

## Electronic Materials and Photonics

**Room 207 A W - Session EM1+AP+CPS+MS+PS+SM+TF-WeA**

### Materials and Devices in Emerging Memories

**Moderators:** M. David Henry, Sandia National Labs, Asif Kahn, Georgia Institute of Technology

**2:15pm EM1+AP+CPS+MS+PS+SM+TF-WeA-1 Impact of Precursor Purge Time on the Performance of Ferroelectric Hf<sub>0.52</sub>Zr<sub>0.50</sub>O<sub>2</sub> Prepared by Plasma-Enhanced Atomic Layer Deposition, Yong Kyu Choi, Benjamin Aronson, Megan Lenox, Liron Shvilberg, University of Virginia, USA; Chuanzhen Zhou, North Carolina State University; Kristina Holsgrove, Queen's University Belfast, UK; Amit Kumar, Queen's University Belfast, UK; Andrea Watson, Stephen J. McDonnell, Jon F. Ihlefeld, University of Virginia, USA**

Hafnium oxide (HfO<sub>2</sub>) shows significant potential for non-volatile memory and energy harvesting applications. However, its monoclinic phase lacks polarization, making it unsuitable for ferroelectric applications. Introducing ZrO<sub>2</sub> into HfO<sub>2</sub> (HZO) helps stabilize a ferroelectric phase. Atomic layer deposition (ALD) is the most widely used film processing technique, offering excellent thickness control, conformability, and relatively low processing temperature. Previous research has explored the impact of various metal precursors, oxidizer precursors, and process temperatures on the ferroelectric properties of HZO. One common observation is that the metal precursor purge time has a large effect on the resulting film phase and performance. However, no clear mechanism has been identified to explain this effect. In this presentation, we will discuss how HZO thin film properties change when the metal precursor purge time varies during plasma-enhanced ALD. Reducing the metal precursor purge time from 90 s to 3 s induced a transition from ferroelectric to antiferroelectric properties with double polarization hysteresis loops, higher endurance and polarization stability, and slightly increased in relatively permittivity. Infrared spectroscopy measurements (FTIR-ATR) confirmed that the antiferroelectric properties are due to the antipolar orthorhombic o-I phase, which is consistent with observations from HRTEM and DPC-STEM. The films deposited with shorter purge times showed carbon impurities as identified by ToF-SIMS analysis. This suggests that residual chemical ligands from incomplete precursor removal during the ALD process, in part, stabilizes the antipolar o-I phase. These results show that phase stability in fluorite oxides is influenced by impurities beyond intentional substituents and that stable antiferroelectric responses can be achieved without deliberately altering the material composition, such as adjusting the Hf:Zr ratio to control phase formation.

**2:30pm EM1+AP+CPS+MS+PS+SM+TF-WeA-2 Effect of Atomic Layer Annealing Duration on Phase Stabilization of Hafnium Zirconium Oxide Thin Films, Nicolas Lam, University of Virginia; Gerald Bejger, John Barber, Virginia Tech; Megan Lenox, Liron Shvilberg, University of Virginia; Christina Rost, Virginia Tech; Jon Ihlefeld, University of Virginia**

Significant research has gone into understanding the stabilizing mechanisms and properties of ferroelectric hafnia. This is largely due to its ability to display ferroelectricity in size scales below 10 nm, incorporation in already existing mass production infrastructure, and complementary metal oxide semiconductor compatibility. Today, hafnium zirconium oxide (HZO) is the most studied hafnia alloy due to its low processing temperature. However, the widespread implementation of HZO as a memory material is hindered by a variety of challenges, such as wake-up, imprint, and retention. A major issue is the inability to make phase pure ferroelectric HZO, a metastable non-centrosymmetric polar orthorhombic structure. Commonly cited impurity phases include the metastable tetragonal, antipolar orthorhombic, and equilibrium monoclinic phases. Previous work using the atomic layer annealing (ALA) technique has shown enhanced crystallinity and remanent polarization in pristine HZO films, circumventing significant formation of the antiferroelectric and tetragonal phases. In this work, thin films of HZO were grown using the ALA technique with various ALA treatment durations, ranging from 0 s up to 59 s. Following a deposition of a metal oxide layer using plasma-enhanced atomic layer deposition, the surface of the film was subjected to additional argon plasma. After synthesis and a post-metallization anneal to form the metastable phase, various structural and electrical measurement techniques were used to characterize the films. Grazing-incidence X-ray diffraction shows no formation of the equilibrium monoclinic phase; Fourier

transform infrared spectroscopy shows increasing ferroelectric phase concentration with ALA time. Polarization hysteresis measurements show an increasing hysteretic response with ALA time as compared to an antiferroelectric reference sample. Positive up negative down measurements quantified the relative amount of wake-up. The reference devices displayed a 200% increase in remanent polarization while the ALA samples displayed an 8% relative increase with the longest treatment time. The results suggest that ALA can modify the local environment of the deposited films, such that the phase fraction of the ferroelectric phase and the amount of wake-up can be tuned. This results in devices that exhibit minimal to no wake-up. This work furthers the understanding of the effect that ALA has on the resultant film's properties.

**2:45pm EM1+AP+CPS+MS+PS+SM+TF-WeA-3 Understanding Time-Dependent Imprint in Hafnium Zirconium Oxide Based Ferroelectric Tunnel Junctions, Megan Lenox, University of Virginia, USA; Samantha Jaszewski, Sandia National Laboratories; Jon Ihlefeld, University of Virginia, USA; M. David Henry, Sandia National Laboratories, USA**

While research into understanding the performance-materials property relationship of hafnium zirconium oxide (HZO) based devices has been accelerated in the past decade, their integration into microelectronic products is challenged by their endurance and imprint behavior. Imprint, or a shift in the coercive field following polarization with an initial applied field, lowers HZO remanent polarization ( $P_r$ ) along the imprint direction, impacting the current transport mechanisms and reducing the overall performance stability when studied in ferroelectric non-volatile memory applications. In these devices, imprint has been hypothesized to result from charge carrier migration at the electrode interface, increasing the charge needed for polarization switching. However, the mechanisms responsible for imprint in ferroelectric tunnel junctions (FTJ) is not understood. To study FTJ imprint phenomena, 7 nm Hf<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> devices with NbN and Nb as the top and bottom electrode, respectively, were fabricated. Polarization-electric field measurements were performed every 2<sup>nd</sup> seconds, showing a + $V_c$  shift with time.

Resistance measurements, using a pulsing scheme composed of a  $\pm V_{max}$  write pulse followed by fifty 0.4 V read pulses at various pulse widths taken every 2<sup>nd</sup> seconds, showed a drift in the ratio of high and low resistance states, and an overall reduction in the binary state memory window with increasing time, characteristic of imprint. Further, these results highlight imprint impacts on multi-state polarization switching used in neuromorphic memory applications. To investigate imprint mechanisms, pulsed hysteresis measurements taken in 0.1 V intervals followed by a reset pulse at  $\pm V_{max}$  showed an 18.1x change in the resistance ratio between the high and low resistance states. However, a similar pulsed hysteresis measurement without the reset pulse had a 11.4x resistance ratio. These results support the generation of time-dependent imprint-free HZO-based FTJs by utilizing selective pulsing schemes, promoting their use in next-generation microelectronics.

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**3:00pm EM1+AP+CPS+MS+PS+SM+TF-WeA-4 Disentangling Gamma-Ray Radiation Effects and Time-Dependent Imprint on Ferroelectric Hafnium Zirconium Oxide-Based Devices, Samantha Jaszewski, Sandia National Laboratories; Megan Lenox, Jon Ihlefeld, University of Virginia; M. David Henry, Sandia National Laboratories**

Ferroelectric hafnium oxide (HfO<sub>2</sub>) enables technological developments in microelectronics, such as the scaling of ferroelectric random-access memory (FeRAM) and new devices like ferroelectric field-effect transistors (FeFETs) and ferroelectric tunnel junctions (FTJs) that were not previously possible with conventional ferroelectrics. This is due to the material's compatibility with silicon and its ability to exhibit a ferroelectric response in films as thin as 1 nm. Understanding the interaction between radiation and ferroelectric HfO<sub>2</sub>-based devices is necessary before these devices can be utilized in radiation-hostile environments. In the literature, it has been reported that gamma-ray radiation can result in a shift of the coercive voltage of ferroelectric HfO<sub>2</sub>-based devices, impacting the memory window and, thus, the reliability of these devices. However, ferroelectric HfO<sub>2</sub>-based

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capacitors have also been shown to exhibit a time-dependent imprint effect in which the coercive voltage shifts over time as a result of the depolarization field in the film, which drives charge redistribution in the ferroelectric layer. As such, it can be challenging to disentangle the effects of gamma-ray radiation and the time-dependent imprint shift when evaluating the performance of these devices.

In this work, ferroelectric hafnium zirconium oxide (HZO) capacitors and ferroelectric tunnel junctions (FTJs) are subjected to 1 and 5 Mrad doses of gamma-ray radiation under grounded and biased conditions. X-ray diffraction and Fourier-transform infrared spectroscopy measurements demonstrate that gamma-ray radiation does not result in phase transformations, further confirmed by capacitance-voltage measurements, which show that the relative permittivity of the HZO capacitors does not change after radiation. Polarization-electric field measurements show shifts in the coercive field after radiation. However, it will be shown that these coercive voltage shifts are due to time-dependent imprint in the material rather than the effects of gamma-ray radiation. This work demonstrates that the structural and electrical properties of ferroelectric HZO-based capacitors and FTJs are not affected by gamma-ray radiation up to doses of 5 Mrad. It also underscores the importance of careful measurement procedures and analysis when evaluating radiation effects in this material.

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