Research on Fatigue Phenomenon and Internal Mechanism of HfZrO₂ Ferroelectric Thin Film Memory

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ABSTRACT: The fatigue effect of the HfZrO₂ thin film sample plays a vital role in its application in the semiconductor field. This article explores the fatigue mechanism inside the thin film sample by studying the effect of various experimental conditions on the ferroelectric properties of the sample, and analyzes the experimental results. Then we study the experimental results to clarify the changes in the micro-physical mechanism inside the sample. Combined with macro-theory and micro-examination, we observe that experimental conditions such as the pulse width of the applied pulse will affect the change of the sample's remnant polarization values during the fatigue cycle. Finally, we try to optimize these conditions to achieve stable remanent polarization. This paper further clarifies the fatigue mechanism of the sample through the mathematical analysis of experimental data and the comparison of existing theories, and points out the direction for optimizing the application of the device.

1. Introduction
As the role of modern information technology in life becomes more and more significant, the requirements for memory in various fields are getting higher and higher, and its performance and factors affecting performance need to be further studied. In order to further meet the development needs of high-density memory, miniaturization and low power consumption, a new type of HfZrO₂ ferroelectric memory with great research prospects came into being. Ferroelectric properties in fluorite-structure oxides such as hafnia and zirconia were first reported in 2011 by Böscke et al. [6, 10]. Since then, there has been increasing interest in the new material. The HfZrO₂ ferroelectric ferroelectric memory can achieve a very fast read and write speed (about tens of ns), it has a relatively low operating voltage and power consumption. The HfZrO₂ ferroelectric memory determines the state of the stored binary data by using the direction of the remnant polarization strength of the ferroelectric material in the ferroelectric capacitor, and has excellent retention and anti-jamming capability[2]. The HfZrO₂ film is not only perfectly compatible with existing semiconductor processes, but also has a sufficiently strong polarization strength at 10 nm. This alleviates the physical limit problem referred to by Moore's Law to a certain extent, and opens a new path for the development of ferroelectric memory [11]. The thin-film device acts as a memory, and the stored data will undergo continuous writing, reading, and modification, which requires the ferroelectric thin film to withstand a large number of switching cycles. So far, the field cycling endurance of the hafnium-based ferroelectric thin film with the best durability has reached $4 \times 10^{10}$, but this is far from the durability of the perovskite material $\left(10^{15}\right)$. The new material itself has some defects, such as low crystallization temperature and high oxygen or impurity penetration[8], especially its fatigue effect seriously restricts its industrial development in semiconductor devices. As a result, the storage of data becomes no longer reliable. The entire fatigue cycle of the device consists of two phases, first the wake-up phenomenon and then the fatigue phenomenon. In the woken-up state, the
remnant polarization enhancement was observed, which was well matched with the results of other studies on the wake-up effect. In the fatigue state, a decrease could be observed in the remnant polarization. In some recent studies, some researchers have observed that the remnant polarization value of hafnium-based ferroelectric thin films will become lower and lower after the device reads and writes about 10^6 times, and the read-write window of the device decreases. This phenomenon is also common in devices based on traditional ferroelectric materials, which affects the normal use of the device. Although many fatigue mechanisms and solutions for ferroelectric materials have been proposed, there is no effective solution to the fatigue problems of emerging materials such as ferroelectric HfO₂.

At present, there are two highly recognized fatigue mechanism theories in academia. The first is the oxygen vacancy redistribution mechanism. They believe that the change in the film ferroelectric parameters is based on the redistribution of the internal oxygen vacancy concentration. Initially, no oxygen vacancies were generated, only the oxygen vacancy redistribution, leading to the remnant polarization to rise. The device generates new oxygen vacancies, the concentration of oxygen vacancies in the device is unbalanced, and the remnant polarization decays. Another researcher proposed the fatigue mechanism of domain pinning [5, 19]. This mechanism is that the device will change the number of switchable domains during the fatigue process, from the initial state to de-pinning to re-pinning, showing that the change in remnant polarization value is consistent with the results of other studies [3, 5].

So far, the fatigue problem is still one of the most serious reliability problems restricting the development of ferroelectric memory, and studying the internal mechanism of device fatigue effect has important practical significance for the development of ferroelectric memory. Although there have been some studies on HfO₂-based memory, the fatigue mechanism still needs to be clarified. In this paper, we will conduct an in-depth study on the 10nm HfZrO₂ film, and gradually fatigue the experimental samples through the tester and waveform generator. In this paper, the test voltage waveforms with different pulse widths are used to perform fatigue tests on the samples to explore the changes in ferroelectric properties. We also studied the electron filling behavior of the device, combined with electron microscopy and other means to deeply reveal the fatigue mechanism inside the sample. When the fatigue effect of the sample occurs, complex physical mechanism changes occur within the sample. The increase and decrease of the remnant polarization value correspond to the opposite changes of these internal microscopic physical mechanisms. To study these internal microscopic changes, to explore the internal mechanism of fatigue effect and to apply it to practice, it is necessary to clarify the influence of various experimental conditions on the internal effects of the device[11].

2. Experimental methods

To prepare samples for this work, HfZrO₂ thin films with a thickness of 10 nm were deposited on (100) Si single-crystal substrates by pulsed laser deposition using a KrF excimer laser. To serve as a bottom electrode, a TiN layer was deposited on the Si substrate. Square TiN top electrodes (100 μm × 100 μm), were deposited on the HfZrO₂ films by radio frequency sputtering through a shadow mask. The rough stacking structure of the samples is shown in figure 1.

A ferroelectric instrument (Radiant precision workstation) was used to measure the polarization (P)-voltage (V) curve of the sample and the polarization-electric field cycles (P-Cycles) of the sample. A semiconductor analyzer (B1500A, Agilent Technologies, USA) was used to measure the current-voltage (I-V) curve and capacitance-voltage (C-V) curve of this sample, and the change of oxygen vacancy concentration and position was analyzed by transient current experiment. Use a transmission electron microscope and other instruments to observe the phases inside the sample.
Figure 1. Schematic diagram of HfZrO$_2$ sample structure

3. Results and discussion

3.1. Fatigue phenomenon of HfZrO$_2$ film

![Graph showing fatigue phenomenon](image)
Figure 2. (a) The square waveform used in the experiment. (b) The pulse waveform used in the experiment. (c) The hysteresis loop of the experimental sample. (d) Relationship between sample remnant polarization ($P_r$) and cycles under square wave condition ($3V$, 1KHz). (e) I-V curve corresponding to Figure d.

Figures 2(a) and 2(b) are schematic diagrams of the square wave and pulse waveforms used in this thesis, respectively. Figure 2(c) shows the hysteresis loops of the samples at different fatigue stages. It is observed in Fig. 2d that the remnant polarization value of the film increases with the number of electric field cycles, which is consistent with the wake-up stage of the fatigue effect. As the number of cycles of the electric field continues to increase, the remnant polarization value of the sample continues to increase. Figure 2e shows the I-V curve of the sample after the electric field with different number of cycles. It can be seen that the leakage current does not change as the electric field cycle increases initially, and then the leakage current becomes larger. The increase of defects such as oxygen vacancies in ferroelectric thin films is the main factor for the increase of leakage current, so the leakage current can be used to characterize the concentration of oxygen vacancies. While the remnant polarization value increases with the number of field cycles, the leakage current also keeps increasing, which shows that the change of oxygen vacancy concentration or position may be one of the internal causes of the fatigue mechanism.

3.2. Fatigue mechanism

Figure 3. The change of $P$ of the sample under the square wave under different frequency waveforms ($3V$), the frequency is from 100Hz to 10KHz.

We apply a square wave waveform to the device, change the frequency of the waveform, and specifically analyze the impact on the thin film device. For waveforms with different frequencies, the lower the
frequency, the faster $Pr$ rises, and the higher the frequency, the greater the limit value of the electric field cycle of the sample, as shown in Figure 3. The lower the frequency, the greater the pulse width and the greater the impact on oxygen vacancies (the same number of fatigue cycles, lower frequency curve, greater residual polarization value), and the faster the homogenization of oxygen vacancy concentration. In addition, the higher the frequency, the smaller the pulse width, and the lower the probability of inducing new oxygen vacancies, so the device shows higher durability.

![Figure 3](image-url)

Figure 3. The lower the frequency, the greater the pulse width and the greater the impact on oxygen vacancies (the same number of fatigue cycles, lower frequency curve, greater residual polarization value), and the faster the homogenization of oxygen vacancy concentration.

![Figure 4](image-url)

Figure 4. (a) Apply a pulse voltage (Voltage: 3V, frequency: 1KHz) to the sample and measure the effect of different waveforms on the film sample $Pr$. (b) Variation trend of $Pr$ in samples with different pulse width.

Change the experimental waveform and use pulse waveform (3V, 1KHz) to perform fatigue test, and obtain the relationship between the remnant polarization value and the number of cycles. The comparison with the square wave (3V, 1KHz) experimental result is shown in figure 4(a). Using pulse waveform at the same frequency and changing the pulse width of the waveform will have a significant effect on the fatigue effect of the sample, which shows that the duty cycle of the experimental waveform also has an effect on the ferroelectric performance of the sample. We provide a pulse waveform for the sample (waveform frequency is 1KHz), change the pulse width of the waveform to carry out the fatigue test on the sample, and then measure the relationship between the remnant polarization value of each fatigue stage and the corresponding number of electric field cycles in the figure 4(b). When the pulse width is less than 0.1ms, almost no wake-up phenomenon is observed in the sample, and the remnant polarization value starts to decrease after a certain period of stability. When the pulse width of the applied experiment waveform reached 0.5ms (duty cycle is 1/2), the sample began to have a significant wake-up phenomenon, but no fatigue occurred, and the sample broke down after a certain number of electric field cycles. Combining with the existing research conclusions, we believe that the voltage applied across the sample electrode will have a microscopic driving effect on the oxygen vacancy inside the sample. When the pulse width of the applied pulse reaches a certain value, it will break the microbalance inside the sample (the pinning effect of the electric dipole, etc.) causes a certain degree of movement of the oxygen vacancy. In theory, there is a value. When the pulse width of the applied pulse is this value, the polarization state of the device can be changed frequently without causing a large change in the remnant polarization of the device.

From the above experimental results, no new oxygen vacancies are generated during the wake-up phase, and only existing defects are redistributed. The redistribution of oxygen vacancies will cause the internal field of the device to become uniform. This aspect may cause the voltage division of the interface layer and the internal part of the device under an applied voltage to change (a larger voltage division may be obtained inside the film). Therefore, a voltage value exceeding the coercive voltage is obtained inside the film, and the film undergoes polarization reversal. More electric field cycles start to generate new oxygen vacancies in the device, so the internal field becomes non-uniform, part of the area cannot change the polarization state, and the remnant polarization value decreases. On the other hand, the redistribution of oxygen vacancies changes the internal electric field, which will break the existing
positive and negative charged combinations such as electric dipoles, resulting in de-pinning of the domain. The number of switchable domains increases, and the remnant polarization value increases accordingly. The oxygen vacancies generated during the fatigue phase lead to an increase in the pinning of the domain and a decrease in the remnant polarization value. The change in oxygen vacancy concentration during the wake-up phase will also induce a phase change, which causes the film to change from the other phase to the ferroelectric phase, and the remnant polarization value increases accordingly. In addition, the continuous increase of oxygen vacancies during the fatigue phase of the sample will lead to an increase in leakage current and breakdown of the device (the sample shown in Figure 2c has breakdown during the wake-up phase) [4].

4. Conclusions
In conclusion, this article uses different electrical conditions to test the film. The film samples used in the above experiments show different performance trends for different voltage waveforms, pulse frequencies, and waveform pulse widths. Regarding the mainstream fatigue mechanism of this sample, there are roughly two opinions currently recognized. The first is that the uneven distribution of oxygen vacancies leads to fatigue, and the second is the field-cycling-induced phase transition. For the original sample, there will be some oxygen vacancies due to various inherent defects, and these oxygen vacancies play a vital role in the ferroelectric properties of HfZrO₂ sample. With the increase of the electric field cycles, the leakage current increases, indicating that the oxygen vacancy concentration increases after a certain cycle, that is, new oxygen vacancies are generated. In the above experiment, the square wave has a larger pulse width in each cycle than the pulse, and the voltage stimulation time for the sample is longer. In the external excitation experiment of the pulse waveform, the larger the pulse width of the pulse waveform, the more obvious the remnant polarization of the sample changes. The external pressure time has an important effect on the performance of the HfZrO₂ film. The longer the applied voltage time, the more obvious the promotion of oxygen vacancies. The remnant polarization value of the sample first increases and then decreases with the increase of the electric field cycles. With the generation of new oxygen vacancies, the leakage current of the sample increases and the sample breaks down. The road for HfZrO₂ samples to be put into real applications is still very long, and its stability and durability need to be further explored and optimized, especially its breakdown with electric field cycles still needs researchers to further solve.

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