Electronic Materials and Photonics
Room 114 - Session EM+AIML+AP+QS+TF-WeM

Ferroelectrics and Memory Devices

Moderators: Samantha Jaszewski, Sandia National Labs, **Erin Cleveland**, Laboratory of Physical Sciences

8:00am **EM+AIML+AP+QS+TF-WeM-1 A Scalable Ferroelectric Non-Volatile Memory Operating at High Temperature***, Dhiren Pradhan,* Department of Electrical and Systems Engineering, University of Pennsylvania*; D. Moore,* 2Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB*; G. Kim,* Department of Engineering Chemistry, Chungbuk National University, Cheongju, Republic of Korea*; Y. He,* Department of Electrical and Systems Engineering, University of Pennsylvania*; P. Musavigharavi,* Department of Materials Science and Engineering, University of Central Florida*; K. Kim, N. Sharma, Z. Han, X. Du,* Department of Electrical and Systems Engineering, University of Pennsylvania*; V. Puli,* Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB*; E. Stach,* Department of Materials Science and Engineering, University of Pennsylvania*; W. Kennedy, N. Glavin,* Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB*; R. Olsson III, D. Jariwala,* Department of Electrical and Systems Engineering, University of Pennsylvania

Non-volatile memory (NVM) devices that reliably operate at temperatures above 300 °C are currently non-existent and remain a critically unmet challenge in the development of high- temperature (T) resilient electronics. There are numerous emerging harsh environment applications including aerospace, space exploration, oil and gas exploration, nuclear plants, mining and others that require complex, in-situ computing and sensing capabilities, for which high temperature NVM is critical. Current Silicon (Si)-based micro(nano)electronics, utilizing complementary metal oxide semiconductor (CMOS) technology, encounter reliability challenges above 200 °C and cannot retain their functional properties at high temperatures. Ferroelectric $Al_xSc_{1-x}N$ exhibits strong potential for utilization in NVM devices operating at very high temperatures (> 500 °C) given its stable and high remnant polarization (P_R) above 100μC/cm^2 with demonstrated ferroelectric transition temperature (T_C) > 1000 °C. Here, we demonstrate an $Al_{0.68}Sc_{0.32}N$ ferroelectric diode based NVM device that can reliably operate with clear ferroelectric switching up to 600 °C with distinguishable On and Off states. The coercive field (E_C) from the Triangle Wave I-V measurements is found to be -5.84 (E_{C-}) and +5.98 (E_{C+}) (+/- 0.1) MV/cm at room temperature (RT) and found to decrease with increasing temperature up to 600 °C. The devices exhibit high remnant polarizations (> 100 μC/cm^2) which are stable at high temperatures. At 600 °C, our devices show 1 million read cycles with On-Off ratio above 1 for > 60 hours. Finally, the operating voltages of our AlScN ferrodiodes are < 15 V at 600 °C which is compatible with Silicon Carbide (SiC) based high temperature logic technology, thereby making our demonstration a major step towards commercialization of NVM integrated high-T computers. NVM characteristics of engineered ferrodiodes with higher On-Off ratios at > 600 °C will also be presented in the meeting.

[a] Dhiren K. Pradhan and David C. Moore contributed equally to this work.

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8:15am **EM+AIML+AP+QS+TF-WeM-2 Oxygen Diffusion Coefficients in Ferroelectric Hafnium Zirconium Oxide Thin Films***, Jon Ihlefeld, L. Shvilberg,* University of Virginia*; C. Zhou,* North Carolina State University

Just over a decade ago, ferroelectricity – the presence of a permanent reorientable dipole – was reported in doped hafnium oxide thin films. This report generated a great deal of excitement as the inherent silicon compatibility of HfO_2, coupled with the extreme thinness of the films that exhibited the ferroelectric response promised to overcome a number of technological hurdles limiting utilization of ferroelectrics in microelectronics. While the material is moving toward mass production, there are lingering issues of insufficient endurance and limited retention. These issues are commonly attributed to oxygen point defects, including the drift of these defects in poled devices. As such, knowledge of oxygen transport in the ferroelectric phase is vital toward overcoming the current shortcomings. In this presentation, we will show the results of experiments using ^{18}O tracers to evaluate the diffusion coefficient of oxygen in the ferroelectric phase. Hafnium zirconium oxide films containing ^{16}O were prepared via plasma-enhanced atomic layer deposition followed by post-metallization annealing to form the ferroelectric phase. Following removal of the metal layer, an ^{18}O-containing hafnium zirconium oxide film was deposited via thermal atomic layer deposition with ^{18}O provided from a $H_2{}^{18}O$ source. Tracer anneals were then performed and the ^{18}O position evaluated with secondary ion mass spectrometry. The results will show that the oxygen diffusion coefficients in the ferroelectric phase are extremely low, with extrapolated room temperature values of only 10^{-26} cm^2/sec derived. The activation energy for oxygen diffusion was calculated to be 1 eV, which is intermediate the values calculated for the equilibrium monoclinic phase and amorphous films. These results indicate that oxygen vacancies may be relatively immobile in ferroelectric hafnia devices and that other charged defects may be the primary source of degradation.

9:00am **EM+AIML+AP+QS+TF-WeM-5 Iridium Etching: Exploring Reactive Ion Etching Parameters for Efficient Electrode Fabrication in Ferroelectric Memory***, Yanan Li, P. Bezard, S. Kundu, F. Lazzarino, X. Piao, Y. Canvel,* IMEC Belgium

Non-volatile Ferroelectric lead zirconium titanate (PZT) are interesting candidates for future memory applications but the fatigue resistance of the electrode material from the capacitors is a challenge. Iridium (Ir) is being investigated as electrode material for its superior characteristic. Thus, a patterning process must be developed. Due to the low volatility of the etch products, etching Ir is typically performed by ion beam etching (IBE). The low-throughput, relative scarcity of IBE chambers in the industry, as well as the limited tunability of the sputtering process are motivations for the development of a plasma-based etching approach.

In this work, we conducted experiments with TiN as a hard mask, following the process flow shown in Figure 1. Preliminary data indicates that Ir can be etched using both fluorine-based and chlorine-based gases. We identify and highlight the primary parameters affecting the Ir etch rate in the RIE process, focusing on gas flow rates, power settings, pressure, and substrate temperature. We also compare the relative contributions of physical and chemical reactions to the etch rate of Ir.

XSEM pictures for those experiments are shown in figures 2 and 3. It is observed that selectivity with a TiN hard-mask is a challenge when using these chemistries. Sidewall residues have also been observed in conditions where ion sputtering is dominant. Therefore, optimization of the etch processes based upon an understanding of the etch mechanisms in place is necessary.

9:15am **EM+AIML+AP+QS+TF-WeM-6 Investigations in Current Transport Mechanisms of Multi-Resistance State Hafnia Zirconia Ferroelectric Tunnel Junctions***, Troy Tharpe,* Sandia National Laboratories*; M. Lenox,* University of Virginia*; S. Jaszewski, G. Esteves,* Sandia National Laboratories*; J. Ihlefeld,* University of Virginia*; M. Henry,* Sandia National Laboratories

Since the discovery of ferroelectricity in doped hafnia (HfO_2) and alloyed hafnia zirconia thin films $(Hf,Zr)O_2$ over a decade ago, fluorite-structure binary oxides have garnered great interest for use within ferroelectric memory devices to realize compute-in-memory (CiM) and neuromorphic applications. With conformal atomic layer deposition (ALD) techniques, process temperatures below 400 °C, coercive fields close to 1 MV/cm, and ferroelectricity down to ~ 1nm, hafnia thin films are ideal candidates for back-end-of-line (BEOL) integration with complementary metal oxide semiconductor (CMOS) circuits. Leveraging these qualities, recent research has extensively focused on charge-based hafnia devices, such as ferroelectric random access memory (FeRAM) and ferroelectric tunnel junctions (FTJs). FTJs are realized by sandwiching a 4-7nm ferroelectric between electrodes to form a metal-ferroelectric-metal (MFM) structure with a voltage-controlled resistance modulated by polarization. Thinner than FeRAM and able to generate multistate resistances, FTJs are poised to enable energy efficient CiM devices and artificial intelligence (AI) hardware accelerators with improved performance and small form factor.

In this work, we study FTJs with 7 nm thick $Hf_{0.5}Zr_{0.5}O_2$ deposited by plasma enhanced ALD, and asymmetric 20 nm niobium (Nb) / 115 nm niobium nitride (NbN) electrodes deposited by magnetron and reactive sputter, respectively. Film ferroelectricity is stabilized by subsequent anneal at 565 °C for 90s in argon ambient. Fig. 1 (a) depicts an optical image of fabricated HZO FTJs while Fig. 1 (b) illustrates a cross section of device layers. Current density vs voltage (J-V) sweeps are taken at 294, 323, 348, 373, and 398 K for HZO FTJs with diameters varying from 74 μm to 117 μm. Fig. 2 (a) shows these J-V sweeps for a 100 μm diameter device, after application of 10 wakeup cycles. Fig. 2 (b) shows high resistance state (HRS) and low resistance state (LRS) trends across temperature for this same device at 0.2V and 0.3V. Fig. 3 (a, b) shows average and outlier resistance ratio (RR) temperature dependence for 4 devices at 0.2 V and 0.3V, respectively. Fig. 3

(c) depicts pulsed hysteresis curves for a 99 µm diameter device at 294 K and 398 K. Device resistance is read at 0.2V and a pulse width of 100ms, following a write pulse progressing from 1.5V to 1.3V and back with 100mV step and 100ms pulse width. The nonlinear HRS, LRS and RR temperature trends indicate a complex conduction system within HZO FTJs, highlighting the need for continued investigation of current transport mechanics for the realization of ferroelectric CiM devices and multistate AI accelerators.

9:30am **EM+AIML+AP+QS+TF-WeM-7 Correlation between Elastic Modulus and Biaxial Stress in Hafnium Zirconium Oxide (HZO) Thin Films**, ***Megan Lenox,*** University of Virginia*; S. Jaszewski,* Sandia National Laboratories*; S. Fields,* Naval Research Laboratory*; A. Salanova, M. Islam, M. Hoque,* University of Virginia*; J. Maria,* Penn State University*; P. Hopkins, J. Ihlefeld,* University of Virginia

The discovery of ferroelectricity in hafnium oxide based thin films has catalyzed significant research focused on understanding the ferroelectric property origins when fabricated in conventional metal-ferroelectric-metal geometries. Studies have revealed that electrode material selection impacts oxygen vacancies, interfacial layers, and biaxial stress, all noted responsible ferroelectric mechanisms. The coefficient of thermal expansion (CTE) incongruency between the hafnia and the electrode material induces an in-plane tensile stress following post-metallization annealing. However, recent work has shown that while the electrode material CTE does have an effect, the overall strain resulting from the device is primarily from the CTE of the silicon substrate and densification of the hafnia film during crystallization. This notwithstanding, comparisons between electrode materials have shown significant differences in ferroelectric remenant polarization (P_r) behavior. This work describes these polarization differences through the lens of the elastic modulus of the electrode material. TaN/HZO/TaN/*M* devices, where *M* is platinum, TaN, iridium, tungsten, and ruthenium, were fabricated using plasma enhanced atomic layer deposition and sputtering for the hafnia and metal layers, respectively. Wafer flexure measurements done using stylus profilometry revealed each metal electrode material was compressive as deposited. Two-dimensional X-ray diffraction, utilized to derive the $\sin^2(\psi)$ in-plane biaxial stress in the HZO, revealed a strong correlation between stress and electrode elastic modulus (E). Further, Polarization-electric field ($P(E)$) measurements at 2.5 MV cm^{-1} field also showed dependence of $P\text{-}_r$ on measured E. Conversely, no correlation exists between the electrode CTE and P_r or biaxial stress, respectively. Increasing modulus results in a greater resistance to deformation of the electrode, which when deposited prior to annealing the HZO to crystallize from the amorphous state, restricts the out-of-plane expansion of the HZO, promoting the stabilization of the ferroelectric orthorhombic phase, in a phenomenon known as the “capping effect”. This work further promotes the acceleration integration of HZO into MFM devices, such a non-volatile memory devices.

9:45am **EM+AIML+AP+QS+TF-WeM-8 Ferroelectric Behavior of ε−Wo3**, ***Mohammad Mahafuzur Rahaman****, A. Annerino, J. Shell, P. Gouma,* The Ohio State University

Designing novel ferroelectric polymorphs having fast and low energy dipole switching responses is crucial for developing next generation’s neuromorphic devices. Reported here a unique binary ferroelectric polymorph called ε−WO_3 and it’s dipole response to electro-optical stimuli, contributed from the stabilization of ε−phase nanoparticles of ∼20 nm grains at RT, previously was at −43ºC in bulk, by our group using FSP. The epsilon phase of the material is confirmed from XRD and Raman analysis. The nano-domains of ferroelectric ε−WO_3 shows switching behavior within few KV/cm electric field. The ferroelectric nanodomains interact with light and shows blue coloration under electro-optical stimuli. The response of these nanodomains with visible light and it’s switching behavior with electric field is studied via C vs V measurement. Furthermore, the origin of the observed “ferro-chromic effect”, the unique, rapid and reversible coloration of the e-WO3 thin films upon application of a voltage in the absence of an electrolyte has been deduced from X-ray Photoelectron Spectroscopy. An important finding for all solid-state single layer ubiquitous displays, energy-saving windows and next generation’s non-volatile memory device for neuromorphic computation.

11:00am **EM+AIML+AP+QS+TF-WeM-13 Innovations in DARPA’s Optimum Processing Technology Inside Memory Arrays (OPTIMA) Program**, ***Todd Bauer,*** DARPA **INVITED**

Fast,compact, and power-efficient compute-in-memory (CIM) accelerators can move machine learning from data centers to edge compute devices, enabling training and inference to be done where the training data is collected. However, conventional accelerators that use vonNeumannarchitectureshave poor area and computationalpowerefficiency and longexecutionlatency.CIMarchitectureswithMultiplyAccumulateMacros(MAMs)canaddressthe power and performancelimitationsof approaches that use von Neumann hardware architectures. To date these MAM implementationshavebeenhinderedbythelargephysicalsizeofmemoryelementsandthehigh-powerconsumptionofsupportingcircuitry.The Defense Advanced Research Program Agency’s OptimumProcessingTechnologyInsideMemoryArrays(OPTIMA)programseekstodeveloparea-andpower-efficienthigh-performanceMAMswithinnovativesignalprocessingcircuits. The key technical challenges that performers are addressing include 1) developing area-efficient, multi-bit memory elements (i.e. 8 bits of storage in a 1T-1C structure) that can be incorporated into compact multiply compute elements (MCEs) and 2) achieving compact, scalable, and power-efficient MAM circuits. This presentation will provide an overview of the OPTIMA program goals and approaches to achieving those goals.

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11:30am **EM+AIML+AP+QS+TF-WeM-15 A Transition Toward Solid-State in TiO_2 Protonic ECRAM**, ***John Hoerauf,*** University of Maryland, College Park*; M. Schroeder,* Army Research Laboratory*; D. Stewart, G. Rubloff,* University of Maryland, College Park

AI and inference learning energy demands are on pace to surpass global energy production[1], but analog in-memory computing hardware can reduce the energy required by up to six orders of magitude[2]. Electrochemical RAM (ECRAM) is a new and promising transistor technology to realize physical neuromorphic analog in-memory computing circuits, achieved on the device level by modifying a thin-film battery stack to measure the impedance of a selected electrode. The impedance is controlled by changing the state of charge of the battery, electrochemically doping the selected electrode with the electrochemically active species. ECRAM that utilizes protons as the electrochemically active species is compatible with existing CMOS devices, has faster programming speed and increased device durability compared to more established Lithium ion ECRAM. As a less well studied system, it is helpful to understand the insertion of protons in and out of the electrode of interest using a more traditional liquid cell before advancing to a solid-state system. In this presentation, the liquid cell electrochemical characteristics and degradation mechanisms in anatase TiO_2 are discussed with and without a capping Nafion film. It is observed that the anatase TiO_2 electrode’s typically quick degradation is suppressed by adding a spin-cast Nafion film, increasing cyclability in an aqueous acetate buffer solution by >10x cycles and altering the H^+ insertion kinetics. Subsequently, TiO_2 is used in an all-solid-state three electrode transistor by splitting the bottom current collector into a source-drain configuration and using PdH_x as the counter electrode and H^+ reservoir. Results toward novel solid state anatase TiO_2 based protonic ECRAM are discussed with a focus on device state modulation by electrochemical doping.

[1] B. Bailey, “AI Power Consumption Exploding,” Semiconductor Engineering. Accessed: May 09, 2024. [Online]. Available: https://semiengineering.com/ai-power-consumption-exploding/

[2] E. J. Fuller et al., “Li-Ion Synaptic Transistor for Low Power Analog Computing,”Advanced Materials, vol. 29, no. 4, p. 1604310, 2017

11:45am **EM+AIML+AP+QS+TF-WeM-16 Effects of Gamma Radiation on the Structural and Ferroelectric Properties of Hafnium Zirconium Oxide Capacitors**, ***Samantha Jaszewski,*** Sandia National Laboratories*; M. Lenox, J. Ihlefeld,* University of Virginia*; M. Henry,* Sandia National Laboratories

Ferroelectric hafnium oxide (HfO_2) presents opportunities for technological developments in microelectronics, such as scaling of ferroelectric random-access memory (FeRAM) and new devices such as ferroelectric field-effect transistors (FeFETS) and ferroelectric tunnel junctions (FTJs), that were not previously possible with conventional ferroelectrics. This is due to its compatibility with silicon and ability to exhibit a ferroelectric response in films as thin as 1 nm. Understanding the interaction between radiation and HfO_2-based ferroelectrics is necessary before this material can be utilized in devices facing radiation-hostile environments. In this work, the effects of varying doses of gamma radiation (1 to 8 Mrad) on the structural and electrical properties of metal-ferroelectric-metal capacitors fabricated with 17 nm thick hafnium zirconium oxide (HZO) layers is investigated. Additionally different electrode materials, titanium nitride and tungsten, will be compared. Polarization-electric field, capacitance-voltage, and leakage current measurements were made after electric field cycling with voltages ranging from 2.6 to 4 V. It will be shown that the devices

experience decreased endurance and a shift in the coercive voltage that scales with the applied gamma dose and depends on the electrode material. Synchrotron nano-Fourier transform infrared spectroscopy measurements demonstrated that no significant phase changes occur after radiation in these films. This work advances the understanding of the interaction between radiation and HfO_2-based ferroelectrics in order to probe the fundamental limits of radiation tolerance in this material.

12:00pm **EM+AIML+AP+QS+TF-WeM-17 Reconfigurable Ferroelectric Field-Effect Transistor Arrays from SWCNTs**, ***Dongjoon Rhee***, *K. Kim, S. Song,* University of Pennsylvania*; L. Peng,* Peking University, China*; J. Kang,* Sungkyunkwan University (SKKU), Republic of Korea*; R. Olsson III, D. Jariwala,* University of Pennsylvania

Ferroelectric field-effect transistor (FeFET) is a promising nonvolatile memory device due to its simple and compact device structure for high-density integration, fast switching peed, and non-destructive readout. Recent progress in FeFETs based on two-dimensional (2D) semiconductor channels and ferroelectric $Al_{0.68}Sc_{0.32}N$ (AlScN) has enabled high-performance nonvolatile memory devices with remarkably high ON-state currents, large current ON/OFF ratio, and large memory windows. However, the wafer-scale synthesis of these 2D semiconductors typically demands growth temperatures exceeding 500 °C, rendering the synthesis process incompatible with back-end-of-line (BEOL) processing and necessitating a subsequent transfer step. Solution-based assembly of semiconducting single-walled carbon nanotube (SWCNT) has shown promise as a strategy to fabricate high-quality semiconducting channels at room temperature, but their integration with AlScN for FeFETs has not yet been achieved. In this work, we present a large array of FeFETs utilizing a dense monolayer film of highly aligned semiconducting SWCNTs and ferroelectric AlScN. Our SWCNT FeFETs can be engineered from *p*-type to ambipolar by changing the contact metals at the metal-semiconducting interface. The ambipolar FeFETs showed high electron and hole current densities, both exceeding 300 μA um^{-1}, along with stable memory retention over 10^4 s and endurance greater than 10^4 cycles. Our devices can also function as reconfigurable *p*- and *n*-FETs by switching the polarization direction of AlScN, potentially enabling multifunctional logic and memory applications at the circuit level.

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