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Monolithic integration and ferroelectric phase evolution of hafnium zirconium oxide in 2D neuromorphic synaptic devices

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ABSTRACT

Hafnium zirconium oxide (HZO)-based ferroelectric field-effect transistors (FeFETs) are three-terminal devices with attractive properties for embedded memory and in-memory computing architectures. We probe the HZO ferroelectric landscape dynamics with materials characterization, device modeling, and electrical measurements. Metal-ferroelectric-metal capacitors fabricated with HZO with Pt contacts were processed at complementary metal-oxide-semiconductor (CMOS)-compatible temperatures near 450 °C. We found that the HZO films do not require field processing for ferroelectricity to arise and have an average remnant polarization between 10 and 20 μ C/cm² and a coercive field of ~0.6 MV/cm. The average HZO grain sizes range from 10 to 15 nm and closely follow the ferroelectric domain size range of 10–20 nm. We further examine the HZO properties by integrating them into back-end-of-the-line (BEOL) FeFET device architectures with WSe₂, a prototypical van der Waals system, and verify their robust synaptic plasticity within a 3.5 order of magnitude conductive range. These discoveries highlight a roadmap for material processing, dimensional scaling, and integration of HZO-based FeFETs.

1. Introduction

Fundamental limits on power and dimensional scaling for Si metal--oxide-semiconductor field-effect transistors (MOSFETs) combined with the von Neumann bottleneck for memory access motivate dramatic changes to the architecture of future computers [1]. Recent efforts bring memory and computation closer through neuromorphic architectures that embed memory near logic elements [2]. This drives a search for materials and devices to best accommodate a new roadmap for the scaling of neuromorphic computing hardware [1]. Transition metal oxides have been studied in two-terminal resistive random-access memory (ReRAM) devices due to their compatibility with complementary metal-oxide semiconductors (CMOS) and their ability to create memory states in circuits using filamentary physics in tunnel junctions [3]. The discovery of ferroelectricity in solid solutions of hafnia steered a new era of ferroelectric memory device research with great potential for impacting future developments in front-end-of line (FEOL) and back-end-of-line (BEOL)-compatible, in-memory computing architectures [4,5].

Hafnia is a high-K dielectric material in typical MOSFETs in advanced (45 nm and below) CMOS nodes [6]. The intricate phase landscape of hafnia is energetically and dynamically complicated. There are six equilibrium phases of hafnia that emerge depending on the growth conditions and post-growth processing [7–12]. Since the equilibrium phases are all non-polar, the presence of ferroelectricity is unexpected, and its exact origin is still under discussion [13,14]. This is further complicated as some hafnia phases found in thin films are metastable [15], which can obscure experimental results. Prior reports assert that the non-equilibrium polar orthorhombic phase Pca21 (o-FE) in hafnia is the main contributor of ferroelectricity [16–18]. Several controlling factors have been explored as kinetic drivers for stabilizing the non-polar orthorhombic phase [19], including doping [20,21], oxygen vacancies [22,23], stress/strain [24,25], quenching strategies [26], and the surface energy [27]. It has also been suggested that the flat

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Received 25 April 2023; Received in revised form 16 June 2023; Accepted 18 July 2023 Available online 24 July 2023 2588-8420/Published by Elsevier Ltd. optical phonon bands in hafnia result in the extreme localization of electrical dipoles and induce ferroelectricity with a pathway to miniaturization down to sub-nanometer levels [28].

The strategic design of hafnia solid solutions uses elements such as Zr to stabilize the orthorhombic phase, allowing access to ferroelectricity in hafnium zirconium oxide (HZO) thin films [29–32]. The full realization of ferroelectric hafnia within computing applications hinges on the development of robust processes for controlling its performance in ferroelectric transistor devices. Device-related properties, such as stable and reproducible non-volatile memory states, device-to-device and cycle-to-cycle variability, and dimensional scaling will decide the fate of this technology; future integration of ferroelectric hafnia are fundamentally rooted in control of the material phase landscape, domain size, grain boundaries, electrical interfaces, and trapping behaviors.

In this work, we use spectroscopy, imaging, and electrical transport measurements to examine how thermal processing affects the structural and ferroelectric properties of HZO. Moreover, we develop a computational framework that bridges materials characterization with piezoelectric force microscopy (PFM) and compact device models based on the multidomain Preisach theory of hysteresis to simulate the ferroelectric response [33]. Our results elucidate the role of multidomain properties in the material's response and paves a path for examining these characteristics for scaled neuromorphic devices. This work informs a baseline understanding of the thermal processing parameter space and the impact of CMOS-compatible thermal limits on the ferroelectric device properties and creates a framework for future improvement in HZO neuromorphic device applications including direct integration with emerging layered semiconductors.

2. Results and discussion

2.1. Stoichiometry and morphology characterization and analysis

We examined the morphology and phase landscape on HZO compositions near Hf_{0.5}Zr_{0.5}O₂. Zirconium supplies a low thermal activation and consistent ferroelectric response within a wide range of concentrations, making it a reasonable choice for device fabrication and processing [34,35]. We grew both undoped hafnia (HO), as a baseline, and HZO layers by atomic layer deposition (ALD) at 200 $^\circ\text{C}$ on sputtered Pt/Ti layers deposited onto commercially available SiO2 (1 µm)/Si (001)-oriented substrates. The use of chemically inert Pt minimizes chemical exchange and oxygen vacancy formation at the contact interface. To avoid growth inconsistencies, we did one deposition run for the hafnia and HZO samples. We then diced each wafer into separate pieces. For both wafers, one piece remained unannealed (UA) as a control and others were thermally processed at annealing temperatures (T_A) of 400 °C, 450 °C, 650 °C, and 800 °C with rapid thermal annealing (RTA). Samples were held at the target temperature for 30 seconds under N₂ ambient). Annealing temperatures near the ALD growth temperature (200 °C) would likely have minimal impact on crystallography. We used 400 °C and 450 °C to assess sample sensitivity to small temperature variations within Si thermal processing budgets. We chose 650 °C due to its likely CMOS compatibility with pulsed laser annealing (PLA) techniques. Establishing a 650 °C baseline for hafnia properties is important for future PLA experiments. The highest annealing temperature of 800 °C likely exceeds the practical CMOS window, but we wanted to assess HZO phase properties and robustness over a wider temperature range. In this text, we refer to the samples by their film (HO or HZO) and their annealing temperature. For instance, HZO (450 °C) refers to the HZO film annealed at 450 °C.

We examined the HZO stoichiometry as a function of different peak temperature thermal processing temperatures using x-ray photoemission spectroscopy (XPS) (Fig. 1a and b). The estimated stoichiometry of all the films approximated $Hf_{0.45}Zr_{0.55}O_2$, regardless of annealing conditions, with no detected sub-oxide phases ($Hf_{0.45}Zr_{0.55}O_{2-x}$). Fig. 1a shows the Zr 3d and Hf 4f core levels overlaid for each of the HZO



Fig. 1. XPS spectra of (a) Zr 3*d* and Hf 4*f* core levels and (b) VBM. Zr 3*d* and Hf 4*f* spectra shifted along energy axis and normalized to Hf 4*f* for comparison. (c) RBS of HZO heterostructures.

samples. For comparison, the data from each sample were shifted along the energy axis and normalized to the maximum intensity of the Hf 4f peak for each sample. Fig. 1b shows the valence band maximum (VBM) of the samples (no energy shifts were applied to VBM spectra). RBS shows (Fig. 1c) that the annealing process induces a minimal change in the estimated stoichiometry (within the resolution of XPS).

To further understand and verify the role of the annealing temperature on the stoichiometry of the HZO films, we used Rutherford backscattering spectrometry (RBS) with a 2.3 MeV beam of ⁴He⁺⁺ ions. The scattering angle, energy resolution, and beam diameter were 163°, 18 keV, and 2 mm, respectively. The experimental data was quantitatively analyzed using SIMNRA [36] and the energy per channel is 1.365 keV/ch, the density of $Hf_{0.5}Zr_{0.5}O_2$ for thickness estimation was taken as 7.2 g/cm³ [37]. The RBS data suggests that HZO films annealed up to T_A = 650 °C are near-stoichiometric with compositions of $Hf_{0.5}Zr_{0.5}O_{2.03}$ while the film annealed at 800 $^\circ C$ is Hf deficient (Hf_{0.41}Zr_{0.5}O_{2.12}). The RBS spectra from Hf and Pt partially overlap due to closeness in atomic number (Fig. 1c). Nevertheless, the RBS spectra from the HZO film annealed at 800 °C shows an asymmetric Ti peak profile suggesting some interdiffusion has occurred at the interface with Pt (Fig. S1, Supplementary Information). We also observed this in the TEM and EDS study (as discussed later, and shown in Supplementary Figs. S2 and S3), which shows the diffusion of Hf into the Pt as well as interdiffused regions of Pt and Ti at their interface. The diffused Hf from HZO into the Pt layer may result in an off-stoichiometric HZO film as noted in RBS measurements for the case of the 800 °C annealed sample.

We estimate that the error bar for the cation stoichiometry is around 2-2.5%. RBS sampling involves averaging through the film thickness while XPS sampling is much more surface sensitive. The error bars for the data collected by each method, along with the different nature of the two techniques sampling methods explain the slight difference in our compositional estimates.

2.2. Phase landscape and grain properties

We examined the phase landscape with coupled 20-w x-ray diffraction (XRD) scans. The scan for HO (UA) (Fig. 2a) serves as a baseline for comparing the other samples in this study. The strongest and narrowest peaks are from the Si substrate and the Ti and Pt metal layers. The Pt and Ti planes oriented with their (111) and (002) planes normal to the growth direction, respectively, although transmission electron microscopy (TEM) images and diffraction patterns (Fig. S4, Supplementary Information) show that there are a variety of in-plane rotation angles in both layers. The Ti layer incorporated O₂ (shown by EDS, see Fig. S5, Supplementary Information) and its XRD features correspond to the anatase phase. For HO (UA), there are very weak features between the Si (002) and TiO₂ (002) peaks that are slightly above the noise floor. Fig. 2a inset scan was collected with a longer acquisition time over the region between the Si (002) and TiO₂ (002) peaks in order to draw out the two film peaks, which are at a much lower intensity than the metal or substrate peaks. The dashed lines under the data curve in Fig. 2a inset show the allowed hafnia diffraction peaks for this range, according to structure factor calculations for films with perfect stoichiometry. The blue lines (l-r) correspond to the calculated (200), (020), and (002) monoclinic peak positions and the vellow lines to the calculated (200) and (020) orthorhombic peak positions.

Fig. 2b is the 2θ - ω XRD scan for HZO (UA). The film peaks discernible from the noise floor are to the left of the Pt (111) and TiO₂ (002) peaks, as shown in the inset. The blue lines (l-r) in the inset correspond to the calculated monoclinic ($\overline{1}11$) and (111) peaks and the yellow line to the calculated (111) orthorhombic peak position.

Although we grew the films under identical conditions and on the same substrates, the HZO planes orient differently than the HO planes.

This is true for as-grown and annealed samples. HfO₂ and ZrO₂ are isomorphic with similar lattice constants and have the same space group within the same phase [38]. The lattice constants of ZrO_2 are slightly larger (~0.8-1.8%) in all dimensions. For HZO alloys with compositions around 50:50, the calculated XRD peaks are at slightly lower 2θ angles ($<\sim 0.5^{\circ}$ difference) relative to the hafnia peaks corresponding to the small increase in the lattice constant. Adding Zr changed the orientation of the films in a manner that increases the lattice mismatch with Pt(111). While the plane's arrangement in the HO films corresponds to a lower lattice mismatch with the Pt, there are other orthorhombic and monoclinic orientations that have an even lower mismatch and still meet the visibility conditions imposed by the structure factor. The absence of other planes that have sufficiently high structure factors tells us that neither the HO nor the HZO films are a truly random polycrystal, which would show all its allowed diffraction peaks with intensities dictated by the structure factor. The fact that the observed planes do not correspond to the lowest lattice mismatch tells us that the orientation preferences are not driven by strain minimization. Zhong et al. [39] also notes that strain from the substrate is not what drives or maintains the presence of specific phases or orientations. Specifically, their HZO grown on SrTiO₃/La_{0.8}Sr_{0.2}MnO₃ preferentially orients along the (111)₀ plane and continues to do so even when lifted off from its substrate.

For illustrative purposes, we show scans of the region between 34 and 42° for HO (UA) and HO (450 °C), normalized to the Pt (111) peak, in Fig. 2c and d. Even for the thermal processing temperature of 450 °C (HO (450 °C)), we can see that the hafnia XRD features are more intense than they were for HO (UA). The intensity of the hafnia peaks increases with thermal processing temperatures up to 650 °C. This suggests that more of the polycrystals are preferentially aligning, more of the film is becoming crystalline rather than amorphous, or that both of these



Fig. 2. 20-00 XRD scans for (a) HO (UA) and (b) HZO (UA). Scans from 34° to 42° for (c) HO (UA) and (d) HO (450 °C) normalized to the Pt(111) peak.

conditions are true.

A completely random HO or HZO polycrystal with monoclinic (m) or orthorhombic (o) grains would have the strongest diffraction peaks, in descending order by relative intensity [40] (all >20% so that the peak is discernible from the noise flow) for $(\overline{1}11)_m$, $(111)_0$, $(111)_m$, $(022)_0$, $(202)_0$, $(202)_m$, $(220)_m$, $(022)_m$, $(002)_m$, $(022)_m$, $(200)_0$ ($\overline{122})_m$, $(020)_0$, $(200)_m$, $(013)_m$, $(020)_m$, $(21\overline{1})_m$, $(20\overline{2})_m$, $(\overline{3}11)_m$, $(130)_m$ and $(102)_m$. The diffraction angles for these planes are all within the range that we scanned. We do not see many planes that are allowed and have sufficient intensity, which further illustrates the preferential stacking of our films.

Overall, the HO peaks trend to slightly higher angles with thermal processing temperature, although the shift is so small that it may not be physically significant. From XRD alone we cannot precisely find the morphology of the crystals as our thin films have sufficiently broad peaks that they could be assigned to more than one reflection. For instance, in the inset to Fig. 2a, Peak 2 could be from either or both of the $(200)_O$ or $(200)_M$. The only substantial change in the XRD with temperature is that the HO peak intensity increases rapidly with temperature, becoming more than four times as strong as the baseline HO (UA) peaks for $T_A = 650$ °C. This indicates that the films are less amorphous and that more of its crystalline regions align along the growth direction, which we verify with TEM as discussed later in this paper. For the highest temperature at 800 °C, the peak intensities drop to around ~3.5 times that of the baseline peaks, likely due to issues with the Ti/Pt breaking down, which we will discuss later in the paper.

There are three predominant film features appearing in the scans for the HZO films, as shown in Fig. 2b and d. Their intensity increases until $T_A = 650$ °C (except for Peak 2, which decreases after $T_A = 450$ °C). For the HZO films, the peak positions shift to slightly lower angles with temperature. The peak positions at higher temperatures are closer to the expected positions for the ($\overline{1}11$) and (111) monoclinic peaks and the (111) orthorhombic peak. The structure of the underlying Ti and Pt layers is unaffected by thermal processing temperatures up to 450 °C, and at 800 °C we see diffusion into the hafnia and HZO layers. TEM images and EDS spectra showing the breakdown of the Ti and Pt layers are shown in Fig. S2 in the Supplementary Information.

We performed high-resolution TEM imaging on all HO and HZO samples grown for this study. (A selection shown in Figs. 3 and 4 as well as in the Supplementary Information). The as-grown hafnia HO (UA) and HZO (UA) films are mostly amorphous with some small crystallites (Fig. 3a and b), consistent with the weak XRD film peaks observed (Fig. 2a and b). The contrast within the small crystalline regions in the unannealed films is diminished by the overlap of the amorphous matrix along the beam direction, making it difficult to determine the polytypes.

Representative high-resolution images of the thermally processed samples are shown in Fig. 4. The monoclinic and orthorhombic phases are present for the thermally processed hafnia and HZO samples. Many regions of the thermally processed samples have overlapping grains of different orientation and/or different polytype along the beam direction, but some single crystalline regions are visible for very thin TEM samples. The extent of crystallinity increases with annealing temperature. We note that the extent of crystallinity for $T_A = 400$ °C and 450 °C is greater in HZO films than in HO films. These results are further confirmed through diffraction patterns measured for HO and HZO films (shown in Fig. S5, Supplementary Information).

The same range of morphologies appear in all of the thermally processed samples, irrespective of temperature. There appears to be more grains with diffraction planes oriented along a preferred growth direction for increasing annealing temperatures. This observation is consistent with the XRD peaks not shifting appreciably with temperature, but becoming more intense.

It is difficult to precisely determine the average grain size. HO (UA), for instance, is primarily amorphous, and the contrast of the weakly organized grains is difficult to distinguish from the amorphous matrix surrounding the grain along the beam direction. We averaged the grain size along the lateral dimension (parallel to the substrate surface) viewed in several TEM images of each sample. There is a large standard deviation for these measurements, as noted by the error bars in Fig. 5a, because the particles are not uniform in size. Fig. 5a shows that the HO (UA) has a grain size of 22 nm, but then it drops and increases with thermal processing temperature for HO (450 °C) – HO (800 °C). The grain sizes, however, increase with temperature for all the HZO films. In all cases, the hafnia grains are larger along the lateral dimension than the HZO grains.

Much of the roughness in the hafnia and HZO surface is likely due to the Pt/hafnia and Pt/HZO interfaces, which in TEM cross sectional profiles appears to be around 2 nm, with considerably rougher interfaces in HO (800 °C) and HZO (800 °C) due to the breakdown of the Pt/Ti layers that begins at $T_A = 650$ °C. The overall trend is that roughness is unchanged (within error bars) with annealing temperature, except for HZO (800 °C) (see Fig. S6, Supplementary Information). TEM and AFM both show that thermal processing does not have a negative effect on our surfaces for temperatures within the CMOS acceptable range.

TEM cannot distinguish between the different orthorhombic phases of HZO and therefore it is impossible to assert if the ferroelectric phase properties of the materials follow this trend. To understand and correlate the crystalline phase landscape of HZO to its ferroelectric phase characteristics we performed PFM experiments using an Oxford Asylum atomic force microscope. As expected, we were not able to decipher any ferroelectric domains in the unannealed samples as they did not exhibit



Fig. 3. HRTEM images of as-grown samples (a) HO (UA) with an amorphous matrix and small polycrystallites, (b) HZO (UA) with an amorphous matrix and polycrystalline grains.



Fig. 4. Representative images of HO and HZO thermally processed samples (a) HO (450 °C), monoclinic grain, (b) HO (650 °C) mixed polytype grains, (c) HO (800 °C) orthorhombic grains, (d) HZO (450 °C) orthorhombic grains, (e) HZO (650 °C) monoclinic grains, and (f) HZO (800 °C) monoclinic grains.



Fig. 5. The evolution of the HZO grain and ferroelectric phase landscape with annealing temperature. (a) Average TEM-estimated HO and HZO grain sizes at different T_A with error bars. The PFM measurements for HZO (450 °C) of the (b) amplitude before poling and (c) phase before and after poling; poled areas highlighted in the white box, (d) the evolution of phase scans of HZO films with T_A . (e) The estimated average HZO ferroelectric domain sizes as a function of T_A .

a response in PFM measurements. The phase measurements for annealed samples clearly show ferroelectric domain property changes across these samples (Fig. 5b and c). The response is shown in volts as an external lock-in amplifier was used to take these PFM measurements and the phase channel output from the lock in was recorded as a varying electrical signal. By applying a 3 V DC bias to the PFM tip, a region was poled

in the middle of the HZO film that was annealed at 450 $^{\circ}$ C, confirming the success of the PFM mapping poling techniques, and clearly demonstrating a ferroelectric response to a poling field (Fig. 5c). We examine the evolution of the ferroelectric phase landscape as a function of T_A.

We see ferroelectric domains in all annealed HZO samples except the

800 °C. This is not surprising given the EDS and TEM observations of the degraded metal contact layers at 650–800 °C. In these results, domains resembling crescents at low T_A values seem to evolve into more regular ferroelectric domain patches at higher temperatures (Fig. 5d). This is most likely related to the gradual alignment of ferroelectric domains with the direction normal to the substrate's growth direction at higher T_A. This is also in agreement with the increased preferential crystalline phase alignment with temperature observed in our TEM and XRD results. We also estimate the average ferroelectric domain size and see a similar trend to the TEM crystal grain analysis, where the HZO ferroelectric domains grew with T_A from ~10 nm–20 nm (Fig. 5e).

2.3. Ferroelectric and neuromorphic device properties

We examined the impact of materials and device processing on the ferroelectric properties of HZO using metal-insulator-metal (MIM) device architectures (The device fabrication is detailed in the Methods section). We examined the material's field cycling phenomena and studied the ferroelectric response over the course of 10^4 cycles (Fig. 6a). There is no field-induced wake-up process for the ferroelectric properties to reach their steady-state. This desired property is beneficial to the design and integration of FeFETs into integrated circuits as the need for and considering of peripheral circuitries for programming the wake-up is not required. Typical HZO research shows that several field cycles, ranging from 100s to 1000s, are needed for the material to reach its optimum ferroelectric properties [41]. In our experiments, the measured remnant polarization is stable from the beginning and throughout our cycling experiments without field-induced wake-up (Fig. 6a). We attribute this to the ordered nature of ferroelectric domains (as also observed by Zhong et al. [39]) and their relative and increased alignment along the growth direction with increasing T_A. However, electrical leakage dominates in the devices processed at 650 °C and above due to the breakdown of the metal layers and interfaces as observed in our TEM experiments (shown in more detail in the Supplementary Information). Our MIM devices break down at roughly 10^5 – 10^7 cycles, similar to other reports on ferroelectric hafnia.

We probed the ferroelectric P-E characteristics of the MIM devices at different field ranges (Fig. 6b and c). The ferroelectric properties for unprocessed samples are dormant, and other than charge trapping behavior represented as hysteresis in our measurements, the HZO behaves as a linear dielectric (Fig. 6b). When we examine the HZO sample processed with rapid thermal annealing at 450 °C, we see an onset of ferroelectricity with a remnant polarization of ~10–20 μ C/cm² and coercive fields of ~0.6 MV/cm (Fig. 6c). The measured values are similar to reported values in the literature and suggest that ferroelectricity can arise in the material within the tight thermal budgets of

CMOS [31].

To enable future simulation of ferroelectric devices in very largescale integrated circuit designs, we developed and calibrated a compact device model for ferroelectric capacitors written in Verilog-A. The details regarding the model are included in the Supplementary Information and is similar to techniques previously presented in literature [33,42–45]. One distinction included within our model is the explicit support for multiple types of ferroelectric domains, each representing a macroscopic average of a particular domain types with unique electronic characteristics. To elucidate the number of domains included within the model, and their corresponding distribution throughout the film, we applied a Gaussian mixture clustering algorithm to the measured PFM phase data from the poled regions of Fig. 5c to categorize similar ferroelectric domains into distinct groups. This analysis was carried out on the poled region of Fig. 5c to qualitatively explore the state of the ferroelectric film during typical ferroelectric device operation where most of the dipoles would be aligned under a poling field of sufficient strength. The resulting analysis is shown in Fig. 7a and b. From the PFM scans and cluster analysis, there are three predominant classes of domains. Based on these findings, we fit our compact device model using three domain types with the same weights provided by the Gaussian mixture model shown in Fig. 7b; this framework is shown schematically in Fig. 7c. The overall analysis culminated in good agreement ($R^2 = 0.968$) with experimental metal-ferroelectric-metal (MFM) characterization as shown in Fig. 7d, with the combined subset of P(E) loops for each domain shown in Fig. 7e. The blue domains demonstrated in-plane alignment with the poling field, red regions in-plane alignment against the poling field, and green regions a mix of in-plane and out-of-plane alignment. As a result, each domain type was fit to a P(E) curve in the compact device model based on its reaction to the poling field. The blue domain type is given a ferroelectric hysteresis curve based on its demonstrated alignment to a poling field. The green domain type maintains a mixed phase after poling and given that the overall ferroelectric phase domains are random in as-processed samples, as shown in the Supplementary Information (Fig. S7), it can be expected that no aggregate ferroelectric response will be observed from these domains and are be treated as a linear capacitor. Lastly, the red domain type opposite in-plane alignment can indicate pinned phases, non-ferroelectric regions of the film due to its polycrystalline nature, or macroscopic averages regions exhibiting varied ferroelectric characteristics due to nanoscale polymorphism in doped hafnia. In these cases, these domains can then be described similarly to a leaky capacitor with a minor P(E) loop. Overall, Figs. 6 and 7 serves as a framework that brings together fundamental materials and device characterization to create a foundation for the accurate representation of ferroelectric MIM devices in analog circuit simulations. This paves the way for 2.5D and 3D



Fig. 6. Ferroelectric properties of HZO. (a) HZO field cycling before and after 450 °C anneal. HZO polarization vs. field loop measurements (b) before and (c) after 450 °C anneal.



Fig. 7. Overview of our PFM-guided compact device model for MFM capacitors. (a) PFM phase image processing for determination of the poled region of Fig. 4c for determining phase landscape probability distribution. (b) Normalized probability distribution of polarization phases in the poled regions of HZO with fitted Gaussian mixture model. (c) Schematic representation of compact device model used in this work comprised of (d) three parallel ferroelectric capacitors. (e) Calibrated compact device model with data from (b) (R2 = 0.968) (f) The three domain archetypes used within the model).

integration of ferroelectric devices within the architecture of CMOS and applications in near-to in-memory computing [46]. As a result, the monolithic integration of HZO into BEOL field effect transistor architectures is an essential step that can shed light on design opportunities in the future. Therefore, a more applied prospective into the HZO properties would be useful through testing of BEOL ferroelectric field effect transistor (FeFET) device architecture. In this approach the ferroelectric states of the HZO are read via a field effect transistor.

As outlined in the Methods section, we fabricated these devices based on exfoliated flakes of WSe₂, which is an excellent candidate for BEOL neuromorphic applications [46] (Fig. 7a) due to the van der Waals nature allowing for layer-by-layer stacking. Our FeFETs demonstrate \sim 4 orders of magnitude on/off characteristics, an estimated memory window for these devices is \sim 1.5 V, with a clear transconductance gain (Fig. 8). Through implementation of a uniform magnitude and programming pulsing scheme (9 V pulses with a width of 1 μ s), we demonstrate the synaptic properties of the FeFET device. A strong threshold switching behavior and a robust plasticity in our devices enables access to 3.5 orders of magnitude in conductance change (Fig. 8b and c). The depression curves measured for this 2D FeFET resolve over 40 pulses with a unique dependency on the read gate voltage values (Fig. 8c). In this depletion mode n-type device, the maximum change in the accessible range of output conductance is at a read gate voltage of V_g, read = -1 V. For better programming of these devices in practical circuit implementations, V_{g,read} = 0 is desired, which requires further interface design and doping of the semiconductor. The insights gained here on the operations of 2D FeFETs demonstrate suitable proof-of-principle FeFET device properties for BEOL integration. The scaling properties of the HZO phase landscape presented here sets the stage for further enhancements in FEOL and BEOL FeFET devices. The synaptic and



Fig. 8. Back-end of line neuromorphic FeFET device characterization. (a) The architecture of a back end of line thin film ferroelectric field effect transistor. (b) The transfer measurements and the pulsing induced threshold switching in 2D FeFETs. (c) The conductivity states and their change as function pulses and the read gate voltage.

programming properties of the 2D FeFETs also motivate further systematic research in the optimization of materials and interfaces to enable their integration into neuromorphic computing architectures.

3. Conclusions

We show the evolution of HZO ferroelectric properties as a function rapid thermal anneal peak temperatures and demonstrate monolithic integration into 2D FeFETs. Direct imaging and spectroscopy results reveal the mixed phase multi domain nature of HZO with small grain sizes in the range of 10–20 nm. Small grains are potentially advantageous for scaling analog properties into advanced CMOS nodes.

Thermal processing at CMOS-compatible temperatures increases the degree of crystallinity; further increases in order and alignment of phases with the out-of-plane directions is present at higher anneal temperatures. Ordered ferroelectric orthorhombic phases are present in the material with CMOS-compatible thermal processing temperatures and exhibit ferroelectric response without a field-induced wake-up process. Polarization-field curves show typical ferroelectric hysteresis behavior. The materials-specific information in our models help more accurately explain the ferroelectric properties of HZO and predict its device behavior. From analysis of PFM phase measurements, we found that the HZO film can be adequately described by three macroscopic domain archetypes and showed that the analysis can be included within a compact device modeling framework to explain experimental metalferroelectric-metal capacitor characteristics. Our FeFET device properties demonstrate promising neuromorphic device properties with a desired synaptic plasticity within 3.5 order of magnitude change in device conductance. The measured small grain and ferroelectric domain sizes, the transistor behavior, and device performance characteristics suggest that these devices can in principle be scalable for advanced node integration.

4. Methods

4.1. Growth

The ALD tool is a commercial Kurt J Lesker Company, Inc. (Jefferson Hills, PA, USA) ALD 150-LX platform. ALD precursors include tetrakis (dimethylamino) hafnium (TDMAH), tetrakis (dimethylamino) zirconium (TDMAZr) and water in alternating pulses with Ar purge of the reaction chamber between pulses. The TDMAH and H₂O were pulsed into the reactor in the following sequence: TDMAH pulse 0.25 s; Ar purge 20 s; 10 s pulse H₂O, and Ar purge 20 s.

4.2. Structural and chemical materials characterization

Coupled 20- ω scans XRD were conducted with a PANalytical X'Pert Pro MRD. The AFM tool is a vacuum-enabled Hitachi 5300 operated in tapping mode. XPS data were collected with a Phi 5000 VersaProbe III utilizing a monochromated Al-k α x-ray source (h ν = 1486.7 eV) with a spot size of 100 µm and a pass energy of 26 eV. Stoichiometry estimates were made using established relative sensitivity factors for the Hf 4f and Zr 3d core levels. XPS spectra were analyzed with kolXPD software [47]. TEM samples were prepared with manual tripod polishing and low temperature Ar⁺ ion milling to electron transparency and then examined in the JEOL ARM 200 TEM. The TEM-EDS data was collected with an Oxford Aztec system. We do not use EDS to find the precise stoichiometry of the hafnia or HZO. If there is insufficient dead-time, the high energy x-rays saturate the detector, washing out the signal from the lower energy x-rays. The inherently thin nature of TEM samples and the high energy electron beam can make it difficult to have sufficient dead time or to make it somewhat equal when comparing a series of samples. Both the Hf and Zr characteristic x-rays are at least an order of magnitude higher than those for O, leading to much more signal from them, which can distort the compositions and make them less precise than RBS or XPS results. EDS is useful for examining profiles, assessing uniformity and/or diffusion and for comparing the chemical abruptness at the interfaces.

4.3. Device fabrication

HZO/HO (40 nm/2 nm) layers were grown using the same conditions as the initial HZO film series studied with materials characterization. The layers were deposited onto patterned bottom Pt substrates for FeFET device fabrication. We employ a Vistec EBPG5000+ES electron beam lithography (EBL) system with automated alignment capability for fabrication of the devices including steps for the marker layer, bottom electrode, source and drain patterning. WSe₂ flakes (SPI) were exfoliated and used for the device fabrication. For the lithography steps, Micro-Chem A4 495 poly(methyl methacrylate) (PMMA) was used as the resist. We spun the resist at a speed of 3000 rpm resulting in an ~200 nm thick PMMA film. After patterning with EBL, the PMMA was developed with methyl isobutyl ketone/isopropyl alcohol (MIBK/IPA) (1:2 ratio) for 90 s. This development recipe was used for all the other steps. The metallization of Au/Ti/In (80/10/40 nm) was carried out in a Kurt J Lesker PVD Evaporator System at mid~ 10^{-6} Torr (mid- 10^{-4} Pa).

A Radiant Precision Premier 2 materials analyzer was used to examine the ferroelectric P-E characteristics of the MIM devices at different field ranges.

Disclaimer

Certain commercial equipment, instruments, software or materials are identified in this paper in order to specify the experimental procedure adequately. Such identifications are not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor it is intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

Author contributions

WS designed the initial experiment parameter space, performed the TEM, XRD, and AFM measurements, and wrote the manuscript draft.

AG developed and calibrated the metal-ferroelectric-metal compact device model and wrote the manuscript draft.

JP performed rapid thermal annealing, ALD materials synthesis, device fabrication and testing.

PL XPS data collection and analysis.

CM performed and analyzed PFM data.

SR performed and analyzed RBS data.

RB performed and analyzed RBS data.

SM performed XPS analysis.

CH analyzed PFM data.

SN conceived the ideas, analyzed and integrated the data, and wrote the manuscript draft.

Declaration of competing interest

The authors declare the following financial interests/personal relationships that may be considered as potential competing interests:

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Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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