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Ferroelectricity and ferroelectric resistive switching in sputtered $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ thin films

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Ferroelectric properties and ferroelectric resistive switching (FE-RS) of sputtered $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO) thin films were investigated. The HZO films with the orthorhombic phase were obtained without capping or post-deposition annealing. Ferroelectricity was demonstrated by polarization-voltage (P - V) hysteresis loops measured in a positive-up negative-down manner and piezoresponse force microscopy. However, defects such as oxygen vacancies caused the films to become leaky. The observed ferroelectricity and semiconducting characteristics led to the FE-RS effect. The FE-RS effect may be explained by a polarization modulated trap-assisted tunneling model. Our study not only provides a facile route to develop ferroelectric HfO_2 -based thin films but also explores their potential applications in FE-RS memories. *Published by AIP Publishing.*
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Ferroelectric HfO_2 -based materials have emerged as one of the most promising candidates to replace the conventional perovskites in the next-generation ferroelectric memories due to their Si-compatibility, scalability, and many other advantages.^{1–3} Recent advances include insights into the origins of ferroelectricity^{4–8} and development of high-performance ferroelectric memory devices.^{9–12} However, several critical issues remain as follows: (i) Overwhelming majority of previous studies used atomic layer deposition (ALD) to fabricate ferroelectric HfO_2 -based thin films.³ Since ferroelectricity was believed to be correlated with a polar orthorhombic (o-) phase rather than the specific ALD process, it would be of necessity to develop ferroelectric HfO_2 -based films using other fabrication techniques. (ii) To date the ferroelectric properties of HfO_2 -based films have been mostly investigated at a macroscopic level. The microscopic study of domain structures and local polarization switching is still lacking.¹³ (iii) In terms of device applications, advanced ferroelectric capacitive memories such as 3D trench capacitors for ferroelectric random access memory (FeRAM)¹⁰ and ferroelectric field effect transistors (FeFET) at the 28 nm node¹¹ have been developed recently. However, the ferroelectric resistive memories based on HfO_2 remain largely unexplored.

Previous studies have shown that ferroelectric $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO) films, a model system from the HfO_2 family, could be developed in a wide composition range¹⁴ and at relatively low temperatures (400–700 °C).¹⁵ In addition, their ferroelectric properties show weak dependence on the effects of capping¹⁶ and good resistance to the degradation during annealing.¹⁷ In this letter, we fabricated HZO films by sputtering, and studied their ferroelectric properties by both

polarization-voltage (P - V) measurements and piezoresponse force microscopy (PFM). The ferroelectric resistive switching (FE-RS) behavior in HZO films was also investigated. Note that according to previous studies, the ALD-deposited HZO films were not suitable for FE-RS memories due to their high resistivity^{17–19} and bulk-limited conduction mechanisms (Poole–Frenkel (PF) emission¹⁸ and phonon-assisted tunneling between traps¹⁹). The high resistivity hinders the reliable detection in the reading process where only a small voltage is applied. Furthermore, the bulk-limited conduction mechanisms are not compatible with the FE-RS because FE-RS relies on the interplay between polarization and interface-limited conduction mechanisms.^{20–24} These two issues may be overcome by sputter-deposition of HZO films. During sputtering, defects (acting as traps), in particular, oxygen vacancies (V_{O}), are easy to form. Increased density of defects facilitates either PF emission or tunneling between traps, thus enhancing the bulk conductivity of HZO and eventually changing the bulk-limited conduction mechanism to an interface-limited one. This renders sputtering a viable method to prepare HZO films with promising FE-RS properties.

HZO thin films with thicknesses of 7.5, 15, 22.5, and 30 nm were deposited on TiN-buffered Si (100) substrates by rf-magnetron sputtering (AJA Orion 8). During the growth of both HZO and TiN layers, sputtering power, growth temperature, and Ar gas pressure were kept at 200 W, 500 °C, and 10 mTorr, respectively. No capping layers were deposited on top of HZO during the cooling process. After cooling, Au dots with a diameter of 200 μm were *ex situ* sputtered on HZO at room temperature. No post-annealing was applied to the Au/HZO/TiN capacitors. Compared with ALD, our sputtering process was simple as capping or post-deposition annealing was not required. The crystal structure and microstructure of deposited HZO films were investigated by

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grazing incidence x-ray diffraction (GIXRD; Bruker D8 Advance) and transmission electron microscopy (TEM; JEOL JEM-2100F), respectively. The P - V hysteresis loops were measured by a ferroelectric test station (Radiant Precision Workstation). Microscopic amplitude and phase images and local hysteresis loops were studied by PFM (MFP-3D, Asylum Research, USA). The DC leakage currents were measured using an electrometer (Keithley 6430). The signs of poling and reading voltages are denoted positive when the top electrode is positively biased.

Figure 1(a) shows the GIXRD results of sputtered HZO films with different thicknesses. All HZO films are polycrystalline, as further confirmed by the cross-sectional TEM image (Figure 1(b)). The diffraction peaks around 30.5° corresponding to tetragonal (t-) and/or o-phases can be easily identified in 15-, 22.5-, and 28-nm films. (The 7.5-nm film shows very weak peaks due to its small thickness reaching the detection limit of our GIXRD system.) Although further distinguishing o-peak from t-peak is difficult, this overlapped t/o-peak can already be regarded as structural evidence for (anti-)ferroelectricity.^{14,15} The fraction of the t/o-phase, as derived from the relative intensities of diffraction peaks, becomes smaller as the film thickness increases. This is due to the surface energy effect that is responsible for stabilization of t/o-phase. This effect weakens with increasing film thickness, resulting in the gradual dominance of the monoclinic (m-) phase.⁷

Although the existence of the t/o-phase in sputtered HZO films was suggested by GIXRD, the existence of (anti-)ferroelectricity needs to be verified. A positive-up negative-down (PUND) method²⁵ was used for the P - V measurements.²⁶ In PUND, a “positive” pulse is applied after negative initialization and it measures the total polarization. A following “up” pulse measures the non-ferroelectric polarizations (including contributions from leakage current and paraelectric responses) and the relaxed polarization. The positive branch of the remnant loop may therefore be obtained by subtracting the half-loop measured by the “up” pulse from that measured by the “positive” pulse. (The same principle applies to extracting the negative branch of the remnant loop). As shown in Figures 2(a) and 2(b), the 15-nm HZO film is quite leaky; however, it still exhibits ferroelectric-like characteristics as suggested by the remnant loop. Additional results confirming the ferroelectricity, including current responses to voltage stimulations measured in a PUND manner and frequency-dependent current responses, are presented in the supplementary material.²⁶ The remnant loops may also be observed in

22.5- and 30-nm films (Figure S4²⁶), but P_r becomes smaller as film thickness increases, which is consistent with the GIXRD results of smaller fractions of t/o-phase in thicker films. Asymmetric polarization switching behavior is found with $|+2P_r| \sim 40 \mu\text{C}/\text{cm}^2$ and $|-2P_r| \sim 20 \mu\text{C}/\text{cm}^2$ ($|-2P_r|$ may be inaccurate²⁶). This asymmetry may be caused by the domains with preferred downward orientation, thus making their upward switching very difficult. In addition, a larger leakage current under negative poling voltage further prevents the upward switching of domains. Compared with the ALD-deposited HZO films of similar thickness,^{14–18} the sputtered HZO films show comparable polarization values despite the existence of significant leakage. The retention properties of those sputtered HZO films are relatively good (Figure 2(c)); however, their endurance properties are poor as indicated by the dramatic polarization reduction after only 100 cycles (Figure 2(d)). This may suggest the existence of a large number of defects (e.g., V_{Os}) in the HZO films, which migrate to domain walls or ferroelectric/electrode interfaces and thus pin the polarization switching.²⁷

To gain further information of ferroelectricity, PFM studies were conducted. The amplitude and phase images in Figures 2(e) and 2(f) were taken after DC poling and subsequent grounded-tip scanning for two times. The $+7\text{ V}$ and -7 V poled regions show different contrasts in both amplitude and phase images, indicating that domains are switched towards opposite out-of-plane directions. The domain switching in the poled regions appears to be incomplete, probably due to the existence of non-ferroelectric m-phase and the relaxation of switched domains. Figure 2(f) shows that the preferred orientations of domains in the as-grown region are mainly downward, which is consistent with previous P - V results. The amplitude and phase loops obtained in the bias-off states exhibit a butterfly shape and a near 180° switching, respectively (Figures 2(g) and 2(h)), demonstrating the occurrence of local ferroelectric switching. The asymmetries in amplitude and phase loops also point to the existence of defects because the asymmetries are known to be associated with an internal field created by non-uniformly distributed charged defects.²⁸ Note that the poling fields used in PFM are larger than those in P - V measurements due to the large tip-sample contact resistance. More comprehensive PFM results and analyses of artifacts²⁹ are found in the supplementary material.²⁶

The significant leakage behavior in the sputtered HZO films, as indicated by the P - V measurements, was then characterized by DC measurements. Figure 3(a) displays a typical DC

FIG. 1. (a) GIXRD patterns of HZO films with different thicknesses. (b) Cross-sectional TEM image of the 15-nm HZO film.

FIG. 2. Ferroelectric properties of the 15-nm HZO film. (a) Positive and (b) negative branches of the P - V hysteresis loops measured by a PUND method with the pulse width of 0.15 ms. (c) Retention properties measured by varying the delay period in the PUND method (no further longer delay period is tested because its upper limit has been reached in our Radiant workstation). (d) Fatigue behavior measured with an applied stress of 2 V. (e) Amplitude and (f) phase PFM images after pooling and subsequent grounded-tip scanning. Local (g) amplitude and (h) phase hysteresis loops.

density-voltage (J - V) curve of the 15-nm film (pre-poled with a -2 V, 0.15 ms triangle pulse) measured in a voltage sweeping mode (delay time of 0.5 s per data point). The high leakage level ($\sim 10^0$ A/cm 2 at 1.3 MV/cm) is about three orders of magnitude larger than that of the ALD-deposited HZO films.^{18,19} The initial J - V curve shows two peaks in the direct course of voltage sweeping ($0 \rightarrow 2$ V and $0 \rightarrow -2$ V), suggesting the occurrence of polarization switching accompanied by redistribution of space charges.^{19,30} However, there are no observable current peaks in the reverse course of voltage sweeping ($2 \rightarrow 0$ V and $-2 \rightarrow 0$ V) because

polarization switching has been completed. To support this, the DC J - V measurements with voltage sweeping from $0 \rightarrow 2$ V and $0 \rightarrow -2$ V were conducted after pulse poling with $+2$ V and -2 V, respectively. As shown in the inset of Figure 3(a), neither current peaks nor diode-like rectifying behavior is observed. In the cycling DC tests, the J - V curves are unstable, and the peaks gradually disappear as the cycle number increases (Figure 3(a)). This may be due to the migration of charged defects to domain walls or ferroelectric/electrode interfaces pinning the polarization switching. This effect has also been regarded as the origin of the fatigue

FIG. 3. Conduction behavior of the 15-nm HZO film. (a) J - V curves measured in a DC sweeping mode. The inset shows J - V curves measured after pulse poling. (b) J - V curves measured from 0 to +1 V after poling in different directions. The maximum voltage is limited to +1 V to avoid polarization switching. (c) Retention and (d) endurance properties of the FE-RS effect. The small reading voltage is +0.3 V. In panels (a)-(d), the applied pulse width is 0.15 ms.

behavior (Figure 2(d)) and becomes more significant in the case of DC voltage sweeping. Therefore, to realize polarization switching with minimized electro-migration of defects, pulse poling rather than DC poling was used.

As simultaneously being ferroelectric and semiconducting (leaky), the sputtered HZO films may show promising FE-RS effects. As shown in Figure 3(b), after +2 V pulse poling, polarization is oriented downward, and the film is switched to a relatively high resistance state (HRS). In contrast, a -2 V pulse poling leads to a relatively low resistance state (LRS). These HRS and LRS are considerably stable under a small reading bias of +0.3 V (Figure 3(c)). The switching endurance is however limited to only a few cycles (Figure 3(d)) that needs significant improvement before realization of practical use.

The current study focused on the possible origins of the observed FE-RS effects. Understanding of the conduction mechanisms is highly desirable. Various bulk-limited conduction models, such as PF emission, typical models of tunneling between traps,³¹ and space charge limited bulk conduction, are used to simulate the experimental current-voltage (*I-V*) curves below 1 V (Figure 3(b)). However, none of these models yields proper fitting or reasonable fitting parameters. This may be qualitatively interpreted as follows. The number of defects (traps) is large in the sputtered HZO films, thus facilitating both PF emission and tunneling between traps. The bulk is quite conductive, and the space charge built within the bulk may be quickly removed at relatively low voltages.^{32,33} The bulk is therefore not conduction limited. In addition, the bulk-limited conduction mechanism is irrelevant to the observed polarization-dependent conduction behavior. The interface-limited conduction mechanisms are then considered. Direct tunneling in the 15-nm film is negligible. Fowler-Nordheim tunneling is unlikely due to the small applied voltages.³⁴ To analyze the feasibility of Schottky emission, the energy band diagram of HZO (n-type semiconductor;^{35,36} bandgap: ~5.8 eV and electron affinity: ~2.8 eV (Ref. 37)) sandwiched between TiN (work function: ~4.7 eV) and Au (work function: ~5.1 eV) is established (Figure 4(a)). The Schottky barriers of TiN/HZO and Au/HZO are ~1.9 eV and ~2.3 eV, respectively, too high to allow for the Schottky emission. The observed *I-V* curves without diode-like rectifying behavior (inset of Figure 3(a)) and HRS obtained under a positive reading voltage in the polarization down state (Figure 3(b)) also rule out the Schottky emission. A trap-assisted tunneling (TAT) model for the HfO₂ films having a substantial number of traps (mainly V_{OS})³³ may be applicable to our observations. In this model, the traps facilitate the electron tunneling from the cathode into the film, which eliminates the need to overcome the high Schottky barrier (Figure 4(a)). The trapped electrons near the cathode/film interface are then quickly transported to the anode through PF emission or tunneling between traps (Figure 4(a)), since the bulk conduction is quite efficient. Therefore, the tunneling from the cathode to the traps becomes the major step limiting the whole conduction process. According to Ref. 33, the TAT current (*I*) is

$$I = N \cdot q \cdot \nu, \quad (1)$$

FIG. 4. (a) Schematic showing the conduction mechanisms in the HZO film containing a large number of traps. Steps 1–4 represent TAT from cathode to traps, Schottky emission, PF emission, and tunneling between traps, respectively. E_b and E_t denote Schottky barrier and trap energy level, respectively. Schematics showing the interactions between (b) positive, and (c) negative polarization charges and positively charged V_{OS} (traps). d denotes the distance between the cathode and nearest V_{OS}.

where N is the total number of nearest unfilled traps that contribute to the conduction, q is the charge quantity, and ν is the transition rate, which is given by

$$\nu = \nu_0 \cdot f \cdot P, \quad (2)$$

where ν_0 is the frequency factor, f is the Fermi-Dirac distribution of the electrons in the electrode

$$f = \frac{1}{1 + \exp\left(\frac{E_b - E_t + F \cdot d}{kT}\right)}, \quad (3)$$

and P is the transmission probability

$$P = \exp\left\{-\frac{4}{3\hbar q F} \sqrt{2m^*} \left[E_t^{1.5} - (E_t - F \cdot d)^{1.5}\right]\right\}. \quad (4)$$

In Eqs. (3) and (4), E_b is the Schottky barrier of TiN/HZO (TiN/HZO is the blocking interface under positive reading voltages); E_t is the trap energy below the conduction band; F is the electric field (the sign is negative when TiN is negatively biased); d is the distance between the cathode and the nearest unfilled traps; kT is the product of Boltzmann constant and temperature; $\hbar$ is the reduced Planck's constant; and m^* is the electron effective mass (~0.1 m_0 in HZO³⁷).

Based on Eqs. (1)–(4), the experimental *I-V* curves in both HRS and LRS (Figure 3(b)) may be fitted through adjusting two key parameters E_t and d , assuming that N is constant. In HRS, E_t is 1.82 eV and d = 1.1 nm; and in LRS, E_t slightly changes to 1.825 eV while d decreases to 1.02 nm. These parameters are consistent with those reported previously.³³ The fitting results may be briefly interpreted using a polarization modulated TAT model. In the polarization down state (after +2 V poling), the positive polarization charges at the TiN/HZO interface repulse the positively charged V_{OS} (traps), resulting in a larger d (Figure 4(b)). This makes the tunneling from the cathode to the traps relatively difficult, leading to a HRS. The reverse situation (Figure 4(c)) may also be analyzed in terms of the interaction between polarization charges and V_{OS}. Note that the real

scenario may be much more complex, because E_t , d , and even N may be simultaneously influenced by polarization charges. Nevertheless, the observed FE-RS behavior can be satisfactorily explained by this polarization modulated TAT model. This model will be invalid if the electro-migration of V_{OS} is significantly involved, since it influences the resistance state in a way opposite to the proposed model. For example, the positive poling drives the V_{OS} towards TiN, facilitating the electron injection from TiN to HZO under a positive reading voltage and thus lowers the resistance.³⁸ This is in contrast to the HRS induced by positive poling via the mechanism of polarization modulated TAT. The electro-migration of V_{OS} may be the origin of the poor endurance properties of FE-RS (Figure 3(d)). To improve the endurance properties, the electro-migration of V_{OS} need to be minimized by either pulse poling with appropriate frequency and amplitude or lowering the temperature to freeze V_{OS} .^{38,39}

In summary, HZO thin films with the desirable o-phase have been fabricated by a facile sputtering method that does not involve capping or post-deposition annealing required by ALD. Although becoming semiconducting due to the presence of V_{OS} , the sputtered HZO films retain ferroelectricity at both macro- and micro-levels, as evidenced by the P - V hysteresis loops measured in a PUND manner and PFM, respectively. The sputtered HZO films show the FE-RS behavior, which may be explained by a polarization modulated TAT model. Our results therefore demonstrate a facile route to develop ferroelectric HfO_2 -based thin films with potential application as FE-RS memories. Future work on the effects of distributions of ions and defects, and local phase compositions on ferroelectric and FE-RS properties^{40,41} is warranted.

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