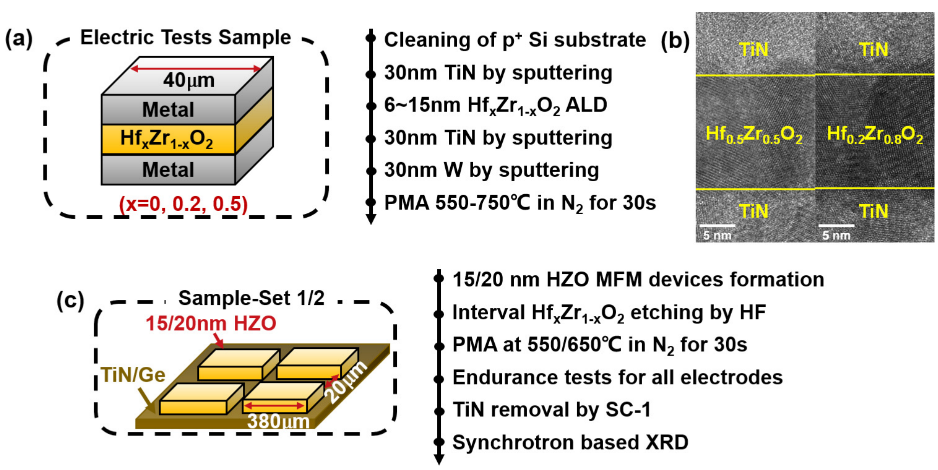

FIG. 1. (a) Structure and process flow of $Hf_xZr_{1-x}O_2$ MFM capacitors with varied thickness, Zr ratio, PMA temperature, and oxidant dose time in ALD. (b) TEM images of 15 nm $Hf_xZr_{1-x}O_2$ MFM capacitors (x = 0.2 and 0.5). (c) Process flow of XRD samples with different sample sets.

and hydrochloric acid. The $Hf_xZr_{1-x}O_2$ and TiN/W deposition method was the same as that described above, but the size of the top electrodes was 380×380 μm^2, and the distance between electrodes was 20 μm. More than 50 electrodes were prepared for each sample, and the $Hf_xZr_{1-x}O_2$ films uncovered by top electrodes were etched by 1:20 hydrofluoric acid for 10 s before PMA. After the polarization switching cycle for all electrodes, the top TiN/W electrodes were removed by SC-1, as shown in Fig. 1(c). Then the crystalline structure of the $Hf_xZr_{1-x}O_2$ films was characterized by synchrotron-based GIXRD at 10 keV ($\lambda_1 = 1.24$ Å) with 2° incidence angle. Finally, XRD data were converted into Cu-Kα form with $\lambda_2 = 1.54$ Å via equation $\lambda_1/\sin\theta_1 = \lambda_2/\sin\theta_2$.

As noted, the AFE-FE wake-up phenomenon has been individually reported to be affected by the oxidant dose time in ALD and film thickness.[25,26] In order to clarify how it can be physically triggered beyond these parameters, the systematic influence of various process factors, including the oxidant dose time in ALD, the Hf contents in the films, and PMA temperatures were studied first. It should be noted that V_O in the $Hf_xZr_{1-x}O_2$ film is controlled by the oxidant dose time in ALD. Figure 2 shows the P–E characteristics of $Hf_xZr_{1-x}O_2$ films in the pristine state and after wake-up cycles with different process parameters. As shown in Fig. 2(a), all of the 6 nm $Hf_{0.5}Zr_{0.5}O_2$ films are pristinely AFE-like, but the transition voltage from the non-polar phase to the polar phase increases, and the polarization of the polar phase decreases with a decrease in the PMA temperature from 700 °C to 600 °C. After 10^6 wake-up cycles, all of the films become FE characteristics. With increased Zr concentrations, similar changes are observed for pristine films, and the AFE-FE evolution trend also occurs for all films, although more cycles (10^{10}) are needed for the $Hf_{0.2}Zr_{0.8}O_2$ film to change to FE-like properties, and the P–E characteristics for ZrO_2 remain AFE-like until the end of the endurance cycles [Fig. 2(b)]. Because the ZrO_2 films are harder to switch, higher field was applied on ZrO_2 compared with other samples. With decreasing ozone dose time in ALD from 10 to 0.5 s for 15 nm $Hf_{0.5}Zr_{0.5}O_2$ films with 750 °C PMA, interestingly, the P–E characteristics change from FE to AFE-like pristinely, and more cycles are needed for wake-up to FE characteristics [Fig. 2(c)]. Comparing three sets of results of varying process factors, although a difference is observed, the trends of change in wake-up effects for $Hf_xZr_xO_2$ films are the same. Namely, the AFE-FE wake-up effect is stronger with lower PMA temperature, higher Zr concentration, and more V_O in the film. This indicates that an intrinsic factor affects the AFE-FE wake-up effect beyond these process parameters.

The endurance characteristics of the aforementioned devices with different process parameters are also characterized as shown in Figs. 3(a)–3(c). In most cases, AFE-FE wake-up is followed by fatigue and breakdown. In the cases of a 6 nm ZrO_2 sample and an $Hf_{0.5}Zr_{0.5}O_2$ sample with 0.5 s zone dose time, breakdown occurs before the end of wake-up. Excluding these two cases, it is found that better endurance is achieved with lower PMA temperatures, higher Zr concentrations, and shorter ozone dose times. That is, better endurance is obtained with stronger AFE-FE wake-up. To obtain quantitative information on how AFE-FE affects the endurance, the cycles of final endurance characteristics are plotted as a function of cycles of wake-up in Fig. 3(d) by extracting the data from Figs. 3(a)–3(c) and excluding the data of a 6 nm ZrO_2 sample and an $Hf_{0.5}Zr_{0.5}O_2$ sample with 0.5 s ozone dose time. Interestingly, the endurance is universally and positively correlated with wake-up in cycles. This suggests that

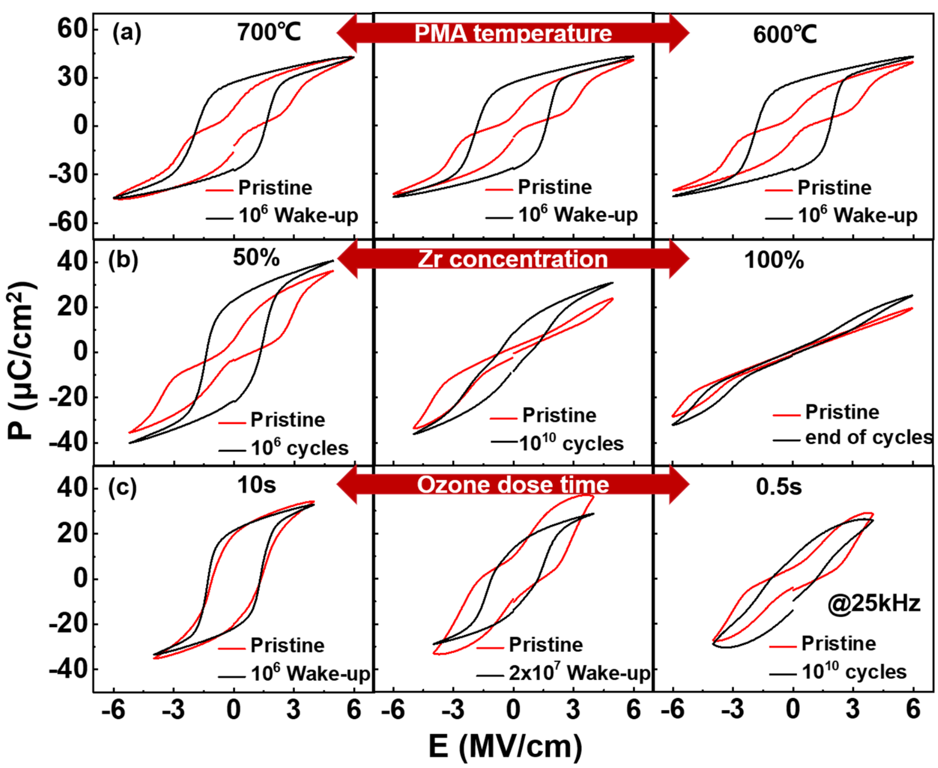

FIG. 2. P–E hysteresis properties of devices in a pristine state and a wake-up state in (a) 6 nm $Hf_{0.5}Zr_{0.5}O_2$ films with 0.5 s H_2O dose time and 700/650/600 °C PMA. (b) 6 nm $Hf_xZr_{1-x}O_2$ films (x = 0.5/0.2/0) with 0.1 s H_2O dose time and 550 °C PMA, and (c) 15 nm $Hf_{0.5}Zr_{0.5}O_2$ films with 10/2/0.5 s ozone dose time and 750 °C PMA.

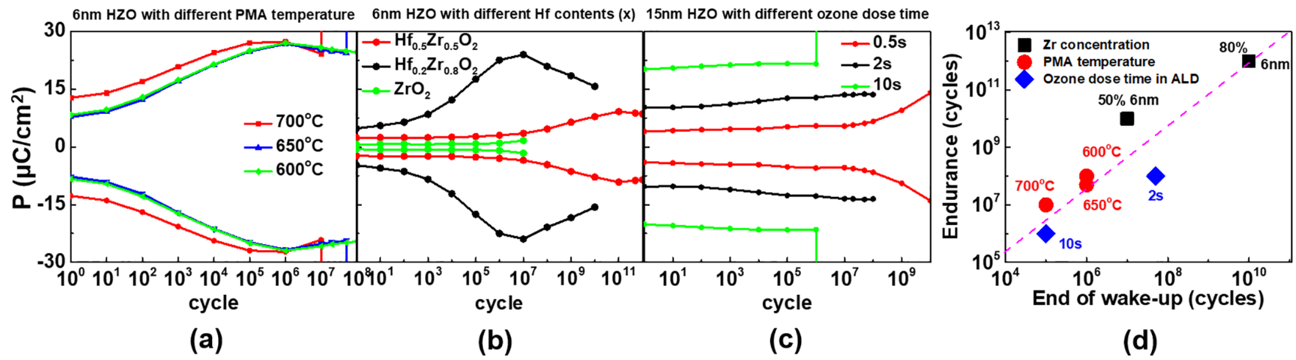

FIG. 3. The endurance performance of devices with 6/15 nm $Hf_xZr_{1-x}O_2$ and different (a) PMA temperatures, (b) Zr concentrations, and (c) ozone dose times in ALD. Lower PMA temperatures, shorter oxidant dose times, and higher Zr concentrations result in better endurance. (d) Endurance cycles as a function of wake-up cycles extracted from (a)–(c).

AFE-FE wake-up generally affects endurance performance, in spite of different process parameters. The physical origin of this influence should be the same with that affecting AFE-FE wake-up intrinsically.

Next, we consider the potential intrinsic factors affecting AFE-FE wake-up as well as endurance performance and what occurs in AFE-FE wake-up from a material viewpoint. It has been clearly shown, both individually and systematically, that T-phase formation is enhanced by a larger concentration of V_O in the film, lower annealing temperature, higher dopant concentration, and thinner film thickness.[8,14,25,26] Combining these results with ours, it can be seen that various process parameters induce the AFE-FE wake-up effect and, hence, affect endurance in the same way with enhancing T-phase transition. Namely, the AFE-FE wake-up effect with better endurance may be intrinsically triggered by a larger T-phase composition in the film in the pristine state. In this case, the phase transition may occur in AFE-FE wake-up.

To experimentally verify possible phase transitions, the precise characterizations of crystalline structures before and after AFE-FE wake-up and after fatigue were carried out [Fig. 1(c)]. Samples on Ge substrates were prepared to confirm the reproducibility of the results. Figures 4(a) and 4(b) show the endurance characteristics of each electrode on two sets of samples with different electrical treatment conditions. Figures 4(c) and 4(d) show the GIXRD results of two sets of samples. Three peaks lying at 2θ around 28.5°, 30.5°, and 31.6° are resulted from M (11–1)-, O- or T-, and M(111)-phase, respectively. Note that the peaks of the O- and T-phases are basically overlapped, but their peak positions are slightly different (O: $2\theta = \sim 30.4°$, T: $2\theta = \sim 30.6°$) as indicated in Fig. 4. It can be found that the peak of the O/T-phase shift from the T-side to the O-side during AFE-FE wake-up for both sets of samples. In addition, it seems that the peak insensitiveness of the M-phase increases slightly relative to the O/T-phase after wake-up. To make these results more intuitive, the peak position of the O/T-phase and the concentration of the M-phase were extracted in Figs. 4(e) and 4(f), where the intensity of each peak was obtained by measuring the peak area and the concentration of each phase was calculated from the ratio of its peak intensities to the total intensity of three peaks. The peak position of the O/T-phase of sample-set-1 shift from ~30.57° to ~30.40° and that of sample-set-2 shifted from ~30.72° to ~30.52° after AFE-FE wake-up. Meanwhile, the M-phase concentration increases from ~32.94% to ~48.72% for sample-set-1 and from ~10.87% to ~27.63% for sample-set-2. The two sets of results clearly demonstrated similar trends of change in AFE-FE wake-up. The difference in absolute values may be due to a large difference in the concentration of the T/O-phase in the pristine film. These results clearly demonstrate that T–O–M phase transition occurs during AFE-FE wake-up. Moreover, this transition provides

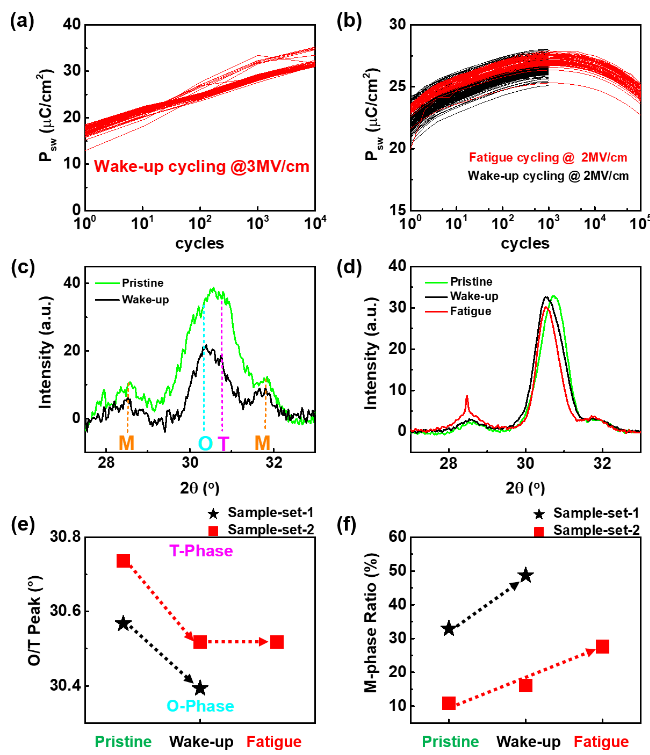

FIG. 4. Endurance characteristics of each electrode in (a) sample-set-1 and (b) sample-set-2. GIXRD results for (c) sample-set-1 and (d) sample-set-2, in the pristine state, after wake-up and after fatigue, are prepared for the investigation of what occurs in endurance tests. (e) O/T peaks position and (f) the concentration of the M-phase of two sets of samples in the pristine state, after wake-up and after fatigue by synchrotron x-ray.

direct evidence that the AFE-FE wake-up effect originates from the larger T-phase composition in the pristine film. When the T-phase transits to the O-phase, P_r increases, and the P–E loop changes to FE characteristics. Because the O-phase is metastable, it can be further transited to the M-phase partly. In the fatigue process, an increase in the M-phase concentration is also demonstrated on sample-set-2. This may be one of the physical origins of fatigue. However, the origins of the fatigue process should be more complicated, as it has been reported that the P_r can be partly recovered after fatigue with a higher field.[29]

In addition, two points should be noted concerning the T–O–M transition during the polarization switching cycling: (i) It may appear only in an $Hf_xZr_{1-x}O_2$ system because AFE-FE evolution is not observed in cycling of HfO_2-based FE-films with other dopants such as Si.[27] (ii) T–O–M phase transition may also have an effect on breakdown. It has been reported that the V_O is more easily formed at the O/M-phase interface which will induce leakage path and, hence, breakdown.[30] Therefore, breakdown probability may increase with an increase in the M-phase concentration.

Finally, based on the above results, a correlation among crystalline phase composition, AFE-FE wake-up effect, and endurance can be established as shown in Fig. 5. Namely, a stronger AFE-FE wake-up effect originates from a larger concentration of the T-phase in a pristine state, enabling better endurance performance. Based on this correlation, a guideline to enhance endurance through phase engineering is clear: to enhance the T-phase composition in the pristine film. Strategies to enhance T-phase formation are available to obtain better endurance characteristics, including decreases in the RTA temperature, oxidant dose time, and film thickness and/or increase in the Zr concentration. Inserting the ZrO_2 layer is also one of the strategies.[31] Note, however, that if the concentration of the T-phase is too large, AFE-like characteristics will appear in a field close to a breakdown field, which will have a negative effect on endurance. This condition will also affect P_r substantially. Thus, various parameters should be simultaneously engineered to obtain an optimized condition.

In summary, our results provide deep insight into the key issue, namely, the physical origin of the AFE-FE wake-up effect of $Hf_xZr_{1-x}O_2$ thin films, which significantly affects the endurance performance of these films. We found that the AFE-FE wake-up effect and endurance performance affected by various process parameters are universally and positively correlated in polarization switching cycles, and the various process parameters induce AFE-FE wake-up effect and improve endurance performance in a similar way to enhance T-phase formation in $Hf_xZr_{1-x}O_2$. In addition, a T–O–M phase transition occurs during AFE-FE wake-up. Thus, a general guideline is established whereby endurance performance can be enhanced by engineering the phase composition of $Hf_xZr_{1-x}O_2$ films.

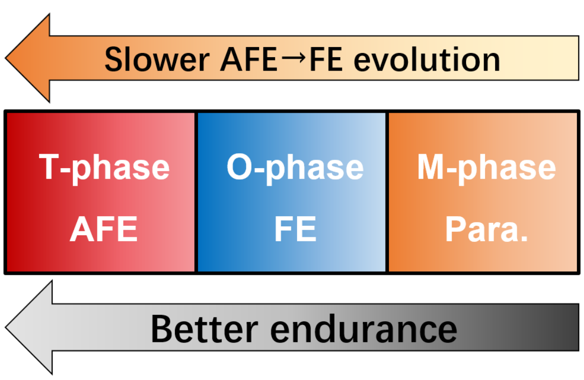

FIG. 5. Schematic correlating process parameters and endurance performance with crystalline structure universally.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Danyang Chen: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Writing – original draft (equal). **Shuman Zhong:** Data curation (equal). **Yulong Dong:** Data curation (equal). **Tianning Cui:** Data curation (equal). **Jingquan Liu:** Funding acquisition (equal); Resources (equal). **Mengwei Si:** Writing – original draft (equal); Writing – review & editing (equal). **Xiuyan Li:** Conceptualization (equal); Funding acquisition (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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