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Observation of inhomogeneous oxygen distribution in electric-field-cycled $Hf_{0.5}Zr_{0.5}O_2$ thin films prepared by atomic layer deposition

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This study investigates the impact of ion distribution, with a particular focus on oxygen ions, on the stability and phase transformation processes of the hafnium zirconium oxide (HZO) ferroelectric phase. Using atomic layer deposition (ALD) to prepare HZO thin films, this research analyzes the microscopic particle distribution of various fatigue aging states from an elemental distribution perspective through spherical aberration-corrected electron microscopy. The results reveal that while the distribution of Hf and O ions remains relatively uniform in fresh samples, notable differences emerge in the distribution of oxygen ions in HZO samples after wake-up and fatigue processes. These findings suggest that the variation in oxygen ion distribution plays a crucial role in the phase stability and transition dynamics of HZO ferroelectric materials.

Keywords: Ferroelectric; hafnium zirconium oxide; atomic layer deposition; oxygen ion distribution.

1. Introduction

The identification of robust scale-free ferroelectricity in MO_2 (M=Hf, Zr) fluorite thin films, doped with various elements on Si or oxide substrates, as well as with noble metal or metal nitride electrodes,[1–3] illuminates the potential for next-generation nanoelectronic memory devices.[4–6] Defects are widely recognized for their significant role in enhancing ferroelectricity and influencing fatigue and bipolar-cycling performance.[7]

Recently, Nukala *et al.*[8] reported a reversible oxygen migration and phase transition in hafnia-based ferroelectric devices where the dielectric layer acts as an oxygen source and sink. This suggests that the ferroelectricity is unmistakably intertwined with oxygen voltammetry. Ma and Liu[9] along with Ma *et al.*[10] theoretically demonstrated that not only the structural polymorphism kinetics was promoted by charged oxygen vacancies, but also a ferroelectric-switching-promoted oxygen ion transport dynamic behavior in HfO_2 was found. The bias-driven successive ferroelectric transitions facilitate ultrahigh oxygen ion mobility at moderate temperature. The correlation between oxygen migration and ferroelectricity switching is evident. To deepen our understanding of the fatigue process under electric field cycling, it is crucial to explore the relationship between the fatigue state and oxygen migration in hafnia-based devices.

In this work, by employing aberration-corrected scanning transmission electron microscopy (AC-STEM), we analyzed the distribution of oxygen ions in $Hf_{0.5}Zr_{0.5}O_2$ (HZO) ferroelectric films under three distinct states: Fresh, wake-up and fatigued. The HZO film is prepared by atomic layer deposition (ALD) following our previous work.[11] Our findings reveal that the distribution of oxygen ions varies significantly across these states. From the fresh samples to the fatigued and aged ones, the distribution of oxygen ions within the HZO film becomes increasingly uneven, with a

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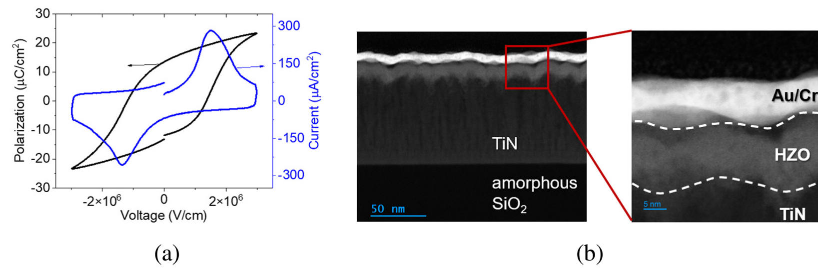

Fig. 1. Thin film preparation of the ALD-prepared HZO film. (a) Ferroelectric polarization hysteresis (PE loop) of the prepared HZO film. (b) Cross-sectional image of the HZO film and it's locally enlarged image of the HZO film interface.

pronounced tendency to accumulate at the top and bottom interfaces of the HZO layer. In the breakdown state, it is evident that oxygen ions have penetrated into the underlying TiN layer.

Initially, the ferroelectric quality of the thin film sample is confirmed by depositing Cr/Au top electrodes and testing their ferroelectric properties. As shown in Fig. 1(a), the thin film exhibits a typical polarization-electric (PE) field hysteresis loop, with a remanent polarization of approximately 10 μC/cm^2. The film also demonstrates two polarization reversal current peaks, and the leakage current is not significant. Figure 1(b) presents a cross-sectional transmission electron microscopy image of the thin film's interface, revealing the multilayer structure within the film, including the TiN/SiO_2/Si substrate, HZO thin film and top electrode. The interface structure is relatively clear, further corroborating the quality of the thin film's multilayer architecture.

Figure 2(a) displays a local structure image of the HZO thin film, with the bright white areas corresponding to the Au/Cr electrodes. Figure 2(b) is an enlarged view of a local area from Fig. 2(a), revealing a clear atomic-scale surface and confirming the structure to be a typical orthorhombic O-phase. This indicates that a relatively stable O-phase has formed within the HZO thin film, which is consistent with

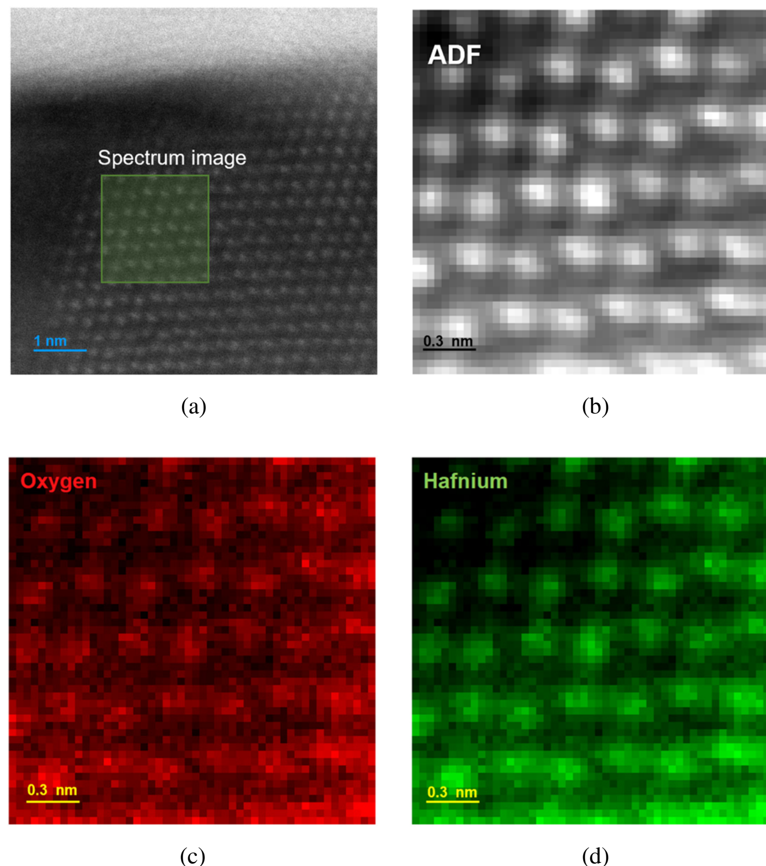

Fig. 2. Microstructure of the HZO thin films. (a) Atomic level image of the film. (b) Magnified atomic level image of the HZO film. (c) Oxygen element distribution of the measured surface corresponds to (b). (d) Hafnium element distribution of the measured surface.

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the ferroelectricity demonstrated in Figs. 1(a), 2(c) and 2(d) show elemental distribution images for O and Hf in the corresponding magnified areas, displaying a clear distribution of O and Hf ions along the lattice. Due to the equal proportion stoichiometric relationship between Hf atoms and Zr atoms in $H_{0.5}Z_{0.5}O_2$, Zr atoms have the same distribution diagram as Hf elements in Fig. 2(d).

Based on the excellent ferroelectric properties and stable ferroelectric phase structure, we conducted a study on the cyclic fatigue aging of the sample. Figure 3(a) clearly shows the ferroelectric polarization cycling test structure of the HZO thin film. Before 10^4 cycles, the sample exhibited a constant remnant polarization with the increase of electric field circulation and almost no wake-up effect. The sample then underwent a process of fatigue aging with a decline in the polarization after 10^4 cycles, and finally broke down after 10^7 cycles. Figure 3(b) presents the (PE) field loop of the sample after the wake-up process, demonstrating that the polarization is still maintained at a level of approximately $10\,\mu C/cm^2$. These cycling numbers are similar to some results reported for HZO prepared using the ALD method.[12–16]

To understand why ferroelectricity changes during fatigue aging under an electric field, especially oxygen ion distribution shifts, we analyzed Hf and O ion distributions in fresh (Fig. 4(b)), wake-up (Fig. 4(c)) and breakdown samples (Fig. 4(d)). They went through 10^0, 10^5 and 10^7 electric field cycles, respectively. The remanent polarization of the film can be referred in Fig. 3. From the process of fresh to wake-up to fatigue and finally breakdown, the distribution of Hf atoms represented by the green band in Fig. 4 is still very

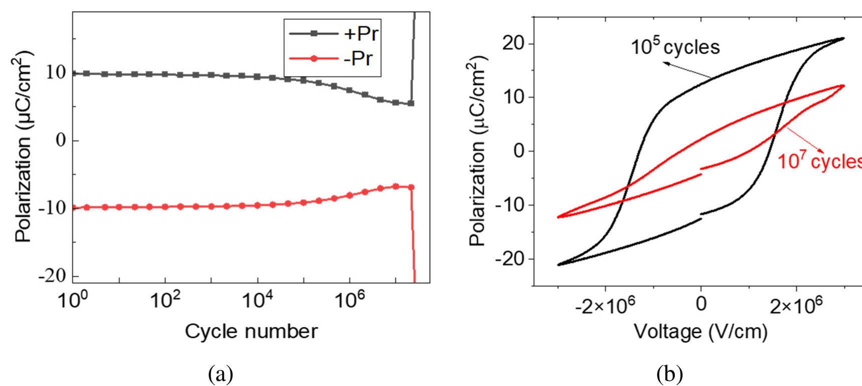

Fig. 3. Polarization fatigue properties of the HZO sample. (a) Polarization as a function of the hysteresis cycle. (b) Polarization hysteresis after the wake-up (10^5 cycles) and fatigue (10^7 cycles) processes.

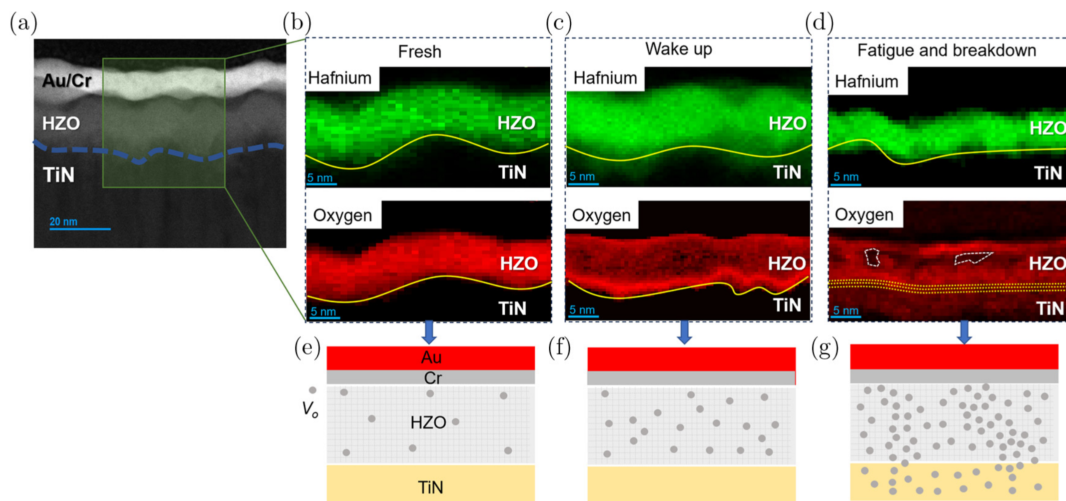

Fig. 4. (Color online) Element distribution (hafnium and oxygen) in HZO samples at different cycling state. (a) Cross-sectional TEM image of the HZO thin films. The dashed blue line represents the interface between the HZO film and the TiN electrode. (b–d) The element mapping of the sample for fresh, wakeup and fatigue states, respectively. The yellow lines represent the interface between the HZO film and the TiN electrode. The irregular white dashed boxes indicate the area with aggregation of oxygen vacancies. (e)–(g) Schematic illustration of the cross-sectional profile of the capacitor devices where oxygen vacancies show different distributions and concentrations corresponding to (b–d), respectively.

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uniform, but oxygen ions become uneven after the wake-up process, accumulating at HZO film boundaries, making the interface between HZO ferroelectric film and the TiN electrode no longer clear. This uneven elemental distribution is even more pronounced in the breakdown sample. As illustrated in Fig. 4(d), for the sample after fatigue and breakdown, more emergent oxygen vacancies can be visually observed. In addition, it is worth noting that such a situation did not occur with the top electrode Au/Cr, which may be due to the reaction between active Cr and the O atom on the surface of the HZO film to form a dense Cr_2O_3 film during the thermal evaporation of the Cr electrode.[17] It is this layer of oxide film that prevents the oxygen atom from being injected into the Au/Cr electrode during the electric field cycling. Moreover, there are aggregations of oxygen vacancies in the local area indicated by the irregular white-dashed boxes. Figure 4(c) also shows that some oxygen ions have appeared in the TiN layer, indicating that oxygen ions have penetrated into the TiN layer. Though the local element distribution may not be accurate enough, these qualitative analyses suggest that the ferroelectricity of the HZO thin film becomes unevenly distributed under the action of an external cyclic electric field, and this unevenness is closely related to the occurrence of the breakdown process. In addition, according to the polarization behavior of the thin film in Fig. 3(a), the polarization of the thin film is almost unchanged when oxygen ions are slightly injected into the TiN electrode during the wake-up process. A large amount of oxygen ions are accumulated in the TiN electrode after fatigue and breakdown processes, while the polarization of thin film changed a little. This indicates that the accumulation of oxygen ions at the interface between the thin film and the electrode has little effect on the polarization performance of the thin film. But a large number of oxygen ions migrate to the inside of the TiN electrode, resulting in the formation of internal conductive defect channels and accelerating the breakdown of the thin film. While we acknowledge the limitations of aberration-corrected transmission electron microscopy in resolving the distribution of oxygen ions, the distribution of oxygen ions in these three states is indeed different, indicating that oxygen ions play a very important role in controlling the ferroelectricity of hafnium-based ferroelectric thin films in the future. This finding is consistent with our recent report on the close relationship between oxygen ion dynamics and the polarization reversal and structural evolution dynamics of hafnium-based ferroelectric oxides.[9,10] It also indicates that in the future fabrication process of HZO ferroelectric memory devices, it is essentially necessary to regulate the thermodynamic behavior of oxygen ions to mitigate the uneven distribution of oxygen ions under the electric field cycling.[18] Additionally, a buffer layer design can be used to prevent the diffusion of oxygen ions into the electrode layer, avoiding more severe uneven distribution of oxygen ions.[19–21]

2. Conclusion

In summary, this study used ALD to create HZO films with good ferroelectricity, confirmed by STEM to stem from the ferroelectric orthorhombic phase. We analyzed oxygen ion distribution in fresh, wake-up and breakdown films. While Hf ions remained uniform, oxygen ions became uneven with cycling, penetrating the TiN layer in fatigue and breakdown processes. In contrast, there is no obvious ion penetration in Cr layer. This impressive oxygen ion penetration in the TiN suggests that during cycling, the TiN tends to be oxidized, playing as a “greedy snake” to chemically absorb the oxygen ions in HZO layer. This indicates that the excess concentration of oxygen vacancies would promote the conduction and breakdown of the HZO thin films. Therefore, in the future, strategies need to be put forward to address the problem of excessive loss of oxygen ions. This clarifies oxygen ions’ role in polarization reversal and fatigue aging.

3. Experimental Section

First, SiO_2/Si substrates were cleaned using acetone, absolute ethyl alcohol and deionized water. Subsequently, the bottom TiN electrodes with thickness of approximately 90 nm was deposited on the SiO_2/Si substrates using physical vapor deposition (PVD). Then, the $Hf_{0.5}Zr_{0.5}O_2$ thin films with thickness of approximately 12 nm were grown at 200°C by ALD on the TiN/SiO_2/Si substrates. The [(CH_3) (C_2H_5) N]$_4$Hf (TEMAH), [(CH_3) (C_2H_5) N]$_4$Zr (TEMAZ), and H_2O were used as the Hf, Zr and oxygen precursors, respectively. Further, the top Au/Cr electrodes, approximately 45 nm and 15 nm, respectively, are deposited by thermal evaporation of Cr and Au in sequence with a shadow mask, yielding a measured electrode area of approximately 77900 μm^2. Finally, rapid thermal annealing (RTP) was performed in N_2 atmosphere for 60 s at 500°C to crystallize the as-deposited HZO thin film.

Microstructures of the $Hf_{0.5}Zr_{0.5}O_2$ thin films were examined by AC-STEM. Energy dispersive X-ray spectroscopy (EDS) was employed to identify the element distributions. The Au/Cr/HZO/TiN/SiO_2/Si capacitors were measured using a precision multiferroic analyzer (RADIANT Tec. Inc.). The P-E hysteresis loops were obtained via simple hysteresis mode and triangular pulses with frequency of 1 KHz were applied to reverse the polarization of ferroelectric HZO layer. The cyclic durability of the film was evaluated using the fatigue mode, where a square wave with a frequency of 100 kHz and an amplitude of 3.0 V were applied.

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