Structural Correlation of Ferroelectric Behavior in Mixed Hafnia-Zirconia High-k Dielectrics for FeRAM and NCFET Applications

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ABSTRACT

The recent discovery of ferroelectric behavior in doped hafnia-based dielectrics, attributed to a non-centrosymmetric orthorhombic phase, has potential for use in attractive applications such as negative differential capacitance field-effect-transistors (NCFET) and ferroelectric random access memory devices (FeRAM). Alloying with similar oxides like ZrO2, doping with specific elements such as Si, novel processing methods, encapsulation and annealing schemes are also some of the techniques that are being explored to target structural modifications and stabilization of the non-centrosymmetric phase. In this study, we utilized synchrotron-based x-ray diffraction in the grazing incidence in plane geometry (GIIXRD) to determine the crystalline phases in hafnia-zirconia (HZO) compositional alloys deposited by atomic layer deposition (ALD). Here we compare and contrast the structural phases and ferroelectric properties of mechanically confined HZO films in metal-insulator-metal (MIM) and metal-insulator-semiconductor (MIS) structures. Both MIM and MIS structures reveals a host of reflections due to non-monoclinic phases in the d-spacing region between 1.75Å to 4Å. The non-monoclinic phases are believed to consist of tetragonal and orthorhombic phases. Compared to the MIS structures a suppression of the monoclinic phase in MIM structures with 50% zirconia or less was observed. The correlation of the electrical properties with the structural analysis obtained by GIIXRD highlights the importance of understanding the effects of the underlying substrate (metal vs. Si) for different target applications.

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INTRODUCTION

Ferroelectricity in hafnium oxide was discovered in 2011 in thin films doped with SiO2 and aided by TiN encapsulation [1,2]. Since then, hafnia with different doping elements and alloying with similar oxides have been under investigation for applications in ferroelectric RAM and negative differential capacitance FETs [3,4]. Further, electric field controlled partial polarization switching in ferroelectric FETs made from hafnia zirconia (HZO) films makes these an interesting candidate for synaptic memory devices for application in neuromorphic computing [4, 5]. At the core of these new-generation technologies is an ALD grown HZO nanoscale film which exhibits ferroelectricity when stabilized in a non-centrosymmetric orthorhombic structure [6]. Hafnia based ferroelectric materials are advantageous over perovskites due to their CMOS compatibility, higher bandgap and scalability. Understanding the details of effect of structural phases on the electrical properties of these materials is extremely important for device engineering for different applications.

Ferroelectricity in hafnia can be observed in ultra-thin films, even in the range of 2 to 10nm [1, 7]. In the bulk form, the most stable phase of hafnia is monoclinic structure (P21/*c*; m-phase) at room temperature and atmospheric pressure. At higher temperature (1700°C and 2600°C), hafnia transforms into tetragonal phase (P42/*nmc*; t-phase) and cubic phase (F*m*3*m*; c-phase) [8]. With hydrostatic compressive pressure, m-phase can be transformed to centro-symmetric orthorhombic phase (o-phase) such as P*bca* and P*nma* [9]*.* Böscke et al.[1] attributed the ferroelectricity to the formation of a polar orthorhombic phase. Sang et al. [10] used detailed transmission electron microscopy to examine the symmetry of HfO2 and confirmed P*ca*21 leads to ferroelectricity in Gd doped hafnia thin films. While there are many factors that help in stabilizing different structural phases, we are particularly interested in investigating alloying and underlying substrate effects. Alloying hafnia with zirconia enables high polarization values for a wide range of composition ratios not seen with various dopants [11]. Here we study the substrate effect on structural and electrical behavior of hafnia-zirconia ultra-thin films.

From the ferroelectric device perspective, it is important to optimize the process and improve the endurance and remnant polarization of both metal-insulator-metal (MIM) and metal-insulator-semiconductor (MIS) capacitor stacks. In our study, we focused on TiN as a metal electrode in MIM and MIS and silicon as the semiconductor in MIS. Further, the electrical and structural properties can be altered by processing conditions [6,12] electrical cycling [13], annealing temperature [6] and types of electrodes [14]. We recently reported ferroelectric behavior in ALD grown HZO films of thickness in the range 7-10nm in MIS stacks with a post-metal anneal [15]. In this previous study, HZO films showed a wide range of electrical properties depending on the ratio of Hf:Zr, transitioning from a linear dielectric for 30% zirconia to a ferroelectric for 80% zirconia.

EXPERIMENTAL DETAILS

The dielectric films of 7nm thick Hf1-xZrxO2 (x = 0-1) were deposited using a thermal ALD process in a 300mm TEL TriasTM cleanroom tool. The zirconia content was modulated by carefully controlling the cycle ratio of the Hf and Zr precursors. H2O was used as the oxidizer. ALD TiN was used as the electrode material. Both blanket and patterned samples of MIM capacitors were fabricated. Electrical measurements were performed on MIM capacitors while blanket MIM films were prepared for physical analysis. All samples in this study were subject to post metallization (after the top TiN electrode) anneal in N2 ambient at 450°C for 5 minutes.

Grazing incidence x-ray diffraction was done at G2 beamline at the Cornell High Energy Synchrotron Source (CHESS) making use of the high synchrotron photon flux. The x-ray beam was in the range of 10.8 -11.3 keV and was incident at 0.5°. The angle of the Soller slits was 0.1° deg. A series of Ω-2ν scans were acquired at different values of tilt of the detectors. The data is collected as grazing incidence reciprocal space maps (GI-RSM) and are converted to grazing incidence d-space maps (GI-DSM) using python codes [15]. Collected GIIXRD spectra were compared to standard reference patterns for monoclinic, tetragonal and orthorhombic structures of HfO2 and ZrO2 from the Standard Joint Committee for Powder Diffraction Spectra (JCPDS) [16-22]. Due to the high stabilization temperature of the cubic phase (~2600°C) [23], the presence of the tetragonal phase is considered to be more likely than cubic phase from the thermodynamic standpoint. There are three different isomorphs of orthorhombic structures that are considered in this study [1, 10, 16, 18, 19]. The TiN layer is observed to exhibit the cubic phase [22].

The MIM sample stacks were patterned to 100x100µm2 for the electrical characterization. The device pads were created via a single lithography step followed by a reactive ion-etch process to remove the top electrode and HZO layer in the field. The electrical characterization was performed via a pulsed based current-voltage (I-V) measurement with a post processing analysis to obtain the polarization properties. To study the ferroelectric response of the samples, polarization measurements involving pulsed switching measurements were performed. A semiconductor analyzer with a waveform generator and fast measurement unit was deployed to apply pulses in the microsecond regime and measure the corresponding current response. The voltage was applied and measured at the TiN top contact and the ground contact served as the measurement point for the current. The ground contact was made to the silicon wafer which is in direct contact to the TiN bottom electrode of the sample stack. The polarization was extracted from the current response in the positive-up negative-down (PUND) measurement scheme as illustrated in Figure 1. The polarization current can be extracted via subtraction of the second from the first pulse and integration over the pulse timing yields the polarization charge. With this relation, the polarization-voltage (P-V) relationship can be plotted. From those plots, the remnant polarization can be extracted at the intersection of the positive and negative polarization (Pr+ and Pr-) with the y -axis.

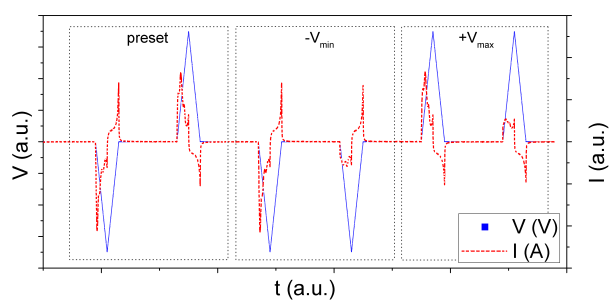


FIGURE 1: Current-Voltage (I-V) example curve. The measurement scheme known as PUND was deployed to extract the polarization. The first 2 pulses are preset pulses to set the polarization to defined level. The following two yield the Pr- component while the second two yield the Pr+ component of the sample stack polarization.

RESULTS AND DISCUSSION

In this study, we have performed GIIXRD measurements for ultra-thin HZO films of 5 different compositions. For studying the substrate effect, we have compared and summarized the GIIXRD data for both MIM and MIS in Figure 2. Pure hafnia exhibits both monoclinic and non-monoclinic features. This is witnessed by three peaks between 2.75A and 3.25A. Pure zirconia displays a pure tetragonal structure. For the samples with 50% zirconia or less we see a marked difference in the aforementioned three peaks indicating differences in relative monoclinic phase amount (figure 2(A-C). There are clear differences in the peak ratio of the main monoclinic peaks (2.86Å and 3.14Å) with the main non-monoclinic peak (2.96Å). We compare the intensity ratios of the peaks for roughly calculating the monoclinic phase and non-monoclinic phase content. The percent values of monoclinic vs. non-monoclinic are tabulated here in Fig 2(F). From these values an increase in the non-monoclinic phase % for MIM vs MIS for 50% zirconia or less is shown. For pure zirconia and 80% zirconia stacks, we do not see any difference in the structural phases between MIM and MIS stack as seen in figure 2(D) and 2(E). This data indicates the substrate plays an increasing role in phase stabilization as the relative amount of hafnia in the mixed films is increased.



FIGURE 2: Summary of the GIIXD comparison data of MIM and MIS samples of the same compositions. Green plots are MIS stack while red plots correspond to MIM stacks. (A) HfO2 (B) Hf0.8Zr0.2O2 (C) Hf0.5Zr0.5O2 (D) Hf0.2Zr0.8O2 (E) ZrO2. The symbols on top of each plots corresponds to the different structural phases identified in these stacks. Black star (**\***) corresponds to P21/*c*; m-phase; Grey letter (**I)** – Orthorhombic P*nma;* Magenta dollar (**$**) corresponds to P42/*nmc*; t-phase; Orange hash (**#)** – Orthorhombic P*bca*; Purple letter (**O**) corresponds to P*ca*21. One symbol may indicate one or a host (multiplicity) of peaks. (F) Table summarizes the monoclinic % content in MIM and MIS stacks for different compositions.

Polarization-voltage behavior in MIM structures was also observed to vary significantly between the sample stacks with different compositions. Starting with pure HfO2, the remnant polarization extracted from the PUND measurement is ~0.04 µC/cm2 with a 3 V peak voltage. This is a significant deviation from the expected non-ferroelectric behavior of un-doped HfO2. A significant increase in polarization can be observed in Hf0.7Zr0.3O2 and Hf0.5Zr0.5O2 with a wide opening of the hysteresis curve (Figure 3(E) and 3(D)) and an extracted remnant polarization of 0.7 µC/cm2 with a 2 V peak voltage and 14 µC/cm2 with a 3 V peak voltage, respectively. A further increase in the Zr content results in a shift from ferroelectric to anti-ferroelectric behavior as can be observed in Figure 3. While Hf0.2Zr0.8O2 seems to have some small ferroelectric component, the pure ZrO2 film is fully anti-ferroelectric in its P-V behavior.

It has been well-established that the ferroelectric behavior in hafnia-based dielectrics is attributed to the non-centrosymmetric polar orthorhombic structure, P*ca*21 [1, 3, 6, 7, 10, 12-15]. While there are two other orthorhombic phases monitored in these materials, they are not polar and do not lead to ferroelectricity. Huan et al [24] also reported calculated values of polarization for hafnia with this orthorhombic structure, further establishing the existence of this particular orthorhombic phase for ferroelectric behavior. However, the theoretical polarization values have not been realized due to the presence of other structural phases. Further, it has been clearly established by theory and experiments that there is a phase transition from monoclinic to orthorhombic phase to tetragonal phase in both hafnia and zirconia. We also see a strong ferroelectric behavior in Hf0.5Zr0.5O2 and Hf0.7Zr0.3O2. Muller et al [25] reported similar polarization values for the HZO with 50% zirconia in 7-9nm HZO samples.

From figure 3 it is clearly shown that ferroelectricity emerges at 30% zirconia and becomes stronger at 50% zirconia while anti-ferroelectricity appears for higher zirconia content in these stacks. We are also reporting the difference in the polarization behavior of MIM here and that of MIS. The important difference is noted for 80% zirconia stacks. From figure 3(C), MIM stack shows an anti-ferroelectric behavior while the corresponding MIS stack shows ferroelectricity as earlier reported [15]. It is believed that this behavior has a strong structural correlation. Similar MIM behavior was reported by Muller et al. and a composition and temperature dependent ferroelectric phase transition was reported in hafnia-zirconia solid solution [26]. Theoretical calculations by Reyes-Lillo et al [27] have shown the tetragonal phase shows anti-ferroelectric behavior in zirconia as it is energetically preferred. The difference in electrical behavior of the 80% zirconia HZO layer in MIS vs MIM can clearly be attributed to the different substrate and differences in applied stress from the bottom TiN electrode vs. semiconductor substrate may play a role in this difference in phase stabilization. Further investigation of HZO layer of similar compositions deposited with other semiconductor substrates such as Ge and different bottom electrodes would be useful to help understand the effect of substrates and bottom electrode on the structure and electrical properties of these materials.

CONCLUSIONS/SUMMARY

We investigated the structural and electrical properties of hafnia-zirconia ALD deposited layers by synchrotron based grazing incidence in-place x-ray diffraction and PUND measurements. These dielectric materials with 5 different compositions with 7nm thickness with two types of stacking (MIM and MIS) were explored. Compared to the MIS structures a suppression of the monoclinic phase in MIM structures with 50% zirconia or less was observed. In MIM stacks, pure hafnia exhibited ferroelectric behavior while pure zirconia exhibited anti-ferroelectric behavior. Similar behavior was seen in films with higher hafnia and zirconia content as well. In the case of 80% zirconia layers, MIM stacks showed anti-ferroelectric behavior and the corresponding MIS stacks showed ferroelectric behavior. Ferroelectric behavior was witnessed for 50% zirconia ultra-thin films as MIM stacks as well. Future research focusing on substrates and bottom electrode layer is required to delineate their exact effect and tailor these dielectrics for different applications.

FIGURE 3: Summary of the GIIXD and PUND measurements of HZO samples as MIM stacks. (A) GIIXD overlay of pure hafnia, Hf0.7Zr0.3O2, Hf0.5Zr0.5O2, Hf0.2Zr0.8O2 and pure Zirconia. Here the symbols on top correspond to different structural phases as explained in Figure 2 caption. PUND measurements shown in (B) pure Zirconia (C) Hf0.2Zr0.8O2 (D) Hf0.5Zr0.5O2 (E) Hf0.7Zr0.3O2 (F) pure hafnia.

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