

Observation of Field-Induced Interface Reactions in HfO₂-Based Ferroelectric Devices by HAXPES

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Ferroelectric HfO₂-based materials are attractive for future nonvolatile memory devices due to their excellent CMOS compatibility and thickness scalability (<10 nm) [1]. However, it remains critical reliability issues such as fatigue and hard breakdown during electric field cycling [2]. These endurance degradations were thought to be mainly caused by the formation of defects such as oxygen vacancies (V_O) in HfO₂-based films [3], but it has been unclear why V_O increases during field cycling. In this study, we investigated the interface reaction between the ferroelectric Hf_xZr_{1-x}O₂ (HZO) film and TiN electrode during field cycling by synchrotron HAXPES to clarify the origin of endurance degradation.

Three different switching cycles, such as pristine for 10⁰, wake-up for 10⁴, and fatigue for 10⁸, were applied to TiN/HZO (10 nm)/TiN ferroelectric capacitors (Fig. 1(a)). Then, chemical states of Ti at the HZO/TiN bottom-electrode interface were evaluated by synchrotron HAXPES with the X-ray energy of 8 keV after removal of TiN top-electrodes (Fig. 1(b)). In the pristine state, Ti-O and Ti-N peaks of Ti 1s spectra were observed, indicating that a TiO_xN_y interfacial-layer (IL) was formed at the HZO/TiN interface. In the wake-up state, no difference of Ti 1s spectra was observed between the pristine and wake-up states. Therefore, the HZO/TiN interface did not change during wake-up field cycling. In the fatigue state, on the other hand, the Ti-O and TiO_xN_y components increased compared to those of the pristine and wake-up states (Fig. 1(b) and 1(c)). This indicates that an oxygen-rich and thicker TiO_xN_y-IL formed at the HZO/TiN interface. Therefore, a field-induced interface reaction accompanied by oxygen diffusion from the HZO film to TiN electrodes should occur during fatigue field cycling, resulting in additional V_O formation in the HZO film (Fig. 1(d)). In conclusion, we clarified one of the origins of endurance degradation by evaluating field-induced interface reactions using synchrotron HAXPES.

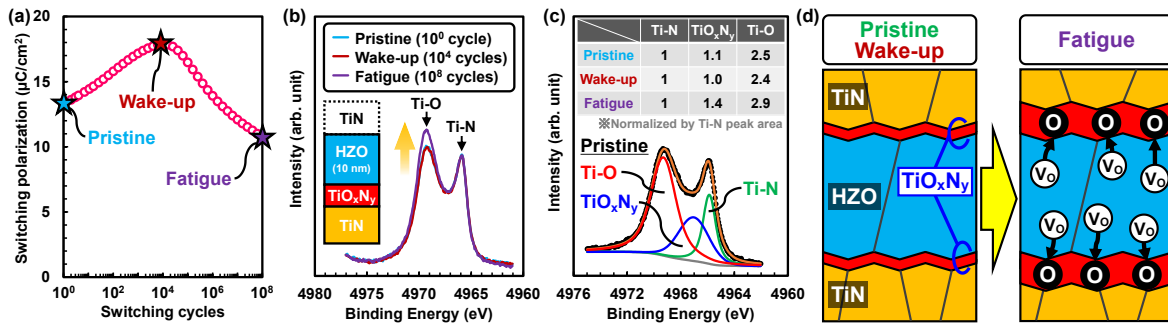


Figure 1 (a) Endurance properties of TiN/HZO/TiN capacitors. (b) HAXPES Ti 1s spectra of the HZO/TiN samples with different switching cycles. (c) Peak area ratios of Ti 1s components estimated by peak deconvolutions. (d) Schematics of interface reactions during field cycling.

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[2] M. Pešić et al., Adv. Funct. Mater. **26**, 4601 (2016).

[3] W. Hamouda et al., Appl. Phys. Lett. **120**, 202902 (2022).

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Supplementary Pages

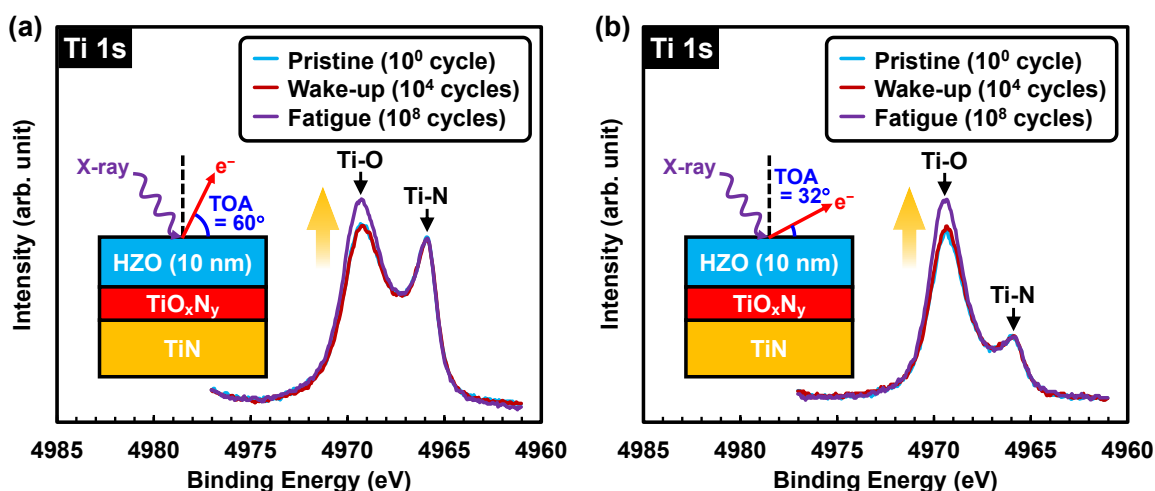


Figure 2 HAXPES Ti 1s spectra of the HZO/TiN samples after applying different switching cycles evaluated at the take off angle (TOA) of (a) 60° and (b) 32° . It is noted that the TiN top-electrode including the TiO_xN_y -IL between the HZO films and TiN top-electrode was fully removed using wet etching process evaluated by laboratory based XPS. In the pristine state, a Ti-O component (~ 4969 eV) was observed as well as a Ti-N component (~ 4966 eV). This is because TiO_xN_y -IL was formed at the HZO/TiN bottom-electrode interface during the atomic layer deposition process of HZO films. In addition, the Ti 1s spectrum evaluated using a surface-sensitive measurement condition (TOA = 32°) showed a higher peak area ratio of Ti-O to Ti-N compared to that evaluated using a bulk-sensitive measurement condition (TOA = 60°). This indicates that the surface region of TiN bottom-electrode contained more oxygen compared to the bulk region. In the wake-up state, the HZO/TiN bottom-electrode interface did not change from the pristine state. Therefore, the wake-up effect is not related to the interface reaction. These suggest that the field-induced phase transformation from the non-ferroelectric phase to the ferroelectric orthorhombic phase [S. S. Fields et al., *ACS Appl. Mater. Interfaces* 12, 26577 (2020).] and domain depinning in the HZO bulk region could be dominant factors for the wake-up [M. Pešić et al., *Adv. Funct. Mater.* 26, 4601 (2016).]. In the fatigue state, the Ti-O component increased compared to those in the pristine and wake-up states regardless of the TOA. These results also support an endurance degradation mechanism driven by field-induced interface reactions at the HZO/TiN interface.