Effects of TiN Top Electrode Texturing on Ferroelectricity in Hf$_{1-x}$Zr$_x$O$_2$

Robin Athle,* Anton E. O. Persson, Austin Irish, Heera Menon, Rainer Timm, and Mattias Borg*

ABSTRACT: Ferroelectric memories based on hafnium oxide are an attractive alternative to conventional memory technologies due to their scalability and energy efficiency. However, there are still many open questions regarding the optimal material stack and processing conditions for reliable device performance. Here, we report on the impact of the sputtering process conditions of the commonly used TiN top electrode on the ferroelectric properties of Hf$_{1-x}$Zr$_x$O$_2$. By manipulating the deposition pressure and chemistry, we control the preferential orientation of the TiN grains between (111) and (002). We observe that (111) textured TiN is superior to (002) texturing for achieving high remanent polarization ($P_r$). Furthermore, we find that additional nitrogen supply during TiN deposition leads to >5× greater endurance, possibly by limiting the scavenging of oxygen from the Hf$_{1-x}$Zr$_x$O$_2$ film. These results help explain the large $P_r$ variation reported in the literature for Hf$_{1-x}$Zr$_x$O$_2$/TiN and highlights the necessity of tuning the top electrode of the ferroelectric stack for successful device implementation.

KEYWORDS: hafnium oxide, III–V, ferroelectric FET, ferroelectric tunnel junction, thin films, CMOS integration

INTRODUCTION

Ferroelectricity in HfO$_2$ has since its discovery in 2011$^1$ been attracting strong interest for applications in nonvolatile memories and negative-capacitance transistors due to its strong remanent polarization ($P_r \sim 20–30 \mu C/cm^2$) and high coercive field ($E_c \sim 1–2 \text{ MV/cm}^2$), as well as being compatible with and already used in complementary metal-oxide semiconductor technology. In addition, ferroelectric (FE) HfO$_2$ can exhibit memristive behavior in ferroelectric tunnel junctions (FTJs) and ferroelectric field effect transistors (FeFETs),$^3$ which indicates its potential for application in neuromorphic computation. The ferroelectricity in HfO$_2$ is believed to originate from a noncentrosymmetric orthorhombic phase (o-phase) Pca$_2_1$, formed when a thin HfO$_2$ film is crystallized under the appropriate stress and annealing conditions. It has been demonstrated that a tensile in-plane stress in the HfO$_2$ induces a transition from the tetragonal phase (t-phase) to the preferred o-phase, thus leading to ferroelectricity.$^4$ This is commonly achieved by doping the HfO$_2$ and has been accomplished with a wide variety of dopants, with Zr being the most common due to its wide range of doping concentrations, yielding FE properties.$^5$ Apart from suitable doping, Böscke et al. highlighted the importance of the top electrode (TE) and its capping ability in achieving the o-phase.$^1$ It is believed that similar to the addition of dopants, the TE induces stress on the underlying Hf$_{1-x}$Zr$_x$O$_2$ film during annealing. The choice of an appropriate TE can thus enhance the FE properties of HfO$_2$. There has since been extensive research exploring various TEs such as Pt,$^6$ Mo,$^7$ W,$^8$ TaN,$^9$ and RuO$_2$, but reactively sputtered TiN is prominent.$^{1,2,5,11}$ Even so, reports are scarce on the effect of varying its microstructure. Deposition conditions such as plasma power, pressure, and gas mixture can strongly influence the microstructure of metals deposited by reactive sputtering, which in turn can affect the strain in the film.

In this work, we study the impact of processing conditions for reactively sputtered TiN, when used as a TE for FE Hf$_{1-x}$Zr$_x$O$_2$. By employing a combination of electrical characterization and grazing incidence X-ray diffraction (GIXRD), we reveal the importance of (111) textured TiN in achieving FE Hf$_{1-x}$Zr$_x$O$_2$. We further use X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure to strengthen our findings. A deepened understanding of the impact of the TE will provide improved reproducibility and performance of HfO$_2$-based FE devices.

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EXPERIMENTAL SECTION

Metal–insulator–semiconductor (MIS) capacitors were fabricated on an InAs(100) substrate ($\rho = 3 \times 10^{-4}$ $\Omega$ cm) with a 100 nm thick unintentionally n-doped InAs epilayer by metal-organic vapor-phase epitaxy. The native oxide was removed using BOE (1:10) immediately before loading the samples into a Picosun Sunale R-100 atomic layer deposition (ALD) chamber to deposit 12 cycles of Al$_2$O$_3$ (~1.2 nm) using TMAI and water as precursors, followed by 100 cycles (~10 nm) Hf$_{0.5}$Zr$_{0.2}$O$_2$ deposited by alternating cycles of TEMA(Zr) and TDMAT(Hf) in order to achieve a Hf/Zr ratio of 1:1, with water as the oxidizing precursor. All ALD depositions were carried out at a temperature of 200 °C. The use of Al$_2$O$_3$ as an interfacial layer reduces the native oxide of InAs and decreases interface defect density.12 Subsequently, a 10 nm thick TiN TE was deposited using RF magnetron sputtering, with a quartz crystal microbalance thickness meter, to control the deposited layer thickness. The deposition was carried out without a temperature controller at a power of 150 W in an AJA Orion system using a TiN target with 99.5% purity at varying chamber pressures and Ar plasmas. The deposition pressure used was 4.0 mTorr (samples A–E). The use of N$_2$ gas is inserted at the top of the chamber, in close proximity to the sample. For readability, the samples will be denoted A–E; see deposition conditions summarized in Table 1. After deposition, the samples were annealed using a rapid thermal processing system at 440 °C for 30 s, followed by an additional device pad definition via lift-off of electron beam-evaporated Ti/Pd/Au (1/5/200 nm). Finally, the TiN between devices was removed using a NaOH$_4$/H$_2$O$_2$/H$_2$O (1:2:5) wet etch for 30 s at 60 °C.

Electrical characterization was performed using a Keysight B1500A parameter analyzer equipped with a B1530A waveform generator fast measurement unit for pulsed measurements. The conventional positive-up-negative-down (PUND) technique was implemented to measure the polarization versus electric field at a frequency of 1 kHz.

| sample | pressure [mTorr] | Ar flow [sccm] | N$_2$ flow [sccm, (%)] |
|--------|------------------|----------------|------------------------|
| A      | 1.3              | 5              |                        |
| B      | 2.6              | 9              |                        |
| C      | 4.0              | 14             |                        |
| D      | 4.0              | 12             | 0.75 (6.25%)           |
| E      | 4.0              | 12             | 1.5 (12.5%)            |

Table 1. Deposition Conditions of TE TiN Samples

Electrical characterization was performed using a Keysight B1500A parameter analyzer equipped with a B1530A waveform generator fast measurement unit for pulsed measurements. The conventional positive-up-negative-down (PUND) technique was implemented to measure the polarization versus electric field at a frequency of 1 kHz. The electric field in this paper refers to the electric field applied across the bilayered structure of Al$_2$O$_3$/Hf$_{0.5}$Zr$_{0.2}$O$_2$. The PUND measurement was always carried out post wake-up cycling of 1000 times using the same voltage used for the PUND measurement. Cycling measurements were implemented using rectangular pulses at a frequency of 10 kHz at various voltages. For CV measurements, an Agilent 4294A impedance analyzer was used, keeping the oscillation amplitude at 50 mV at frequencies between 10 kHz and 10 MHz. For structural characterization, a Bruker D8 diffractometer with a Cu Kor X-ray source was used for GIXRD measurements with an incidence angle of 0.3–0.5° to determine the crystallographic texturing. A ZEISS Gemini 500 scanning electron microscope with an energy-dispersive X-ray spectroscopy (EDX) detector was used to determine the stoichiometry of the TiN TE.

Furthermore, the samples were examined using synchrotron-based X-ray techniques, XPS and near-edge X-ray absorption fine structure (NEXAFS), at the FlexPES beamline of the MAX IV Laboratory in Lund, Sweden. XPS was performed for O 1s, Ti 2p, N 1s, Zr 3d, and Hf 4f core levels at varying kinetic energies for characterization within the top 2 nm. Looking deeper with NEXAFS (~10 nm), N K- and Ti L-edge absorption spectra of total and partial electron yield were measured by recording electrical current from the sample.

RESULTS AND DISCUSSION

The polarization–electric field (P–E) characteristics at 3.5 MV/cm of samples with differently deposited TiN TEs are presented in Figure 1a. The evolution of the P–E with increasing field for sample E is presented in Figure 1b. The corresponding data and current–voltage characteristics of samples A–E are provided in the Supporting Information, Figure S2. In Figure 1c, the progression of the remanent polarization at increasing electric field of all samples is summarized. The $P_r$ values in Figure 1c are extracted from the P–E curves presented in the Supporting Information, Figure S2. The observed leakage currents are much smaller than the switching currents for all the samples, facilitating...
increased to 2.6 mTorr (sample B), the (002) re-
orientations are present. However, when the pressure is
with increasing chamber pressure. For sample A deposited with
pressure of 4.0 mTorr, there is no longer a distinct re-
orientation. The similar inclinations of the two re-
sections are inclined at 18.25 and 21.25° under the same conditions as used for the MIS samples (see Table 1). Sputtered TiN tends to have a preferential grain orientation (texturing) either with (111) or (002) aligned to the sample surface normal depending on the processing
conditions.13 The (111) and (002) reflections for cubic TiN are found at 2θ = 36.5° and 2θ = 42.5°, respectively.14 The measured data in Figure 2a indicate that both (111) and (002) reflections are present in the films to different extents depending on the sputtering parameters used. Due to the limited diffraction signal of thin polycrystalline films in the regular Bragg geometry, we are forced to utilize GIXRD geometry here, in which the measured (111) and (002) planes are inclined at 18.25 and 21.25° with respect to the surface normal. The similar inclinations of the two reflections allow us to obtain an indication of the preferential grain orientation from the relative peak intensities. A clear trend is observed with increasing chamber pressure. For sample A deposited with the lowest pressure of 1.3 mTorr, both (111) and (002) grain orientations are present. However, when the pressure is increased to 2.6 mTorr (sample B), the (002) reflection is reduced. Finally, for sample C with the highest deposition pressure of 4.0 mTorr, there is no longer a distinct reflection from (002) oriented grains, and the (111) reflection is lower in intensity compared to A and B, indicating lower degree of overall TiN crystallinity. This corresponds well with previously reported trends for TiN sputtering in literature and can be explained by a decreased ion energy with higher deposition pressures.13 The preferred texturing of TiN is decided by overall energy minimization, which for TiN becomes a competition between the low strain energy of the (111) plane and low surface energy of the (002) plane.35 At low ion energy (high pressure), the strain energy dominates and (111) overall energy minimization, which for TiN becomes a preferred (002) texturing. Therefore, by means of GIXRD. Figure 2a compares the measured data in Figure 2b, highlights the impact of the TiN texturing. The desired FE o-(111) reflection is expected at 2θ = 30.4° whereas the non-FE m-(111), is found at 2θ = 28°. A clear trend between predominately TiN (111) texturing and the intensity of the FE o-(111) reflection of the Hf1−xZrO2 can be observed. For sample D with a low N2 flow and predominantly (002) textured TiN, the lowest intensity of the o-(111) reflection is measured. Overall, the crystallinity is weak in this sample. On the contrary, sample B with (111) textured TiN has the strongest o-(111) reflection. As is typically reported for Hf1−xZrO2 the strong

Figure 2. (a) GIXRD of TiN on silicon between 30 and 50° with dashed vertical lines indicating the position of the (111) and (002) reflections from unstrained TiN, (b) GIXRD of Hf1−xZrO2 between 25 and 33°. Positions of the monoclinic m-(111), o-(111), t-(101), and m-(111) reflections are indicated. (c) Correlation between TiN(111) texturing, Hf1−xZrO2 o-(111) phase volumetric fraction and the remanent polarization \(P_r\).
correlation between the peak height of the α-(111) reflection and the remanent polarization $P_r$ magnitude. By accounting for the TiN TE, we provide further insights, revealing the additional interplay between the strength of the TiN (111) texturing and the strength of the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ α-(111) reflection. This correlation is highlighted in Figure 2c. For information regarding the calculation of the relative peak intensities, we refer to the Supporting Information.

It is important to understand why the conditions yielding predominant (111) texturing of the TiN also lead to a strong FE response of the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ film, while the FE response diminishes with stronger (002) texturing. A possible explanation for this lies in the induced strain from the TiN on the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ during the crystallization process. For TiN with (002) texturing, there will be compressive stress (up to $\sim 0.7$ GPa) acting on the underlying $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ whereas in the case of (111) texturing, a tensile stress (up to 1.4 GPa) is present instead.4,16 Indeed, we here extract a $\sim 1\%$ out-of-plane tensile strain from the TiN peak positions in samples A–C, confirmed by wafer curvature measurements. In samples D and E, we instead observe $\sim 1\%$ compressive strain (Supporting Information, Figures S3 and S4). Thus for samples A–C, we expect the out-of-plane tensile strain in the TiN to induce an in-plane tensile stress in the underlying $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ layer. There are many reports of in-plane tensile stress enhancing the out-of-plane FE properties since it allows for the transformation between the $c$-axis of the tetragonal phase into the a-axis of the orthorhombic FE phase.4,16–20 It is worth noting that despite having predominantly (002) texturing, sample E with TiN deposited with 12.5% N$_2$ exhibits a relatively strong α-(111) reflection and in turn, a $P_r = 17 \mu$C/cm$^2$ at 4 V bias. Clearly, for this sample, the TiN texturing cannot explain the out-of-plane FE properties since it allows for the transformation between the $c$-axis of the tetragonal phase into the a-axis of the orthorhombic FE phase.4,16–20

Complementing the electrical measurements, NEXAFS and XPS were conducted to investigate compositional differences between samples. MIS structures with 2 nm thin TiN layers were processed using the same deposition conditions as before (see Table 1) to accommodate the surface sensitivity of these techniques. Figure 3 shows X-ray absorption spectra (XAS) comparing the nitrogen K-edges of samples with varying N$_2$ gas flows. Samples D (dark green, 6.25% N$_2$ flow) and E (bright green, 12.5% N$_2$ flow) are juxtaposed with nitrogen-free deposition, sample C (dark red, 100% Ar flow). Increasing the nitrogen flow increased the sharp, high-energy shoulder at 400.8 eV, which is characteristic of the N 1s $\rightarrow$ 1π$^*$ transition of molecular nitrogen.21 It is noted that this signal was present even in sample C without N$_2$ flow, evidence of a byproduct of oxidation. Nonetheless, the peak size was comitant with flow, indicating that nitrogen gas had incorporated into the samples. This is reinforced by high-resolution NEXAFS spectra which exhibit the vibrational characteristics of N$_2$ trapped in lattice interstices22 (Supporting Information, Figure S5). The molecular nitrogen peaks were diminished in the more surface-sensitive partial electron yield NEXAFS and absent from XPS, indicating that N$_2$ was mainly incorporated close to or even in the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ layer, not in the strongly oxidized surface of the TiN layer. The inset of Figure 3 quantifies a more salient point; the entire N K-edge was integrated to get an estimate of the total nitrogen content. Whereas increasing gas flow from 0 to 6.25% N$_2$ resulted in approximately the same amount of nitrogen signal (samples C, D), further increasing it to 12.5% (sample E) came with a nearly 40% increase in nitrogen. Combined with the diffraction data, we interpret this as clear evidence of added N$_2$ gas flow changing the TiN chemical composition and even introducing molecular N$_2$ into the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$. As was previously hypothesized,23 interstitial N$_2$ may induce the necessary stress to facilitate the phase transition into the FE phase, explaining the high $P_r$ observed in sample E, despite having predominantly (002) TiN texturing.

Next, we evaluate the impact of the TE processing conditions on the cycling endurance of the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ films. In Figure 4a, we present the $P$–$E$ characteristics of sample E in its pristine state after 10$^3$ and 10$^4$ cycles. Corresponding measurements were done for samples A–D, where the evolution of the $P_t$ with cycling is presented in Figure 4b. The endurance data were measured by cycling rectangular pulses with an amplitude of 3 V at a frequency of 10 kHz. The polarization was measured with the PUND technique at a frequency of 1 kHz once per decade up to 10$^4$ cycles, followed by more frequent measurements up to 10$^6$ cycles. It is clear that the “wake-up” effect in the samples is different, possibly due to variations in the oxygen vacancy distribution. Three devices of each sample were measured, and similar results were achieved for all devices of a sample. In general, we observe that the endurance of the samples is limited by the InAs bottom electrode, known for a large interfacial defect concentration.23

![Figure 3. XAS and integrated intensity of nitrogen K-edges. Spectra are of TiN deposited with (C) 0% N$_2$, 100% Ar flow (dark red), (D) 6.25% N$_2$ flow (dark green), and (E) 12.5% N$_2$ flow (bright green).](https://dx.doi.org/10.1021/acsami.1c01734)
mean free path of the photoemitted electrons that was sufficient for characterizing the top 1–2 nm (Supporting Information, Figure S8). Although significant oxidation of TiN occurred upon exposure to ambient air, titanium oxide and oxynitride components were deconvoluted and their relative components quantified. The addition of high levels of nitrogen during TiN deposition (sample E) led to more (and presumably more thermodynamically stable) Ti–N species, which were less prone to oxidation. Supporting details are summarized in Table S2 and Figure S9.

To further explore the potential accumulation of defects in the Hf1–xZrO2 upon voltage cycling, capacitance–voltage (CV) characteristics were investigated. In Figure 5a–c, the measured CV data for samples B, D, and E are presented, where the bias is first swept from −3 to 3 V (solid) and then back to −3 V (dotted) while measuring the small signal response with an AC signal of varying frequency and amplitude of 50 mV. The frequency dispersion per decade in accumulation is investigated between the three samples in Figure 5d. Sample B in Figure 5a behaves as expected for a regular MIS structure with high capacitance when the semiconductor is in accumulation (>1 V) and by applying a negative voltage to the top contact the InAs is driven into depletion, leading to a decreased capacitance. Due to thermally excited minority carriers, there is an increase in capacitance again once the bias is reduced below −1 V, which is typical at room temperature for narrow band gap III–V materials such as InAs.27 As the frequency is increased, the capacitive contributions from minority carriers and defect states are reduced. For both samples B (Figure 5a) and E (Figure 5c), the typical “butterfly”-shaped CV curves are measured, exhibiting two distinct peaks arising from the increased capacitance during polarization switching. From the CV characteristics of the samples, the frequency dispersion per decade in accumulation can be extracted (Figure 5d). The dispersion between measurement frequencies allows one to qualitatively compare the distribution of defects in the dielectric from their time constants. From Figure 5d, it becomes evident that the introduction of N2 during deposition results in a smaller frequency dispersion per decade, with both samples D and E having lower dispersion up to 1 MHz. These results could indicate that a N2-rich TiN reduces oxygen vacancy defects in the Hf1–xZrO2 film, which reduces the capacitive influence of defect states. At the higher frequencies of 1–10 MHz, the dispersion becomes similar for all three samples. At these high frequencies, only defects with short tunneling lengths can respond. Hence, the contribution becomes dominated by defects located close to the semiconductor interface, which in this case would originate from the thin Al2O3 interface layer for all the measured samples.

**CONCLUSIONS**

This paper highlights the importance of the deposition conditions for sputtered TiN when used as a TE for FE Hf1–xZrO2. It is found that the remanent polarization of Hf1–xZrO2 films is heavily impacted by the texturing of the TiN film, ranging from almost zero for majority (002) texture up to 30 μC/cm² for the majority (111) texture. Moreover, additional N2 flow during TiN sputtering yields improved endurance and a lower CV frequency dispersion. XAS, EDX, and XPS measurements confirm the increased nitrogen incorporation in the TiN with additional N2 flow. Finally, we hypothesize that the disparate results in the literature, with
regard to the magnitude of remanent polarization, ranging from $10^{30}$ to $26 \mu \text{C/cm}^2$, obtained with essentially the same material stack, could be a result of varying processing conditions for the TiN electrodes, rather than differences of $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ itself.

**Figure 5.** Capacitance–voltage characteristics between $-3$ and $3 \text{ V}$ for frequencies between 10 kHz and 10 MHz for samples B (a), D (b) and E (c). The arrows below the curves indicate the sweeping direction of the measurement. In (d), the frequency dispersion per decade of the corresponding samples is presented.

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c01734.

Measured current voltage characteristics of PUND measurements and corresponding $P-V$ and $I-V$ curves of samples A–E; extraction procedure of bar height in Figure 2c; microstrain calculations derived from the measured GIXRD data of the TiN(111) and (002) reflection; stress determination by wafer curvature measurements; vibrational oscillations of molecular nitrogen in NEXAFS results; cycling endurance comparison between MIM and MIS structures (sample B); relative compositional changes of the TiN TE in samples C–E derived from the EDX data; and deconvolution of the XPS data and relative peak components of samples C–E for Ti 2p (PDF)

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**Notes**

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