Abstract: HfO$_2$-based ferroelectric materials have been widely studied for their application in ferroelectric FETs, which are compatible with conventional CMOS processes; however, problems with the material’s inherent fatigue properties have limited its potential for device application. This paper systematically investigates the effects of tensile stress and annealing temperature on the endurance and ferroelectric properties faced by Zr-doped HfO$_2$ ferroelectric film. The remnant polarization ($P_r$) shows an increasing trend with annealing temperature, while the change in the coercive electric field ($E_c$) is not obvious in terms of the relationship with tensile stress or annealing temperature. In addition, the application of tensile stress does help to improve the endurance characteristics by about two orders of magnitude for the ferroelectric material, and the endurance properties show a tendency to be negatively correlated with annealing temperature. Overall, although the effect of stress on the ferroelectricity of a HZO material is not obvious, it has a great influence on its endurance properties and can optimize the endurance of the material, and ferroelectricity exhibits a higher dependence on temperature. The optimization of the endurance properties of HZO materials by stress can facilitate their development and application in future integrated circuit technology.

Keywords: Hf$_{0.5}$Zr$_{0.5}$O$_2$; ferroelectric; endurance; tensile stresses; annealing temperature

1. Introduction

Doped ferroelectric HfO$_2$ materials have been widely studied alongside low power logic devices and non-volatile memory due to their scalability and compatibility with traditional CMOS processes [1–4]. Meanwhile, they are widely used in micro- and nanofluidic devices [5,6]; however, there are still problems regarding the fatigue or poor ferroelectricity in ferroelectric materials that prevent full application, so the optimization of modification for ferroelectric materials has been an important challenge for ferroelectric materials [7], e.g., with baseline technologies the write cycles of SRAM or DRAM is more than $10^{16}$, whereas the endurance of HfO$_2$-based FeRAM is about $10^5$ to $10^{10}$ [8–10] and Hf-based ferroelectric devices have so far been unable to achieve an endurance comparable to that of the conventional memory devices [11]. The endurance characteristics of ferroelectric FETs originate from two main sources. One is the fatigue of ferroelectric materials, caused by internal material stress, space charge, and electric domain pinning [12,13]. On the other hand, it is also caused by the degradation of the reliability of the gate stack, where the high electric field will lead to an increase in the defect density in the interface layer and result in deterioration of the quality of the interface layer [14]. The current research on the optimization of ferroelectricity mainly includes doping [15–22], the annealing temperature [23,24], changing electrode materials [25,26], the optimization of material growth methods [27] and so on. According to existing studies [28,29], stress may change the generation of crystalline
phases in ferroelectric materials and thus affect the formation of ferroelectric domains. Consequently, stress may have an effect on the ferroelectricity and fatigue characteristics of ferroelectric materials; however, little research has been reported on the effect of stress on the ferroelectricity of Hf-based ferroelectric materials.

In this paper, we systematically investigate the effect of stress on the ferroelectricity of HZO ferroelectric materials by characterizing three aspects: remnant polarization, the coercive electric field, and endurance characteristics and obtain results for the regulation of stress regarding ferroelectricity for ferroelectric materials by comparing the properties of ferroelectric materials under different annealing temperatures. A 10-nm HZO capacitor structure with stress conditions at an operating voltage of 3 V with 2P between 30–45 µC/cm² endurance characteristics operating in 10⁹ cycles without breakdown is demonstrated. The optimized effect of stress on endurance greatly increases the potential of HZO ferroelectric materials for future applications in high performance low power devices.

2. Materials and Methods

Figure 1a shows the key steps in the preparation of HZO thin film-based ferroelectric capacitors. The process started with an 8-inch Si wafer. After the complete cleaning of organic matter and impurities on the wafer, a 20-nm layer of TiN was deposited as the bottom electrode. Following that, a 10-nm HZO layer was deposited by ALD at 300 °C. Hf[N(C₂H₅)CH₃]₄, Zr[N(C₂H₅)CH₃]₄ and H₂O were used as Hf, Zr, and O sources. The ratio of Hf and Zr was controlled by controlling the cycle of depositing one layer of Hf followed by one layer of Zr, after which the top 20-nm TiN electrode was grown. This was followed by the deposition of the top electrode W. The stress applied to the HZO film can be controlled by controlling the pressure at which the top electrode W grows. The specific theory of stress regulation by W electrodes has been studied in detail by our group, as shown in [30,31]. It must be noted here that the W electrodes grown at both pressure conditions (323 MPa and 2726 MPa) introduced exotic stresses, but the latter was several orders of magnitude larger relative to the former, and therefore we defined both as stress-free and stressed structures, respectively. In this article, we took this method and used it directly. Finally, the capacitor structure was prepared by annealing at different temperatures. Rapid thermal annealing (RTA) was used for the heat treatment process, where the temperature was rapidly increased to the corresponding temperature in an N₂ atmosphere, held for 30 s, and then rapidly cooled to room temperature. The structure of the prepared capacitor with stress is shown in Figure 1b. Figure 1c,d clearly show the HZO capacitance sandwich structure between the two electrodes and the butterfly C–V curve which confirms the ferroelectricity.

In this paper, capacitance–voltage (C-V) measurements were taken using the 4200 semiconductor parameter analyzer, and all capacitance-based ferroelectricity and endurance characterization measurements were performed based on a TF3000 analyzer.
3. Results and Discussion

3.1. Ferroelectricity Characterization

First, the effect of stress on the ferroelectricity of thin HZO films at a 600 °C annealing temperature in MFM structures as test devices were investigated. Figure 2 illustrates the P–E hysteresis curves of ferroelectric films under different electric field conditions, where (a) and (b) denote the two cases with and without stress, respectively. The test voltage amplitude gradually increased from 1 V to 3.5 V. As shown in Figure 2, the remnant polarization ($P_r$) increased with the voltage amplitude for both conditions. At the same time, the hysteresis loops clearly show observable ferroelectricity in both capacitors. Figure 2c,d show $P_r$ and $E_C$ as functions of the test electric field, respectively. The results show that the overall $P_r$ magnitudes were similar in both conditions, but $P_r$ in the stressed condition was larger than that in the unstressed condition when the electric field strength was below 3 MV/cm, while an opposite result was obtained when the electric field strength was higher than 3 MV/cm. The $E_C$ values under the two conditions were also close, but the $E_C$ with stress was slightly smaller than the $E_C$ value without stress.

The $2P_r$ values at different annealing temperatures were measured to further investigate the effect of stress on the ferroelectricity of HZO materials as shown in Figure 3a,b. As the annealing temperature increased, the remnant polarization charge of the HZO capacitor was gradually enhanced, and the $2P_r$ value increased from about 35 µC/cm$^2$ at 450 °C to about 45 µC/cm$^2$ at 650 °C. The remnant polarization improved by approximately 30%, which is illustrated in Figure 3c. The remnant polarization charges at different annealing temperatures with and without stress were similar and showed a higher ferroelectricity dependence on temperature, indicating that the enhancement of ferroelectricity by stress may not be significant and that the samples have similar ferroelectricity. Figure 3d shows the variation of the coercive electric field with different annealing temperatures. The results show that $E_C$, with the stress condition was slightly smaller than that without stress, and $E_C$ varied little with temperature.
Figure 2. P–E loops of (a) HZO capacitor with stress and a (b) HZO capacitor without stress, respectively. Evolution of (c) $P_r$ and (d) $E_c$ of HZO capacitor with and without stress.

Figure 3. Comparison of P–E loops (a) in the stress free and (b) with stress conditions under different annealing temperatures. (c,d) The extracted remnant polarization and coercive electric field the of two capacitor structures at different annealing temperatures, respectively.
3.2. Endurance Characterization

Furthermore, the endurance properties of HZO ferroelectric materials under the two conditions have been investigated. Figure 4 depicts the variation of P–E loops of the HZO capacitor in both the (a) stress free and (b) stressed conditions with the polarization number at an annealing temperature of 450 °C, respectively. The measurement of P–E curves was carried out under a constant voltage of 3 V. The cycle signal was set to a square wave signal with a frequency of 1 MHz and featured an amplitude of ±3 V. The P–E loop results show that the capacitor varied little with the reversal of cycles under the condition of stress; however, it changed significantly in the absence of stress, showing that stress has a significant effect on the endurance properties of HZO materials. The variation of \( E_c \) and \( P_r \) with reversal cycles corresponding to the two stress conditions was extracted as shown in Figure 4c,d. Although the capacitive structures under the two conditions exhibit certain fatigue characteristics, the results for the stressed capacitive structures were significantly better than those for the unstressed ones. The interpolated results indicate that under stressed conditions, the \( P_r \) value does not change significantly until \( 10^8 \) operation cycles, which is an improvement of nearly two orders of magnitude when compared to the change in \( P_r \) at \( 10^6 \) cycles under unstressed conditions. This can be attributed to the introduction of the top electrode W, which makes the stress at the top and bottom electrodes asymmetric, and greater stress may make the defect density at the grain boundaries in the HZO material smaller, thus enhancing the endurance. Besides, according to previous studies [32,33], there is a contradictory relationship between the endurance of the material and the remnant polarization strength, which is called the polarization-endurance dilemma, i.e., the endurance properties are weakened by increasing the remnant polarization charge; however, in our stress experiments, we found that the \( P_r \) of the stressed and unstressed capacitance structures are basically the same, and the stressed one is also a little larger, so the introduction of stress enhances the endurance of the material without sacrificing \( P_r \), which can be a great improvement on the material properties.

![Figure 4](image-url)

**Figure 4.** Variation between the absence of stress (a) and stress (b) for P–V curves with polarization cycles at a 450 °C annealing temperature. (c,d) The extracted endurance property values.
The endurance measurements for HZO capacitance at different annealing temperatures were taken in order to further explore the endurance characteristics of HZO materials. In general, according to the requirement of the endurance of the memory device, the $P_r$ reduction of the material should be less than 10% after $10^9$ to $10^{12}$ cycles. We chose the operation cycle corresponding to the degradation of the remnant polarization to 90% of the initial polarization charge as the judgment criterion of capacitance endurance, and the extracted endurance results are shown in Figure 5. The vertical axis represents the operation cycle at each annealing temperature when $2P_r$ degrades to 90% of the corresponding initial value. The results show that the endurance properties of the material show a gradual weakening with the increase of the annealing temperature, where it can be seen in Figure 3c that the $P_r$ value for the material increases as the annealing temperature increases. The endurance will weaken according to the polarization-endurance dilemma; however, on the other hand, the effect of stress on the optimization of the endurance properties at each temperature is obvious, where the endurance with the stress condition at each temperature is significantly better than that of the endurance without the stress condition. Besides, the endurance properties degrade more slowly with increasing temperatures while in the presence of stress.

![Figure 5. Comparison of endurance characteristics of the two capacitor structures at different annealing temperatures.](image)

4. Conclusions

In summary, this paper has investigated the effect of tensile stress applied through the top W electrode on the ferroelectricity of HZO ferroelectric materials. The article has systematically analyzed the effect of stress from three aspects: remnant polarization charge, coercive voltage, and endurance. The results at different annealing temperatures show that although the effect of stress on the remnant polarization charge and coercive voltage is not significant, the endurance is well optimized and can be improved by two orders of magnitude at the same annealing temperature without sacrificing the $P_r$ value ($450 \degree C$). This is useful for the later research of HZO ferroelectric materials for application in integrated circuits.
Author Contributions: Conceptualization, Y.C., Q.Z., Z.Z., H.Y.; Data curation, Y.C. and Z.Z.; Funding acquisition, H.Y. and Q.Z.; Methodology, Y.C., Q.Z., Z.Z., G.X., Z.W., J.G., J.L., J.X.; Project administration, H.Y. and Q.Z.; Supervision, H.Y. and Q.Z.; Writing-original draft, Y.C.; Writing-review & editing, Y.C., Q.Z., Z.Z., H.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported in part by the NSFC under grants 92064003, 61904194, 91964202 and 61874135, in part by the Youth Innovation Promotion Association, Chinese Academy of Sciences under grant YQYQ01R004, in part by the Opening Project of Key Laboratory of Microelectronic Devices and Integrated Technology, Institute of Microelectronics, Chinese Academy of Sciences under Grant E0YS01X001 and E0290X03. The review of this letter was arranged by xxxx.

Institutional Review Board Statement: Not applicable for studies not involving humans or animals.

Data Availability Statement: The data presented in this study are available on request from the corresponding authors.

Acknowledgments: We thank the Integrated Circuit Advanced Process Center (ICAC) at the Institute of Microelectronics of the Chinese Academy of Sciences for the devices fabricated on their advanced 200 mm CMOS platform.

Conflicts of Interest: The authors declare no conflict of interest.

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