NDnano Summer Undergraduate Research
2024 Project Summary

1. Student name & home university: **John Howe, University of Notre Dame**

2. ND faculty name & department: **Kai Ni, Department of Electrical Engineering**

3. Summer project title: **Fabricating Ferroelectric HfO_2 Capacitors for Next Generation Nonvolatile Memory**

4. Briefly describe new skills you acquired during your summer research:
I learned many components of semiconductor device fabrication, including:
   - **Magnetron Sputtering**
   - **Electron Beam Evaporation**
   - **Atomic Layer Deposition**
   - **Reactive Ion Etching/Inductively Coupled Plasma Etching**
   - **Photolithography**
   - **Rapid Thermal Processing**

5. Briefly share a practical application/end use of your research:
Practical applications include applications in ferroelectric random-access memory (FeRAM) and in ferroelectric transistors (FeFETs). These ferroelectric devices have the potential to revolutionize our current solid state memory devices.

6. 50- to 75-word abstract of your project:
Hafnium Zirconium Oxide (HZO) based Metal-Ferroelectric-Metal (MFM) capacitors are fabricated with various electrode materials to evaluate the choice of the electrode material on device performance characteristics as well as how the material interfaces with a ferroelectric interlayer. Both TiN and W electrode MFMs are fabricated using a combination of magnetron sputtering and consecutive plasma enhanced atomic layer deposition (C-PEALD) methods

7. References for papers, posters, or presentations of your research:

[1] T. S. Böscke, J. Müller, D. Bräuhaus, U. Schröder, and U. Böttger, "Ferroelectricity in hafnium oxide thin films," Applied Physics Letters, vol. 99, no. 10, Sep. 2011.

[2] D. Tian, H. Xu and J. Zhang, "Method for improving endurance and breakdown characteristics of metal/ferroelectric/metal capacitor by modulating deposition cycle ratio," 2022 IEEE International Conference on Artificial Intelligence and Computer Applications (ICAICA), Dalian, China, 2022, pp. 445-449.

[3] A. Sünbül, D. Lehninger, M. Lederer, T. Kämpfe, K. Seidel and L. M. Eng, "Improved polarization by interface layer insertion in ferroelectric HfO2-based MFM capacitors," 2023 IEEE International Symposium on Applications of Ferroelectrics (ISAF), Cleveland, OH, USA, 2023, pp. 1-4.

[4] Q. Wang et al., "Improved Symmetry of Ferroelectric Switching in HZO Based MFM Capacitors Enabled by High Pressure Annealing," in IEEE Journal of the Electron Devices Society, vol. 10, pp. 1009-1014.

[5] J. -H. Hsuen et al., "Demonstration of Large Polarization in Si-doped HfO2 Metal–Ferroelectric–Insulator-Semiconductor Capacitors with Good Endurance and Retention," 2023 International VLSI Symposium on Technology, Systems and Applications (VLSI-TSA/VLSI-DAT), HsinChu, Taiwan, 2023, pp. 1-2.

[6] M. I. Popovici et al., "High-Endurance Ferroelectric (LA, Y) and (LA, GD) Co-Doped hafnium zirconate grown by atomic layer deposition," ACS Applied Electronic Materials, vol. 4, no. 4, pp. 1823–1831, Apr. 2022.

[7] J. D. Anderson, J. Merkel, D. Macmahon and S. K. Kurinec, "Evaluation of Si:HfO2 Ferroelectric Properties in MFM and MFIS Structures," in IEEE Journal of the Electron Devices Society, vol. 6, pp. 525-534.

[8] Y. -K. Liang et al., "Demonstration of Highly Robust 5 nm $Hf_{0.5}Zr_{0.5}O_2$ Ultra-Thin Ferroelectric Capacitor by Improving Interface Quality," in IEEE Electron Device Letters, vol. 42, no. 9, pp. 1299-1302.

[9] A. Sünbül et al., "Impact of ferroelectric layer thickness on reliability of Back-End-of-Line-Compatible hafnium zirconium oxide films," Advanced Engineering Materials, vol. 25, no. 4, Oct. 2022.

[10] D. Zhou et al., "Wake-up effects in Si-doped hafnium oxide ferroelectric thin films," Applied Physics Letters, vol. 103, no. 19, Nov. 2013.

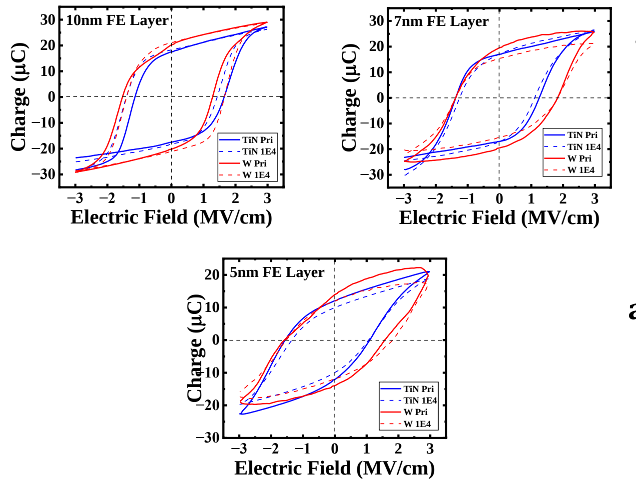

Fig. 1. Ferroelectric *Q-V* hysteresis loops for (a) 10nm, (b) 7nm, and (
5nm HZO thicknesses for 50μm x 50μm area TiN and W MFMs.
Measurements taken at 50kHz.

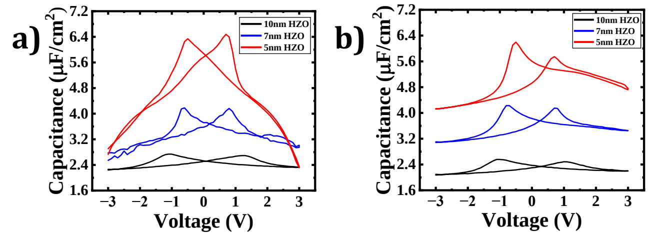

Fig. 2. W/HZO/W MFM (a) and TiN/HZO/TiN (b) MFM *C-V* Curves.

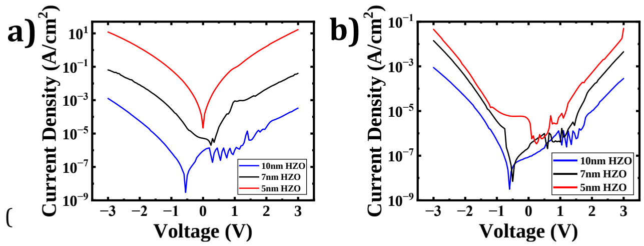

Fig. 3. W/HZO/W (a) and TiN/HZO/TiN (b) *DC-IV* Curves.

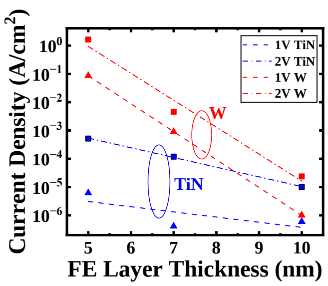

Fig. 6. Leakage current at +1V and +2V for both TiN and W MFMs as a function of FE thickness, normalized for capacitor area.

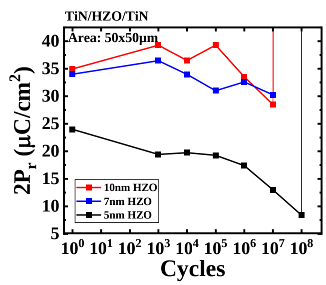

Fig. 4. $2P_r$ endurance for TiN/HZO/TiN MFMs under increasing endurance cycles

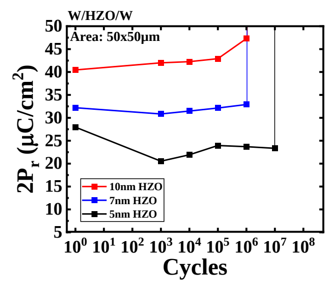

Fig. 5. $2P_r$ endurance for W/HZO/W MFMs under increasing endurance cycles

One of the critical hindrances of implementing ferroelectrics into modern memory devices is their relatively poor performance and endurance compared to necessary requirements for commercial manufacturing standards. Metal-Ferroelectric-Metal (MFM) capacitors, for instance, often begin to break down on the order of 10^6 to 10^7 ferroelectric switching cycles, when industry implementation would require magnitudes near 10^14 cycles. Additionally, capacitors may vary in their ability to withstand higher voltage differences and allow higher magnitudes of undesirable leakage current.

Many methods have been devised to increase the endurance, such as doping the ferroelectric hafnium oxide (HfO_2) interlayer with materials such as zirconium oxide (ZrO_2) and aluminum oxide (Al_2O_3), regulation of the growth of an interfacial oxide layer, and varying the methods of deposition, however little focused is put on how the electrode material affects device performance on an overall scale. We evaluated two common electrode materials: Tungsten, which is commonly used in vias as well as interconnects, and Titanium Nitride, a commonly used electrode material in industry applications.

MFMs were fabricated to have similar structures, mainly concerning symmetry about a ferroelectric layer. The ferroelectric layer thickness, as well as the electrode thickness, was varied in devices ranging from 10x10μm to 100x100μm capacitor electrode areas. For W MFMs, the bottom electrode was first deposited by magnetron sputtering only. Then, Hafnium Zirconium Oxide (HZO) was deposited via Atomic Layer Deposition (ALD). Finally, the top electrode was pattered and deposited, followed by post metallization annealing (PMA) at 500°C for 1 min in an N_2 atmosphere. For TiN MFMs, both the top and bottom electrode were deposited by a combination of magnetron sputtering with ALD, where top of the bottom electrode and the bottom of the top electrode were deposited via ALD before and after ALD deposition of HZO. By this method, the interfacial quality of the TiN with HZO improved, which improved device performance. TiN MFM electrodes, combining the thickness of both deposition methods, were the same thickness as the W MFM electrodes. TiN MFMs were also annealed in the same conditions.

Both sets of MFMs demonstrated similar capacitance through their *C-V* curves (Fig. 2 (a) and (b)), with TiN MFMs revealing a possible oxide layer (TiO_xN_y) between the TiN and the HZO, causing a possible imprint that leads to additional possible charge trapping. This charge trapping layer becomes more apparent as the thickness of the HZO layer decreases. Ferroelectricity is demonstrated through each device's *Q-V* loops (Fig 1 (a), (b), and (c), respectively). TiN MFMs display reduced polarization and coercive field compared to their W MFM counterparts. This trend is consistent as the Ferroelectric Layer (FE layer) decreases in thickness as well. One of the most significant differences between the two types of devices is their leakage current, with TiN MFMs demonstrating significantly reduced magnitudes of leakage current (Fig 3 (a) and (b)), even as FE layer thickness decreases. By Fowler Nordheim Tunneling (Fig. 6), TiN MFMs also display a reduced electron tunneling barrier which indicates that its leakage current is less dependent on the barrier thickness and therefore retains its superior properties as the dimensions of the device are scaled down. When the devices are subjected to varying electrical field cycling, TiN MFMs also display increased endurance. MFMs with a 10nm thick and 7nm thick FE layer saw an improvement of two orders of magnitude additional cycles (10^6 in W MFMs versus 10^8) before breaking down while 5nm devices endurance over 10^8 endurance cycles without approaching breakdown, while their W MFM counterparts broke down at this amount of cycling, as shown in Fig 4 and Fig. 5, respectively.

These results imply that TiN is a superior electrode material for scalable ferroelectric capacitors, and that while W can lead to an increase in polarization, TiN continues to function more effectively at smaller dimensions, a trait which is desirable for commercial manufacturing applications.