

Investigation of Electronic Mechanisms in Sputtered Thin-Film Oxides for Next
Generation Computational Devices

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Degree

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ABSTRACT

The increasing demand for data processing, alongside the tapering of Moore's Law, poses a critical challenge for the continued advancement of computing technologies. As energy consumption by information technology rises rapidly, there is an urgent need to develop new materials and device architectures that enable energy-efficient, high-density, and scalable memory and logic solutions. This dissertation investigates the mechanisms underlying resistive and ferroelectric switching in metal-oxide thin films, with a focus on tantalum oxide (Ta_2O_5), zirconium oxide (ZrO_2), and hafnium-zirconium oxide ($\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$) systems.

A combined conductive atomic force microscopy (C-AFM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) workflow was used to directly observe field-driven ion migration in $\text{Ta}_2\text{O}_5/\text{Ta}$ memristive devices. The study reveals three dominant mechanisms: charge trapping, oxygen vacancy migration, and irreversible breakdown. Each of these mechanisms is associated with distinct voltage and current regimes. This understanding provides a foundation for tuning operational windows to promote reversible switching behavior.

A combinatorial approach is employed to synthesize and characterize $\text{Zr}_x\text{Ta}_{1-x}\text{O}_y$ thin films across a range of compositions. This enables high-throughput exploration of how cation chemistry affects electronic trap depth, ionic motion, and switching performance. The results demonstrate that optimal switching behavior occurs near 30% Zr content, where hysteresis and current levels are maximized. These findings are

supported by ab initio molecular dynamics simulations, which reveal enhanced ionic mobility at this composition.

Ferroelectric switching was investigated in sputtered $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films. Structural analysis reveals a reduction in the monoclinic phase and emergence of orthorhombic and tetragonal phases with increasing Zr content. Electrical measurements indicate that charge trapping and interface effects contribute to the observed switching behavior, with phase composition and electrode-induced stress playing critical roles.

This work advances fundamental understanding of the structure-property relationships governing oxide-based resistive switching and ferroelectric devices. The insights gained provide principles for designing and fabricating the next-generation, energy-efficient computing systems based on tunable oxide thin films.

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INTRODUCTION

There are numerous mechanisms where electric fields cause ionic interactions. This thesis will focus on electric field driven ionic motion in transition metal oxide materials for memory storage and computation applications. Along with resistors, inductors and capacitors, the memristor was theorized as the fourth basic circuit element in 1971 by Leo Chua[1]. Chua stated that the three basic circuit elements that had been realized in the lab (resistors, inductors and capacitors), could be used to control the four fundamental circuit variables current (I), voltage (V), charge (q) and flux-linkage (ϕ), with a resistor controlling the relationship between V and I , an inductor controlling the relationship between ϕ and I , and a capacitor controlling the relationship between q and V . The memristor was theorized as the missing element that could control the relationship between ϕ and q . Over time, this definition of a memristor has lost the connection to the magnetic flux and now represents non-volatile devices that change resistance states with applied electric fields. These resistance states can then be read and can act as a type of digital or analog memory.

The two main mechanisms of memristive switching are the valence charge mechanism (VCM) and electrochemical metallization (ECM)[2–5]. The VCM postulates that electric fields induce motion of negative ions toward the positive cathode/active layer interface, which reduces the Schottky barrier height in the depletion region, subsequently increasing electron tunneling and conductivity. The VCM generally occurs with inert metal electrodes and requires higher voltages when compared to the ECM. In transition

metal oxides, this mechanism is based on a uniform transport of oxygen in the active layer. The buildup of oxygen at the electrode/active layer interface induces space charge and reduces the Schottky barrier height for electron tunneling in the depletion region, resulting in an increase in current. This mechanism can be seen in mixed valence state materials with smooth interfaces between the electrodes and active layers. The specific smoothness of the interfaces needed is still unknown, but if the interfaces are rough, the roughness localizes the electric field and makes filament formation more likely. This mechanism can be observed in I-V curves as a smooth transition to a more conductive state with a saturation current that represents all the active oxygen in the system built up at the interface.

The ECM is a more common mechanism and generates a conductive filament through the active layer, effectively short circuiting the device. This ECM is essentially a reversible dielectric breakdown of the insulating transition metal oxide active layer. Dielectric breakdown of thin film materials is a phenomenon that has been studied since resistors were implemented into circuits. Any insulating material can be broken down by a high enough electric field. This breakdown is caused by large amounts of ionic motion and joule heating. This breakdown creates a metallic filament through the insulating film and effectively short circuits the active layer of the device. This filament can be composed of either electrode ions that dissolve into the active layer (Ag) or active layer metallic ions. This mechanism can generally be observed in I-V curves as a sharp jump in conductivity that corresponds to when the filament connects both electrodes.[5–10] The interesting

memristive behavior is not the initial breakdown of the films, but the reversibility of this breakdown. This reversibility is caused by a breaking of the conductive filament, thus breaking the ohmic conduction path and reverting the film back to an insulating state. This “reversibility” is generally not fully reversible, since the conducting filament is not fully dissolved, but only partially broken. In order to observe reversibility of the resistive switch, the material bonding must be flexible and reconfigurable. This means that mixed valence transition metal oxides (Ta, Va) are prime candidates for this reason. This allows oxygen ions to move easier through the material and allows the thin film to take on multiple states. These two mechanisms cause the VCM to generate more analog switching while the ECM generates digital switching.

A third, introductory mechanism has been shown in nanoporous Ta₂O₅/Ta, and MoO_x, and CuInP₂S₆ that can be a precursor to VCM switching.[4,11,12] Gunuk Wang et. al. suggests that his type of resistive switching in nanoporous Ta₂O₅ is due to oxygen migration across the pore boundary.[4] Guangyu Wang et. al. suggest that this abnormal resistive switching in MoO_x devices is driven by induced dipoles that act against the external field, this drives the minimum conductivity below the device conductivity at zero applied voltage.[12] **Figure 1** shows the polarity resistive switching IV characteristics that drive interfacial resistive switching in Pt/MoO_x/ITO devices. Wu et. al demonstrated this abnormal resistive switching in flakes of CuInP₂S₆. [11] They attribute this abnormal resistive switching to Cu⁺ motion within the active layers.

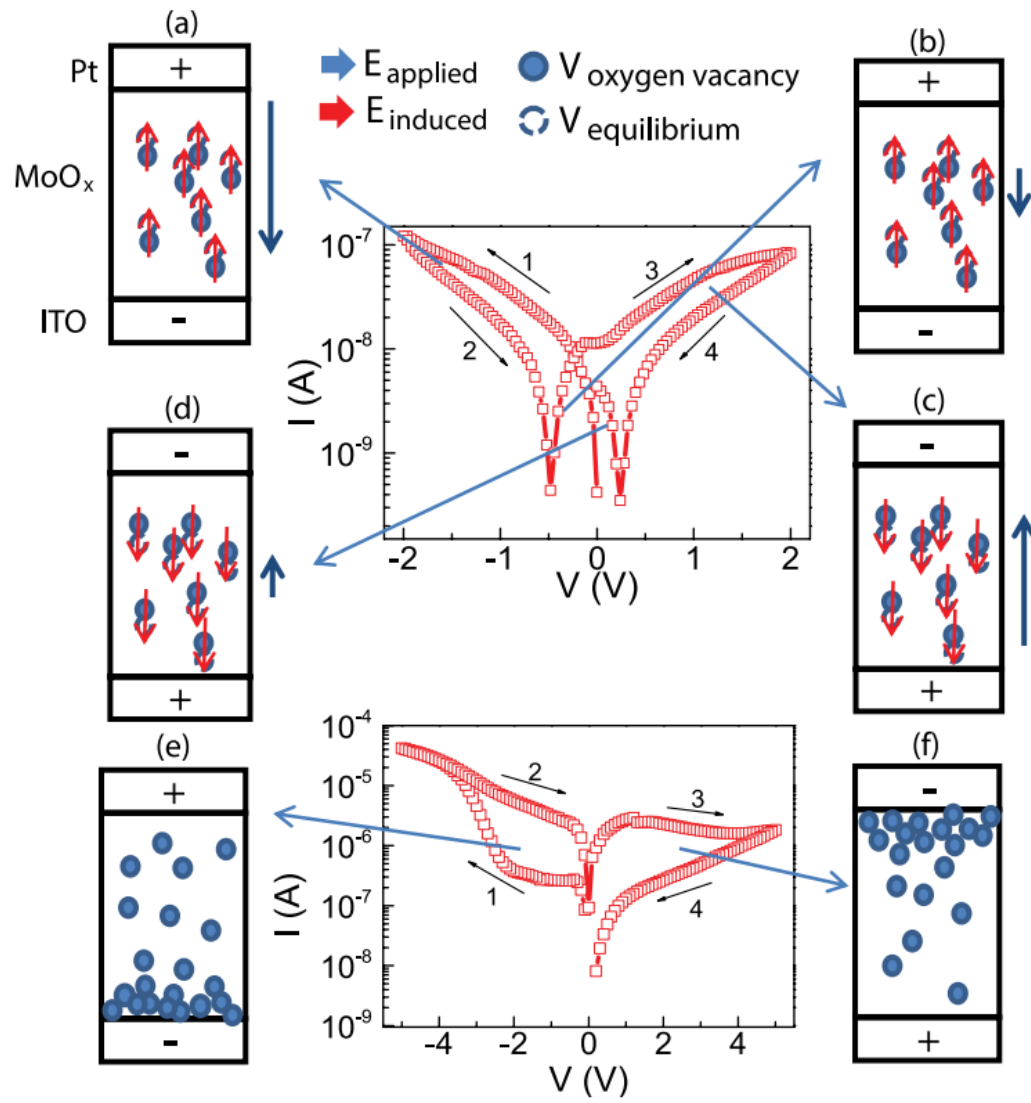


Figure 1. shows polarity driven resistive switching that drives interfacial resistive switching in Pt/MoO_x(277nm)/ITO devices[12]

Memristor Theory

Memristors were first proposed in 1971[1] and are fundamentally a resistor with a “memory” of the previous circuit history. These resistance random access memory (ReRAM) circuit elements change conductance states with applied electric fields, which makes these materials interesting candidates for non-volatile multi-state memories. These types of memories could also allow for advances in in-memory and analogue computing. Similar to the resistance changes in the human brain, these memristive circuit elements could be the basis for complete computational redesigns based on neuromorphic computing. A diagram of the resistive switching mechanism in biological systems can be seen below in **Figure 2**. These stable conductivity changes are based in ionic motion. This ionic motion is caused by the voltage drop across the oxide active layer that induces the transport of negative ions in the opposite direction to the electric field.

ReRAM Materials

Oxides

Amorphous mixed valence oxides (TaO_x , ZrO_x) [3,4,6,14,15] and bulk phase change materials ($\text{VO}_2/\text{V}_2\text{O}_5$)[16] are showing the most potential as active layer ReRAM materials. These oxide materials have the potential to replace complementary metal oxide semiconductor (CMOS) systems and are also compatible with existing CMOS fabrication methods.

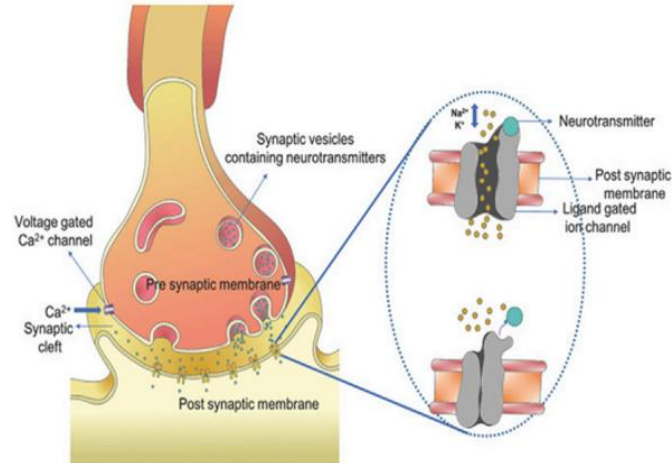


Figure 2. Shows biological synapse that utilizes neurotransmitters to migrate Na^+ and K^+ ions causing conductivity changes between the pre synaptic and presynaptic membranes.[13]

Ta_2O_5 has shown sub-nanosecond switching[17], low switching voltage ($\sim 1\text{V}$), long state retention (< 10 years) and switching endurance ($> 10^{10}$ cycles)[6]. Arrays of

Pd/TaO_x/Ta/Pd devices were shown to solve difficult computational tasks, such as partial differential equations.[18]

The resistive switching mechanisms in these materials is driven by oxygen migration and usually require an initial electroforming step, where the film is initially switched from a high resistance to a low resistance state. This electroforming step is not fully understood in computational models[19], and is not always required for stable resistive switching[20], but is generally considered to initiate the onset of oxygen motion in highly insulating oxide films. This oxygen motion can be lateral or horizontal in the film stack. The oxygen migration mechanism and the resulting resistive switching IV characteristics were shown by Mayong-Jae Lee et. al. and can be seen below in **Figure 3a**. This mechanism shows a local movement of oxygen from the Ta₂O_{5-x} layer into the TaO_{2-x} layer, forming metallic filaments through the Ta₂O_{5-x} layer and a buildup of oxygen at the Ta₂O_{5-x}/TaO_{2-x} interface[6]. This mechanism is represented in the IV characteristics by a sharp increase in current at the set voltage (V_{set}) where the metallic filaments are formed. Meyong-Jae Lee et. al. followed up this study that focuses on the active layers of the devices[6] with a second study that focuses on the electrode materials and processing.[3] In this study, in-situ transition electron microscopy (TEM) was used to image the oxygen motion in the active layers. These images, along with schematics of the electrode materials, can be seen below in **Figure 4**.

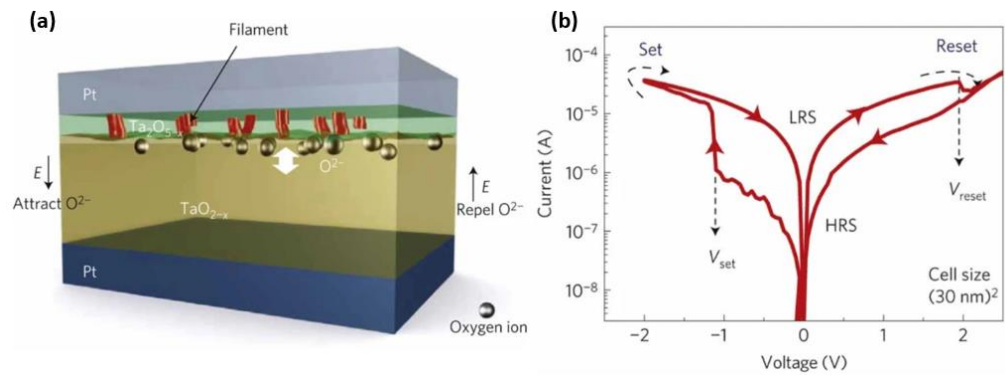


Figure 3. Shows the mechanism of oxygen movement in a Pt/Ta₂O₅/TaO_{2-x}/Pt device stack (a) and the resulting IV characteristics (b).[6]

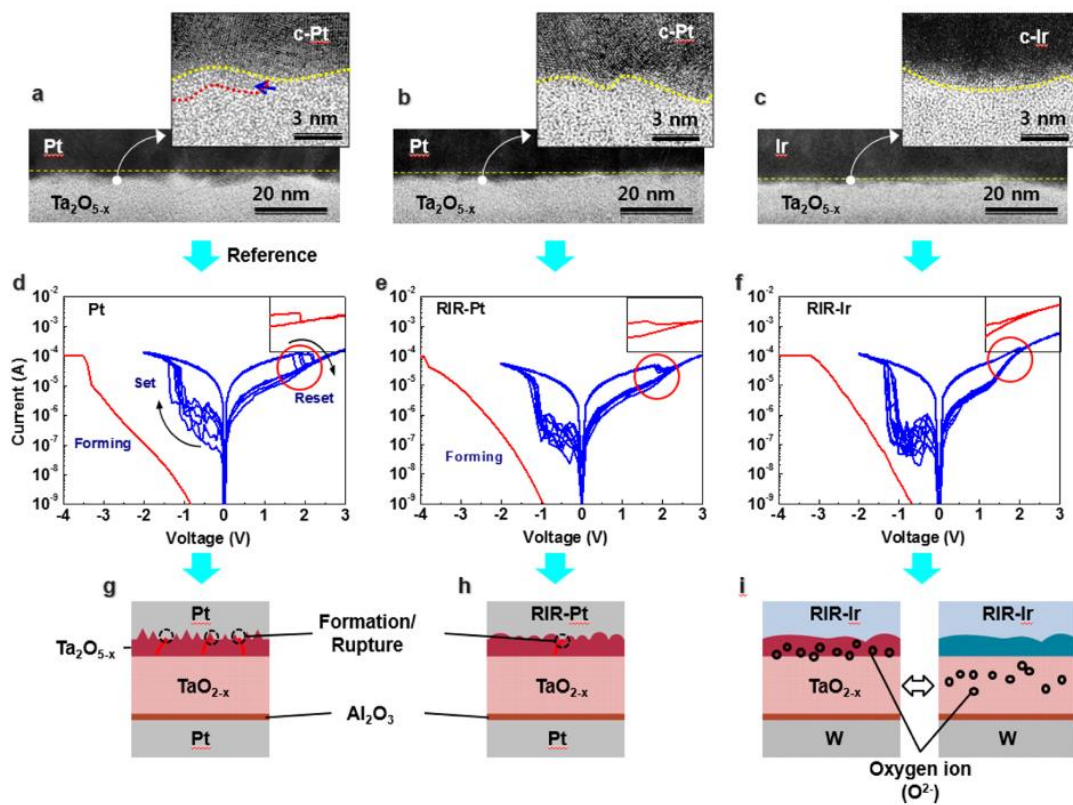


Figure 4. Shows different resistive switching mechanism that are induced in $\text{Ta}_2\text{O}_{5-x}/\text{TaO}_{2-x}$ active layers with different various electrodes[3]

These TEM images show that by decreasing the interface roughness between the top electrode and the $\text{Ta}_2\text{O}_{5-x}$ layer, the devices transition from a filament dominant mechanism to an interfacial oxygen buildup mechanism. This suggests that the rough interfaces enable localization of the electric field and drive filament formation. The activation energy for filament formation in Ta_2O_5 was shown to be reduced with Si doping.[7]

Nanoporous Ta_2O_5 and ZrO_2 capacitors showed different resistive switching compared to other previously referenced Ta_2O_5 films.[4,15] These resistive switching mechanisms appear to be driven by polarization and generate opposing internal electric fields that need to overcome by the external field in order to switch resistive states. These opposing electric fields can be seen as two local minimums in the current-voltage sweeps that generate higher resistance compared to the zero-voltage state.

Perovskites

Hybrid perovskite materials have shown hysteretic resistance changes with applied electric fields.[5,21–29] Weak bonding in hybrid perovskite materials allows for very low switching voltage, but this low switching voltage also reduces the device endurance and state stability. Inorganic perovskites show the most promise for active layers in memristive devices, due to increased bonding strength and stability. These inorganic materials have can also exhibit electrochemical metallization and valence charge mechanisms depending on the chosen electrode materials.[5] Figures of these two mechanisms and the corresponding current-voltage curves can be seen below in **Figure 5**

and **Figure 6**. Hybrid perovskite materials were first introduced as photodetectors, so these types of materials do present an interesting potential for light sensitive resistive switching.

2D materials

Resistive switching in 2D materials has been studied in WS_2 , MoS_2 , PdSe_2 and CuInP_2S_6 and has generally shown to be driven by vacancy motion.[11,30–35] Though the 2D nature of these materials generates very different properties when the 2D layers are parallel to the electric fields compared to when the layers are perpendicular to the electric field. The Vander-walls bonding of these 2D materials make them very insulating and cause a large energy barrier for ion diffusion between layers. Vacancy motion can be generated within the 2D layers, but in MoS_2 , Sangwan et. al. showed that this intraplanar vacancy diffusion requires significant voltages.[32] Ion migration from active electrode materials has shown to cause very low voltage switching ($< 200\text{mV}$) in vertical MoS_2 devices.[36] These 2D material systems show promising results as active layers for memristive data and computation applications. The main drawback to these materials being accepted into the market is they cannot be synthesized easily with standard CMOS processes.

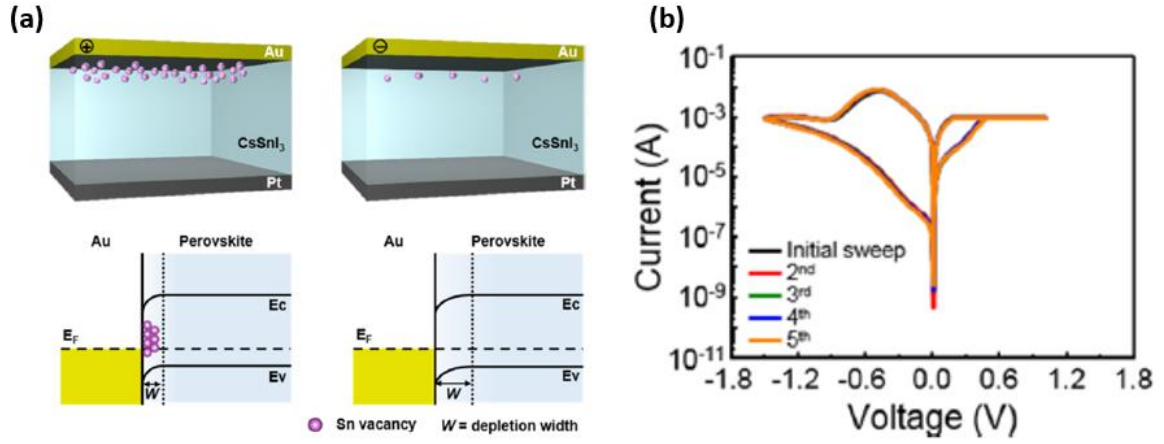


Figure 5. Shows valence charge mechanism (VCM) (a) and resistive switching IV characteristics (b) of an Au/CsSnI₃/Pt device stack[5]

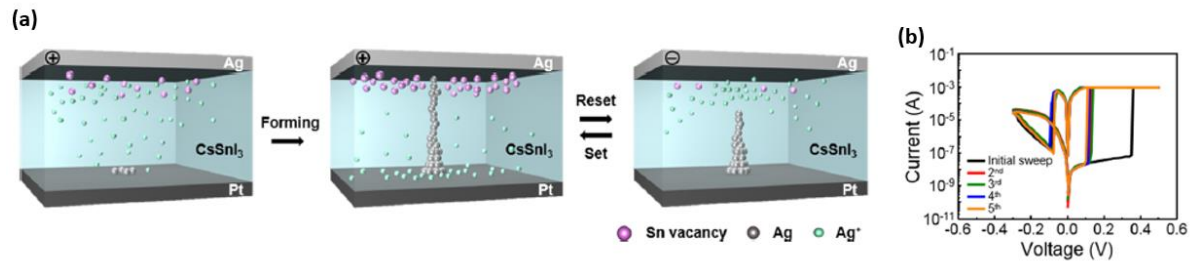


Figure 6. Shows electrochemical metallization mechanism (ECM) (a) and resistive switching IV characteristics (b) of an Ag/CsSnI₃/Pt device stack[5]

Magnetron Sputtering

Sputtering is a process where an electric field is induced at a cathode (sputtering target) in a system held at an appropriate pressure to induce a plasma. A plasma is a state that contains a mix of ionized gas (typically positively charged), electrons, ground state gas atoms or molecules that is globally neutral. A typical glow discharge plasma, contains a region of high electric field near the cathode surface, which accelerates ions that drift into the high field region. The ions gain energy and strike the target material. One by-product of the energetic ion-surface interaction are secondary electrons that are generated and are accelerated in the opposite direction away from the cathode. In the case of magnetron sputtering, a subsequent magnetic field generates a Lorentz force and elongates the otherwise line of site trajectory of the electrons and confines the trajectory in the near surface region of the target, thus increasing the plasma density. Importantly, another interaction of the energetic ion-target surface is the ejection of near surface atoms/ions – which is the sputtering process. Generally, argon (Ar) is used as the primary ions because argon is a noble gas and will not react with the secondary ions and it has reasonable mass to induce elastic energy transfer to the target material. The secondary atoms and ions are ejected from a material target and these ions form a physical vapor towards the substrate. The secondary atoms and ions then condense on the substrate, forming a film.[37] The sputter yield (atoms or ions sputtered/incident ion) increases with ion energy and the total sputtering rate is a function of the sputter yield and ion current and thus the applied power and plasma characteristics. The film

thickness is thus dependent on the power applied to the target and the deposition time. A diagram of an operation magnetron sputter chamber can be seen below in **Figure 7**. Film thickness can be made more uniform by rotating the substrate during the deposition. Simulating film thickness can be done in order to predict film thickness and chemistry. The sputter chamber geometry is very important when simulating film thickness across the sample. In our system we use a 100 mm wafer. A figure of the important angles and relevant distances can be seen below in **Figure 8**.

The mass of material deposited per unit area dM_s/dA_s at a specific location on the substrate can be calculated with equation 1 below. This equation assumes the target normal at the center of the target intersects with the substrate a location on the substrate and the projected flux can be estimated by the appropriate geometric parameters relevant to the system.

$$\frac{d\overline{M}_s}{dA_s} = \frac{\overline{M}_T(n+1)\cos^n\phi\cos\theta}{2\pi r^2}$$

Equation 1. Mass of material deposited per unit area at a specific area during the magnetron sputtering process

M_T is the total mass sputtered from the target, while ϕ is the angle between the target surface normal and a point on the substrate. The value r represents the distance from the center of the target to a given point on the substrate and θ represents the angle between the target normal and the substrate normal. The value of n is the degree of flux peaking and is dependent on the gun geometry.

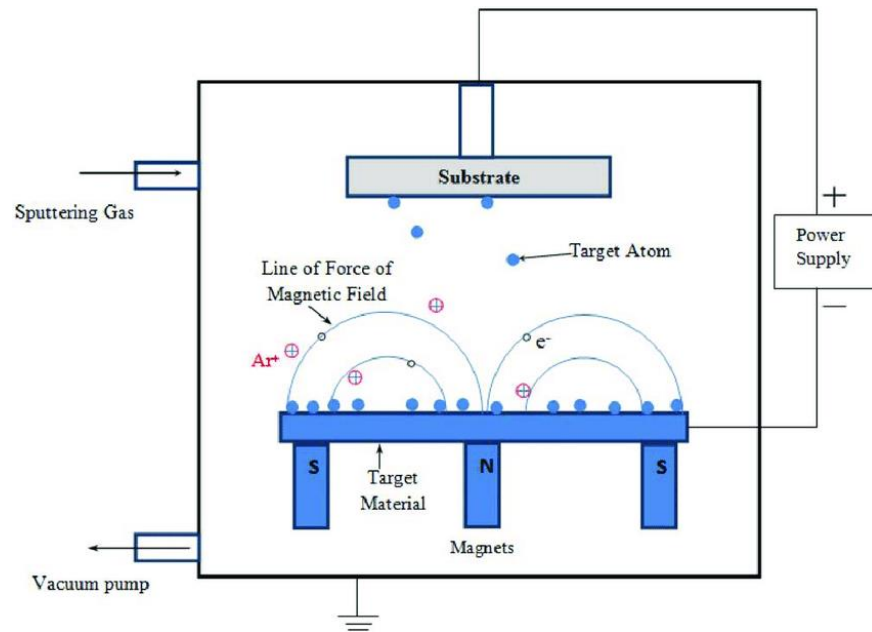


Figure 7. Diagram of Magnetron sputtering chamber[38]

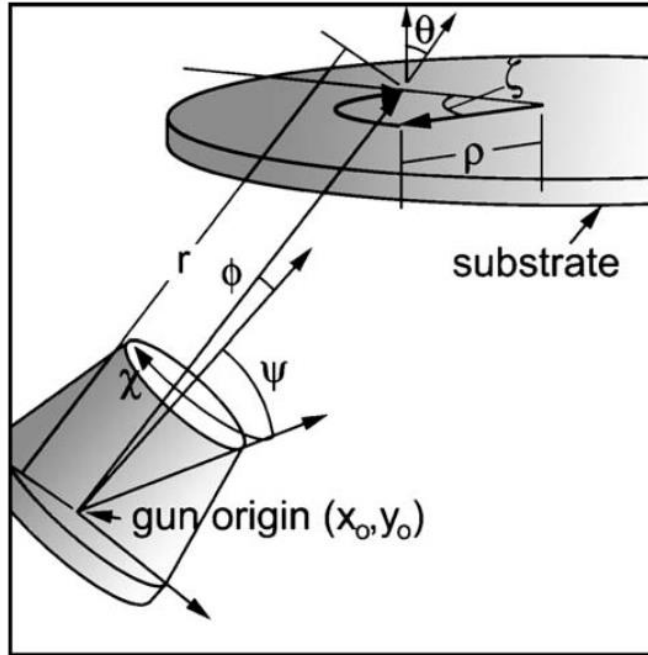


Figure 8. Schematic of relevant distances and angles needed to calculate theoretical film thickness[39]

Since the targets are set into 50 mm tubes to keep the sputtering atoms from depositing onto other targets in the system, the value of n is 12 for the system being used for these studies.[39] The distributions from multiple sources can be summed for cases where multiple targets are used at the same time to deposit alloyed films; importantly if the substrate is rotated a uniform film with metal stoichiometry proportional to the sputtering rates is achieved, or combinatorial libraries with a composition and thickness gradient can be achieved if the wafer is fixed during the deposition.

Characterization Methods

Atomic Force Microscopy

Atomic force microscopy (AFM) is one of the most versatile imaging techniques. AFM is a physical imaging technique that employs a small physical probe mounted to a cantilever. Similar to a record player, this probe is dragged along the surface of the sample. The position of the cantilever is tracked by a laser that deflects off top of the cantilever and is detected by a photodetector. The height of the cantilever is tracked while the probe is rastered across the sample surface and a topographical image is generated. Electrically conductive probes can be used to probe local conductivity of the sample and, in the case of memristive materials, locally switching the conductance state of the film. The force applied to the tip/surface interface is generated by a voltage applied to a piezoelectric material. In the case of contact mode, direct voltage is applied in order to maintain the pressure on the sample. A schematic of a standard AFM can be seen below in **Figure 9**.

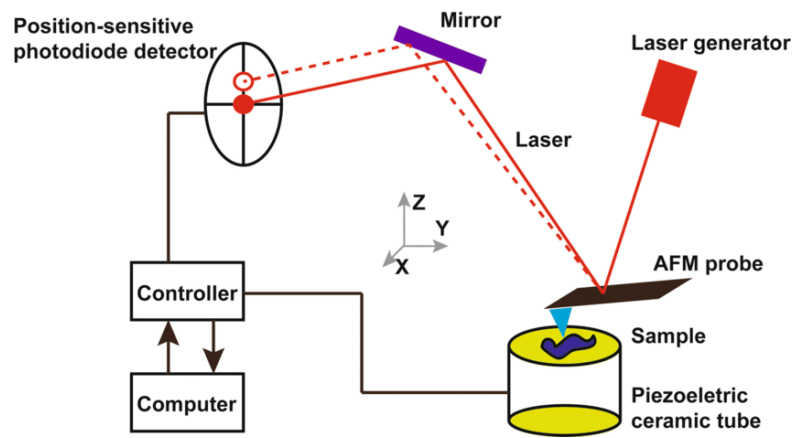


Figure 9. Schematic of AFM working principle[40]

In the case of tapping or AC mode, an AC bias is applied to the piezoelectric material in order to generate a waveform at the tip/surface interface proportional to the applied AC bias. This AC mode is useful for generating topographic information on force sensitive samples, or for measuring local surface potential differences in the sample. Using kelvin probe force microscopy (KPFM), the contact potential difference (CPD) between the sample and the tip can be measured. This is done by measuring the surface topography in AC mode, then lifting the tip slightly off the surface while applying voltages to the tip and measuring the attraction/repulsive force on the tip. The voltage applied to the tip that generates no attractive/repulsive force is considered the CPD between the tip and surface.

ToF-SIMS

Time-of-Flight secondary ion mass spectrometry (ToF-SIMS) is a chemical imaging technique. This technique is conducted in high vacuum (10^{-6} - 10^{-8} torr) and can be used to collect the spatially resolved mass spectra of a material. Secondary ions are sputtered from the sample surface by 30 keV Bi ions. The sputtered ions generate are subsequently attracted to the charged detector. Since the ions are generated at the same time, and the larger ions will take longer to reach the detector compared to the smaller ions, which generates a time-of-flight charge/mass spectrum. Focusing, pulsing and rastering the primary Bi ion beam, enables a spatially resolved chemical image of the layer to be taken and by stitching multiple layers together generates a tomograph of the sample to be imaged. In the system used for these studies the ions used for milling through the sample are Cs and O₂. Alternate milling ion gun and the chemical imaging ion guns provides the

depth profile of the chemistry in the SIMS. A limitation to ToF-SIMS is that the detector can only be charged in one polarity per experiment, therefore only positive or negative ions can be collected for each experiment. The spatial resolution of ToF-SIMS is about 100 nm but this resolution requires skilled operation of the tool. ToF-SIMS has been used previously to track ionic motion in thin films.[5,41] A schematic of a spatially resolved ToF-SIMS tool can be seen below in **Figure 10**.

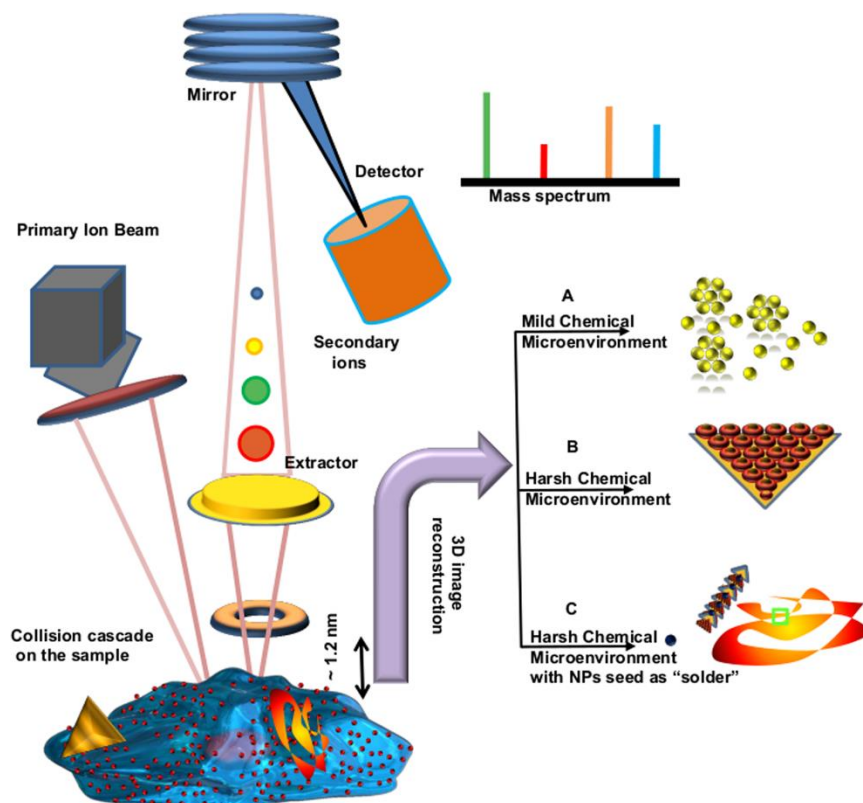


Figure 10. Shows the components and general geometry of a ToF-SIMS system[42]

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CHAPTER I

DIRECT VISUALIZATION OF CHARGE MIGRATION IN BILAYER

TANTALUM OXIDE FILMS BY MULTIMODAL IMAGING

Direct Visualization of Charge Migration in Bilayer Tantalum Oxide Films by Multimodal Imaging

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Author Contributions

This work was originally published in *Advanced Electronic Materials*. Matthew Flynn-Hepford was the lead writer and experimentalist of this paper. Matthew conducted the AFM and ToF-SIMS experiments present in the article. Philip Rack acted as the main editor. Ivan Kravchenko and Steven Randolph did the ion irradiation. Jong Keum did the XRD and XRR experiments. John Lasseter assisted on ion irradiation calculations. Bobby Sumpter conducted the modeling simulations. Alec Talin, Stephen Jesse, Petro

Maksymovych assisted on editing and arguments. Matthew Marinella's fabricated the tantalum oxide films. Anton Ievlev supervised ToF-SIMS measurements and assisted in editing. Olga Ovchinnikova obtained funding and assisted in editing.

Abstract

Inspired by biological neuromorphic computing, artificial neural networks based on crossbar arrays of bilayer tantalum oxide memristors have shown to be promising alternatives to conventional complementary metal-oxide-semiconductor (CMOS) architectures. In order to understand the driving mechanism in these oxide systems, tantalum oxide films are resistively switched by conductive atomic force microscopy (C-AFM), and subsequently imaged by kelvin probe force microscopy (KPFM) and spatially resolved time-of-flight secondary ion mass spectrometry (ToF-SIMS). These workflows enable induction and analysis of the resistive switching mechanism as well as control over the resistively switched region of the film. In this work it is shown that the resistive switching mechanism is driven by both current and electric field effects. Reversible oxygen motion is enabled by applying low (<1 V) electric fields, while high electric fields generate irreversible breakdown of the material (>1 V). Fully understanding oxygen motion and electrical effects in bilayer oxide memristor systems is a fundamental step toward the adoption of memristors as a neuromorphic computing technology.

Introduction

Fundamental physical principals limit future scaling of semiconductor technology according to Moore's law and lead to a prohibitive increase in energy cost for future

computing. The global energy demand of computational applications is projected to increase to approximately 20 percent by 2030.[1] This is driven by inefficiencies built into conventional complementary metal-oxide-semiconductor (CMOS) architectures. Furthermore, industrial processing is reaching the theoretical limit of transistor size (2-3nm), which, together with increasing challenge of heat dissipation, caused Moore's law to start failing around 2010.[2, 3] This theoretical limit is dictated by the scale where transistor physics transitions from conventional to quantum physics dominating the carrier transport. As a strategy to address the growing computation needs associated with artificial intelligence, analog memory computing approaches using various tunable resistor device concepts are emerging, including ferroelectrics, phase change, electrochemical and filament forming valence change memories.[4, 5] Resistive switching random access memory (ReRAM) devices or memristors, have many advantages compared to other emerging non-volatile memory (NVM) device types, including extreme scalability, compatibility with CMOS, excellent retention, and the realization of up to 2048 (11 bit) analog states.

Tantalum oxide (TaO_x) based ReRAM devices have an operational voltage around ± 1 V and have been widely studied as candidates for analog NVM due to their outstanding retention (> 10 years) and endurance ($> 10^{10}$ Cycles).[6-10] These properties allow for integration with conventional CMOS architectures, which shortens the barrier to implement this technology to a wider market.[11-13] Nevertheless, challenges associated with wide spread adoption of TaO_x ReRAM analog NVM remain. For example,

‘denoising’ procedures that can dramatically increase the analog state density are required after each ‘write’ operation, which greatly complicates training.[14]

These materials demonstrate resistive switching by two main mechanisms; the valence charge mechanism (VCM) and electrochemical metallization (ECM). The ECM has been demonstrated by a transition from a high resistance state (HRS) to a low resistance state (LRS) caused by the formation of a conducting filament of metallic ions that percolates through the TaO_x active layer, effectively short circuiting the otherwise insulating oxide layer.[7, 10, 15] This phase change is driven by a localization of the electric field by interface roughness resulting in joule heating and breakdown. ECM is not observed in *in situ* scanning transition electron microscopy (STEM) experiments if the electrode/active layer interface has a low surface roughness, suggesting that conductive filaments need a localized electric field caused by interface roughness in order to form, but the threshold of roughness needed is still unclear.[8] The VCM can be observed by a smooth exponential transition from the HRS to the LRS.[8, 9] This formation-free resistance change is caused by a buildup of cation vacancies at the electrode/active layer interface, which reduces the Schottky barrier height, and increases the probability of electron tunneling. Devices that operate via the VCM generally operate at a higher voltage compared to those that operate by the ECM, however the devices are more stable relative to devices driven by filament formation.

Kim et. al. showed that Si doping can improve the on/off ratio of TaO_x devices at only 2.7 at% Si.[10] An increased on/off ratio in a filamentary device is caused by a thicker

filament in the LRS and a wider depleted gap between the filament and electrode in the HRS; both of which suggests a higher oxygen ion mobility. For silicon-doped TaO_x devices, this higher oxygen mobility was justified by Si induced ion conductivity channels. These weak bonding channels are caused by strong bonding in proximity to the Si ions, allowing for weaker bonding away from the Si ions and faster oxygen ion motion in the material overall. These ion conductivity channels can be simulated by the atomic structure, utilizing density functional theory (DFT), but this method can be inconclusive in amorphous oxide materials, since it is challenging to accurately simulate amorphous structures. Though doping presents an enticing path to tuning resistive switching in oxide films, the VCM and ECM mechanisms must be understood in TaO_x in order to fully understand the effects of doping.

Characterization of memristive oxides requires a means to electrically inducing and detecting ion motion. Atomic force microscopy (AFM) is a prime candidate to both induce and detect local ion motion. AFM has been used to investigate resistive switching along with local IV measurements.[16, 17] Conductive atomic force microscopy (C-AFM) has also been used to induce and measure low and high conductance states in oxide films.^[16] In thin films, kelvin probe force microscopy (KPFM) can also detect ion motion through changes in contact potential difference (CPD) between the tip and sample surface, though interpretation of the corresponding results is complicated by a number of auxiliary phenomena, such as charge trapping and surface potential (ionic motion). These phenomena cannot be investigated by AFM means alone. In order to study them here, we

use spatially resolved time-of-flight secondary ion mass spectrometry (ToF-SIMS) to characterize possible chemical changes in tantalum oxide devices. ToF-SIMS can be used to collect the depth profiles of chemical species and thus be used to visualize ionic motion in memristive films or devices.[18-23] Previous work using a combined workflow using C-AFM/ToF-SIMS demonstrated that it was possible to track oxygen motion induced by C-AFM in a SiO_x active layer, but showed that C-AFM in ambient conditions is prone to driving moisture into the active layer.^[24] Therefore, to capture true oxygen motion a C-AFM/ToF-SIMS workflow needs to be conducted in the same high vacuum environment to allow for induction and measurement of the ionic motion in the active layers without the effects of ambient oxygen or moisture. This experimental workflow also allows for a sputter cleaning of the surface prior to C-AFM measurements to ensure good probe contact with the active layers.

In-situ STEM characterization of a 40nm TaO_x device operation was analyzed by Ma et. al.[25] A 10-20nm wide oxygen deficient filament formed between the top and bottom TiN electrodes. Lateral oxygen movement by temperature-driven Fick's diffusion was suggested to be the driving mechanism for filament formation, rather than vertical diffusion in the active layer. Oxygen was not observed to move in or out of the electrode in the EDS maps shown. This study contributes evidence of how tantalum-rich filaments form in a single layer TaO_x sandwich device structure and shows that lateral diffusion of oxygen is possible in these systems.

In this study we utilize multimodal chemical imaging to investigate charge trapping and ionic motion effects in poled amorphous Ta₂O₅/Ta bilayer films. To accomplish this, films were dynamically poled using C-AFM and subsequently analyzed by KPFM and ToF-SIMS in order to measure changes in CPD and ionic motion, respectively. These experiments help illuminate the mechanisms that contribute to resistive switching in tantalum oxide films. KPFM showed a nonlinear CPD response. Under vacuum, low applied voltage (< 1V) during C-AFM measurements show reversible ionic motion that could be observed in ToF-SIMS measurements. Larger applied voltage (> 1V) generated irreversible breakdown of the film, which was also corroborated by ToF-SIMS measurements. These results provide insight into the different mechanisms that are present in these bilayer oxide films and enable better understanding of resistive switching in these materials.

Results and Discussion

In order to simulate the energy needed for oxygen and tantalum to diffuse, an amorphous Ta₂O₅ structure was created and ion activation energies for diffusion processes were simulated using plane-wave density functional theory (DFT) and molecular dynamics (MD), respectively. Plane-wave DFT calculations were carried out using VASP and the projector augmented wave (PAW) pseudopotentials for electron-ion interactions.[26] Exchange-correlation interactions were accounted for using the generalized gradient approximation (GGA) functional of Perdew-Burke-Ernzerhof (PBE).[27] Starting with crystalline Ta₂O₅, we used a supercell structure containing 168 atoms (i.e.,

$\text{Ta}_{48}\text{O}_{120}$ [28,29]) with optimized lattice constants of $x = 14.635 \text{ \AA}$, $y = 12.377 \text{ \AA}$, and $z = 11.761 \text{ \AA}$. During structural optimization, both atoms and cell volume were allowed to relax until the residual forces fell below $0.02 \text{ eV \AA}^{-1}$, with a cutoff energy of 520 eV and Gamma-point only k-point sampling. Next a melt-and-quench approach was used in ab-initio molecular dynamics (AIMD) simulations to generate an amorphous $\text{Ta}_{48}\text{O}_{120}$ structure and its amorphous derivative structures with different oxygen vacancy concentrations, including $\text{Ta}_{48}\text{O}_{119}$, $\text{Ta}_{48}\text{O}_{96}$, and $\text{Ta}_{48}\text{O}_{84}$. [30,31] We note that this model has shown very good results, agreeing with experiments based on cathodoluminescence (CL), electron energy loss spectroscopy (EELS) and scanning microwave impedance microscopy. For the amorphous $\text{Ta}_{48}\text{O}_{119}$ (see **Figure 15**, Supporting Information), we then ran AIMD using a Nose-Hoover thermostat for 5 different temperatures, ranging from $300\text{--}2000 \text{ K}$ and used the mean square displacement (MSD) of Ta and O via Einstein's relation to find the respective diffusion coefficients. Using the Arrhenius equation, we then determined the activation energy for the diffusion process. Oxygen vacancy migration for the amorphous model was found to be $\approx 1.2 \text{ eV}$, which is in accord with other simulation results.[31] The diffusion barrier for Ta was considerably higher, $\approx 4 \text{ eV}$. The origin of the relatively low activation energy of oxygen vacancy migration has been previously detailed by Hur.[33] As highlighted, the large mobility of oxygen vacancies predicted by a switching model can be explained by the relatively low activation barrier of positively charged oxygen vacancies. As described below, this is in good agreement with our experimental findings.

Inducing and measuring electric field driven oxygen vacancy migration was first done via C-AFM/KPFM. After using C-AFM to apply a range of electric fields to the surface between ± 4 V, a large change in CPD is observed in the subsequent KPFM scan. A slight swelling of the film is observed in **Figure 11** (< 1 nm) after applying a positive C-AFM bias, while negative applied bias resulted in virtually no topography change. The cause of the film swelling under positive bias is unclear, but is most likely associated with pulling negative charge to the surface. At tip voltages between 4 and -4 V, only the 4 V region showed measurable current readings during the C-AFM scans, but significant changes in CPD were observed in the subsequent KPFM scans at all applied voltages. The change in CPD is observed in **Figure 11d,e,f** for pristine and silicon irradiated regions.

An increase in CPD is observed after a positive electric field is applied and naturally, the CPD decreases when a negative field is applied. This effect is due to electrons being pushed and pulled to the near surface region and being trapped. Trapped electrons at the surface of the material, result in a higher work function because of the negative space charge induced at the surface. Conversely, a negative electrical bias applied to the AFM probe depletes the near surface region of electrons, resulting in a positive space charge and lower work function. The asymmetry in the CPD difference for positive versus negative polarity is not clearly understood but could be due to the asymmetry in the number of surface states versus bulk states.

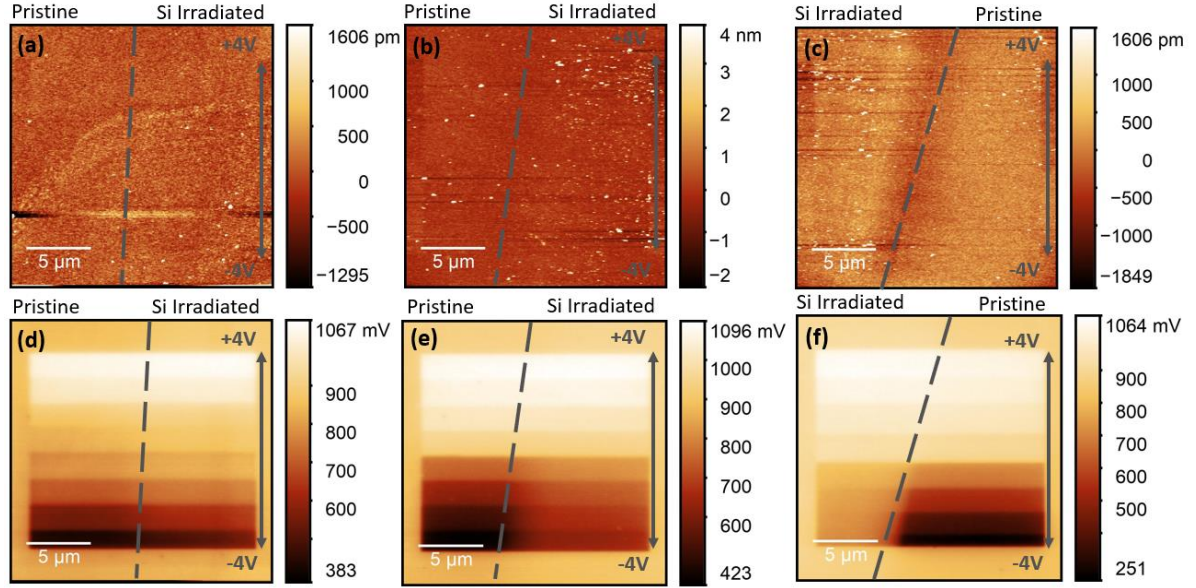


Figure 11. Topography (top a-c) and relative CPD (bottom d-f) measured by KPFM after applied tip bias in contact mode. The 15 μm biased area was poled from 4 to -4 V in 1 V increments. (from the top of each scan: 4, 3, 2, 1, -1, -2, -3, -4V). Irradiation doses of 5 (a and d), 10 (b and e) and 50 (c and f) ions/ nm^2 . Note the irradiated/pristine areas are flipped for (c) and (f).

The regions exposed by silicon are not as susceptible to CPD change by the negative applied bias which suggests less positive space charge. To elucidate the effect of the silicon irradiation, SRIM simulations (**Figure 16**, Supporting Information) were performed and the silicon doping was estimated by normalizing the implanted Si concentration to the areal dose applied to the samples. As shown in **Figure 17** (Supporting Information), the concentration of silicon in the Ta₂O₅/Ta layers is negligible (< 1.4 at. %Si) and thus well below the doping levels reported by Kim et al (2.7 at. %Si).[10] We attribute the changes in the observed KPFM to ion-induced defects caused by electronic and nuclear energy loss, namely damage accumulation induced by the ion beam, which produces deeper traps and thus less mobile charge. The charge trapping effects are significant and appear to dominate over ion motion effects as the CPD dissipates noticeably over 14 hours (**Figure 18**, Supporting Information). Our calculated activation energy for thermal driven diffusion in an amorphous TaO_x system shows that oxygen vacancies require less energy to diffuse compared to Ta ions and although electric field driven ion migration is different than thermally driven ion migration, it is possible that oxygen vacancies are being pulled or pushed through the film by this applied AFM tip polling. In order to separate charge trapping and ionic motion effects, ToF-SIMS was employed to directly measure ion contrast in the films. The C-AFM and ToF-SIMS workflow described above was employed to induce and image ionic motion effects respectively. This workflow also enables induction of electric field driven ion motion by C-AFM and direct measurement of the ion motion by ToF-SIMS in the same

area of the film without breaking vacuum. The ToF-SIMS depth profile of the 50×50um C-AFM area shows that oxygen ions appear to be the primary species that are moved by the generated electric field. This oxygen migration can be seen below in **Figure 12**, where the Cs_2O^+ ion count (**Figure 12a**) at the $\text{Ta}_2\text{O}_5/\text{Ta}$ interface is presented. **Figure 12b** shows a sum of oxygen ion and normalized tantalum oxide ion counts (O^+ ion count, TaO^+ normalized with the Ta^+ ion count and TaO_2^+ ion count normalized to the Ta^+ ion count). This C-AFM/SIMS data agrees with the previously calculated thermal diffusion activation energy for oxygen vacancies and tantalum in an amorphous Ta_2O_5 system. This thickening of the Ta_2O_5 layer under applied positive polling is also consistent with in situ STEM work done by MyongJae Lee et. al.[8] where oxygen is observed moving in the opposite direction to the applied electric field, effectively increasing the Ta_2O_5 layer thickness.

The trace and retrace images from the C-AFM measurement (**Figure 19**, Supporting Information) show an increase in current from the trace to the retrace, suggesting this thickening of the Ta_2O_5 layer was enough to increase the conductivity of the film stack. The ion profiles of other relevant ions in the film stack are plotted in **Figure 20** (Supporting Information). Unlike oxygen, the other ions in the stack (Ta^+ , TaO^+ and TiN^+) do not seem to move under these low electric fields, suggesting that the barrier for oxygen motion under applied electric fields is lower compared to the other ions in the system.

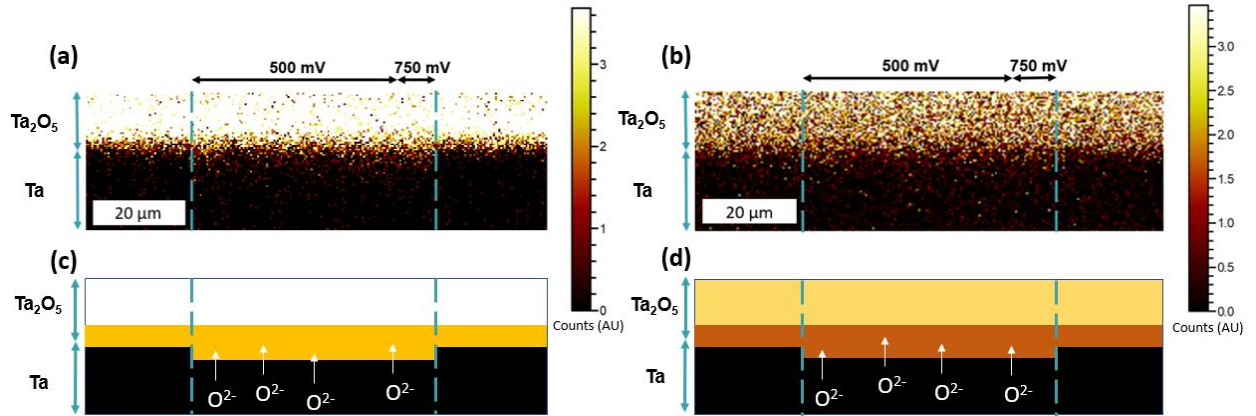


Figure 12. ToF-SIMS depth profile showing the Y-Z slice of Cs₂O⁺ ion counts (a) and the sum of the O⁺ ion count, TaO⁺ normalized with the Ta⁺ ion count and TaO₂⁺ ion count normalized to the Ta⁺ ion count (b). A 500mV electric field was applied to the surface using C-AFM in the region between the dotted lines. Oxygen buildup can be seen at the Ta₂O₅/Ta interface. Cartoons of this SIMS data (c, d) shows the direction the oxygen ions are pulled to the surface from the induced electric field.

A second C-AFM/ToF-SIMS experiment was done in order to investigate reversibility of observed ion motion. The first C-AFM scan of this experiment was done to induce reversible ionic motion without breaking down the film stack, employing low applied voltages of 0 to 1 in 0.25 V increments. The current maps from this first C-AFM scan can be seen in **Figure 21** (Supporting Information). The pristine RMS surface roughness, taken from the top 1/5th of the C-AFM scan where no AFM tip bias was applied was 9.61 nm. The RMS roughness of the subsequent regions corresponding to tip biases of the 0.25, 0.5, 0.75, and 1 V regions were 6.09, 3.28, 6.14, and 11.01 nm, respectively (**Figure 22**, Supporting Information). The total roughness of the entire scan was 17.19 nm. This low surface roughness suggests the film did not experience dielectric breakdown or filamentary resistive switching. A second C-AFM scan was done that overlapped with the first, but the scan direction was rotated 90 degrees. This second scan attempts to reverse the ionic motion induced by the first scan by applying low negative voltages of 0 to -1 V in 0.25 V increments. Subsequent ToF-SIMS measurements show that applied electrical bias moved small amounts of oxygen from the Ta/TiN interface into the Ta layer with an applied positive bias (**Figure 13a**).

In order to visualize oxygen motion through the material stack, the ion counts for tantalum oxide species (sum of TaO^+ , TaO_2^+ , Ta_2O_5^+) were normalized with the respective tantalum species (sum of Ta^+ , Ta_2^+). These visualizations are shown in **Figure 13**. The average normalized oxygen ion count in the TiN layer under the 0.5 to 1 V bias region was found to be 19.5% lower compared to the total average oxygen ion count in

the unbiased TiN layer. Subsequently, the oxygen ion count in the area above this oxygen deficient region was found to be 7.5% higher compared to the total oxygen ion count in the Ta layer. This change in oxygen concentration in the 0.5 to 1 V biased area is attributed to oxygen movement toward the positively charged electrode. Depth profiles of this biased region compared to a pristine region can be seen in **Figure 23** (Supporting Information). No oxygen motion is observed in **Figure 13** at 0.25 V which suggests that this is below the activation voltage needed to initiate this oxygen motion. Above 0.25 V, oxygen can be seen migrating toward the positive surface. This redistribution of oxygen through the film stack is enough to noticeably change the conductivity of the film stack. This change in conductivity can be seen by the difference between the current trace and retrace of the C-AFM scans that induced the oxygen motion (**Figures 21, 22**, Supporting Information).

When a subsequent negative bias (-0.25 V) is applied to the adjacent region, the oxygen migrates into the TiN electrode interface. This can be seen by a 9.1% increase in the oxygen ion counts under the biased area in column 2. Though this oxygen movement is subtle and different from the oxygen movement observed in the first C-AFM/ToF-SIMS experiment (**Figure 12**), it is consistent with expectations that oxygen moves in this Ta₂O₅/Ta bilayer system under small (< 1 V) applied electric fields. Migration of TiO⁺ into the TiN electrode at every negative applied bias can be seen in **Figure 25** (Supporting Information) along with breakdown of the film from -0.5 to -1 V. This suggests oxygen motion away from a negatively charged surface.

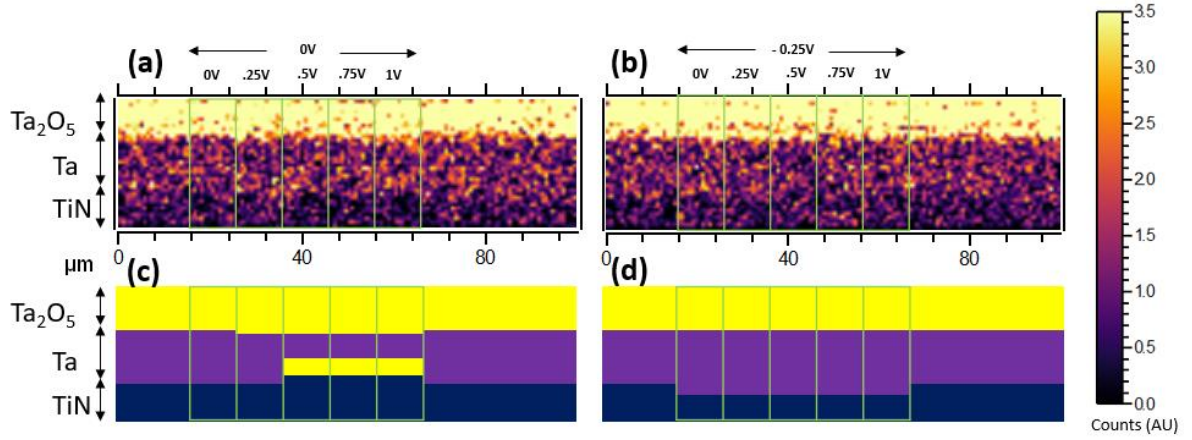


Figure 13. Shows YZ depth profiles of the Ta₂O₅/Ta/TiN interface for column 1 (a) and column 2 (b). The ions counts potted include: The O⁺ ion count, TaO⁺ normalized with the Ta⁺ count, TaO₂⁺ ion count normalized to the Ta⁺ ion count and the Ta₂O₃⁺ ion count normalized with the Ta₂⁺ ion count. The green lines indicate the border of each 10 μm bias area (these YZ slices correspond to column 1 and 2 in **Figure 20**). The cartoons below the depth profiles (c and d) show the rough movement of oxygen across the biased regions. The applied voltages are shown above each bias area where the bottom row indicates the voltage applied in the first scan and the top bias indicated the voltage applied during the second scan. (An absence of oxygen can be seen at the bottom of **Figure 13a** that is reversed in **Figure 13b**)

The average oxygen counts as a function of depth for columns 1 and 2 are shown in **Figure 13**, along with corresponding schematics of the overall oxygen movement. During the second C-AFM scan of the oxygen motion reversibility C-AFM/ToF-SIMS experiment (negative bias applied to the surface), breakdown of the film began to occur in the -0.5 V region and persisted for the remainder of the scan. Breakdown occurring at -0.5 V and not at $+0.5$ V demonstrates an asymmetric electric field polarity effect in this system. This effect can be seen in point current-voltage measurements of an oxygen cleaned area, where a negative applied electric field results in a larger current compared to an equal positive electric field (**Figure 26**, Supporting Information). Relevant ion profiles from this experiment can be seen in **Figure 27** (Supporting Information). Upon applying higher voltages (± 4 V), these systems undergo irreversible breakdown where the applied energy is higher than the activation energy for diffusion of tantalum and oxygen, resulting in atomic motion for all species present in the system. When the voltage increases to the point of breakdown, a third mechanism driven by joule heating emerges. Larger voltages lead to breakdown of the entire film stack, where the breakdown is localized to directly under the AFM tip since a straight line between the AFM tip and bottom electrode will predominantly be the shortest circuit distance. The migration of O^{2-} is demonstrated by the TaO^+ ion count shown in **Figure 14**. A swelling of the film at positive applied bias can also be seen in the topography post poling (**Figure 14b**), suggesting a similar charge trapping mechanism to the ambient C-AFM/KPFM experiment discussed earlier.

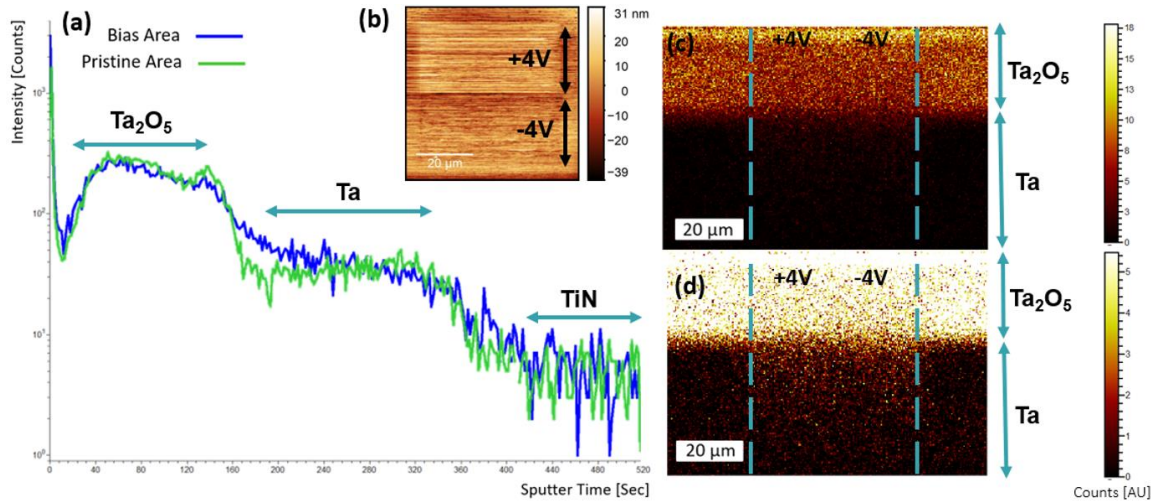


Figure 14. A comparison of the TaO^+ depth profile in the biased area vs the pristine area (a), the resulting topography change (b) by AFM and a YZ slice of ion counts of: TaO^+ , CsO^+ , Cs_2O^+ , CsTaO_2^+ across the biased region highlighting oxygen depletion the Ta_2O_5 layer (c) and the oxygen insertion in the Ta layer (d). Line scans of the topography image (b) can be seen in **Figure 35**. Note that both (c) and (d) are the same dataset with different scale.

There was no significant variation in ion counts between positive and negative biased areas (**Figure 28**, Supporting Information), suggesting the breakdown mechanism is primarily current driven. This breakdown is the driving mechanism of filament formation in these amorphous tantalum oxide films. Filaments are prone to breaking when an opposite electric field polarity is applied, returning the film to its high resistance state. Therefore, electric field effects must be, at least partially, involved in filamentary resistive switching as well. When applying these larger electric fields to the surface (C-AFM), this breakdown mechanism is easily observed by significant changes in topography (average RMS surface roughness of 29.58 nm) and significant ion migration through the stack (**Figure 30**, Supporting Information). An increase of TaO^+ concentration in the Ta layer of the film stack correlates to an increase in oxygen in the Ta layer. The oxygen appears to build up at the $\text{Ta}_2\text{O}_5/\text{Ta}$ interface, which supports previous proposed mechanisms for filament induced resistive switching. The TaO^+ depth profile of the biased and pristine regions is shown in **Figure 14a**, next to the depth profile of oxygen species in the film stack.

Conclusions

The tapering of Moore's Law in the coming decade, combined with ever increasing demands on data processing, will greatly accelerate the energy consumption of information technology (already the fastest growing consumer of energy worldwide) in order to maintain growth in computing power. To sustain continued increase in computing power at a significantly reduced energy consumption, fundamental materials

research must be undertaken to underpin and enable transition to new computing principles and new types of computing devices. In this work we investigate the switching mechanism in tantalum oxide memristive devices by directly visualizing ion migration via a unique workflow combining C-AFM and ToF-SIMS. We found that by applying an electric field across a Ta₂O₅/Ta film stack results in an interplay of several mechanisms including: nonlinear charge trapping, reversible oxygen motion and irreversible breakdown. The degree to which these mechanisms dominate depends on the amount of current generated by the applied voltage. If an electric field is applied and accompanied by a low current through the system, charge trapping is the dominant mechanism. If the electric field is excessive, a large current is generated, and the film breaks down by joule heating and ions from the film and electrodes start to intermix. At modest voltages (<1 V) a mechanism associated with field assisted the migration of oxygen/oxygen vacancies in the film can cause changes in conductivity but does not irreversibly breakdown the film. This type of electric field driven oxygen diffusion is more stable if it can be controlled. In the future, more effort will be placed into understanding this sub-breakdown ionic motion and its potential in resistive switching devices. Changes in film thickness and/or chemistry will also be investigated in order to vary the resistance of the films. This change in resistance will enable clearer separation of the electric field effects from the current effects. Molecular dynamic simulations of these structures could also be useful. Simulating the energy needed to migrate each ion type through TaO_x layer could define the operational window for these devices where the lower boundary of the operational

window would be defined by the minimum energy needed to migrate oxygen and upper boundary would be the minimum energy needed to migrate tantalum.

Experimental Section

In order to investigate the driving mechanism of resistive switching in bilayer memristive oxide devices, thin films of tantalum oxide + tantalum on a titanium nitride electrode (Ta_2O_5 (10 nm) / Ta (15 nm) / TiN (20 nm)) were deposited on an 8-inch P-type silicon substrate via a combination of reactive DC magnetron sputtering and inert gas sputtering (see [32] for overview of reactive sputtering of Ta_2O_5). The entire deposition was done without breaking vacuum. The 15 nm Ta layer acts as a gettering layer, which removes oxygen from the neighboring Ta_2O_5 layer. The functional bilayer of Ta_2O_5 /Ta was shown to be ≈ 25 nm total (10 nm/15 nm each, respectively) and no crystalline peaks were identified in the structure as measured by X-ray reflectivity (XRR) and X-Ray diffraction (XRD), respectively (**Figure 31**, Supporting Information). XRD and XRR measurements were conducted on a PANalytical X'Pert Pro MRD equipped with a proportional Xenon counter. For the XRD and XRR measurements, the X-ray beam was generated at 45 kV/40 mA, and the X-ray beam wavelength, λ was $\lambda = 1.5406 \text{ \AA}$ (Cu $K\alpha_1$ radiation). The step size ($\Delta 2\theta$) was 0.01° and the exposure time at each step was 20 seconds. In XRR, the x-axis was converted from scattering (diffraction) angle, 2θ to qz , where $qz = (4\pi\sin\theta)/\lambda$. A functioning film stack without the top electrode enables experimental flexibility of how an electric field can be applied to the stack. An atomic force microscopy tip was used as a top electrode to apply an electric field across the film stack

in specific areas. This dynamic way of applying an electric field to the film enables induction of the resistive switching mechanism in a designated area. While the uniformity of an electric field between electrodes is dependent on the interface roughness, the uniformity of the field generated during a C-AFM scan is dependent on parameters that determine surface contact, such as scan speed, tip shape and surface roughness. In order to investigate the effects of charge trapping on the mechanism of resistive switching, selected areas were irradiated with Si^{++} using a Raith VELION FIB-SEM at doses of 5, 10 and 50 ions nm^2 with an accelerating voltage of 35 KeV (70 KeV landing energy). KPFM images were taken in ambient conditions using an Oxford Cypher AFM, measuring topography during the trace scan and driving the tip to the null voltage (voltage where the attractive/repulsive force equals zero) between the tip and substrate during the retrace scan. A 15 μm ambient C-AFM scan was done at a range of voltages (+4 to -4 V) across the boundary of each irradiated area in an attempt to switch the film. C-AFM scans were measured across the boundaries of the irradiated areas to probe both the Si irradiated regions and pristine, unexposed, regions of the film for reference. The topography and current maps from the ambient C-AFM scans can be found in **Figure 32** (Supporting Information) and the average change in CPD from the applied C-AFM can be seen in **Figure 33** (Supporting Information). To directly probe electrically driven ionic motion in this $\text{Ta}_2\text{O}_5/\text{Ta}/\text{TiN}$ system, C-AFM measurements were done under high vacuum (10^{-8} mbar) followed by ToF-SIMS in the same location. The instrument used (A ToF.SIMS 5 by iONTOP from Munster, Germany), enables measurements of

conductive properties of the film stack by C-AFM while subsequently depth profiling through the area of interest with ToF-SIMS without the film leaving the vacuum chamber. This C-AFM to SIMS workflow in vacuum enables the induction of ion motion via the C-AFM and subsequent measurement of the resulting ion distribution with the ToF-SIMS without breaking vacuum. An oxygen sputter cleaning was done prior to all C-AFM biasing at 1 keV for 20 s in order to remove surface contaminants and ensure good contact to the Ta₂O₅ active layer. Oxygen surface cleaning was critical to generate any C-AFM or local current/voltage measurements. A ToF-SIMS depth profile of a 1 keV oxygen beam sputtering the Ta₂O₅/Ta/TiN system is shown in **Figure 34** (Supporting Information). A stopping range of ions in matter (SRIM) simulation [33] was also calculated for 50 000, 1 keV oxygen ions interacting with a 10 nm Ta₂O₅/15 nm Ta/20 nm TiN/100 nm Si target and is shown in (**Figure 35**, Supporting Information) and illustrates the 1 Kev O₂ does not penetrate past the Ta₂O₅ layer. A 10 MΩ resistor was also added in series with the AFM tip and sample in order to reduce the current of the circuit and damage to the AFM tip/surface junction. All C-AFM and ToF-SIMS measurements were collected with a resolution of 256 × 256 points and lines. The first C-AFM/SIMS experiment employed small, applied voltages of 750 and 500 mV during a 50 × 50 μm C-AFM scan in order to induce oxygen motion without breaking down the film stack. The chemistry change induced by the C-AFM scan was imaged using a ToF-SIMS depth profile. The profile was formed by repetitive scans from a Bi₃⁺⁺ liquid metal ion gun at 30 keV for surface analysis followed by a 500 eV Cs ion sputter. The second C-

AFM/ToF-SIMS experiment was designed to image oxygen motion reversibility. Two 50 μm C-AFM scans were conducted, followed by a 100 μm ToF-SIMS depth profile. The first scan used a 0-degree scan direction, applying increasing bias in the negative Y direction from 0 to 1 V. The second scan used a 90-degree rotation scan and applied increasing negative electric field from 0 to -1 V in an attempt to reverse any ionic motion induced by the initial scan. These two scans generate a 5×5 array of 10×10 μm squares on the surface of the Ta_2O_5 film that is ideal for investigating reversibility of ionic motion through the film stack. A diagram of the applied electric field pattern is shown in **Figure 24** (Supporting Information). The C-AFM scans employed a scan rate of 10 $\mu\text{m}/\text{sec}$ with voltage changes every 52 lines for a total of 256 lines. Similar to above, the SIMS depth profile employed repetitive scans from a Bi_3^{++} liquid metal ion gun at 30 keV for surface analysis followed by a 500 eV Cs ion sputter. When significant electric fields ($> |1|$ or $|-0.5|$ V applied to Ta_2O_5 surface) are applied to the device stack, the film exhibits irreversible dielectric breakdown. To investigate the effect of dielectric breakdown, high electric fields (± 4 V) were applied to the AFM tip during a 50×50 μm contact mode scan. The breakdown/electroforming region of the $\text{Ta}_2\text{O}_5/\text{Ta}$ bilayer film was subsequently mapped via a ToF-SIMS depth profile, using the same parameters as mentioned above. This breakdown is driven by joule heating and is the most significant mechanism that drives tantalum-rich filament formation.

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Appendix

Supporting Information

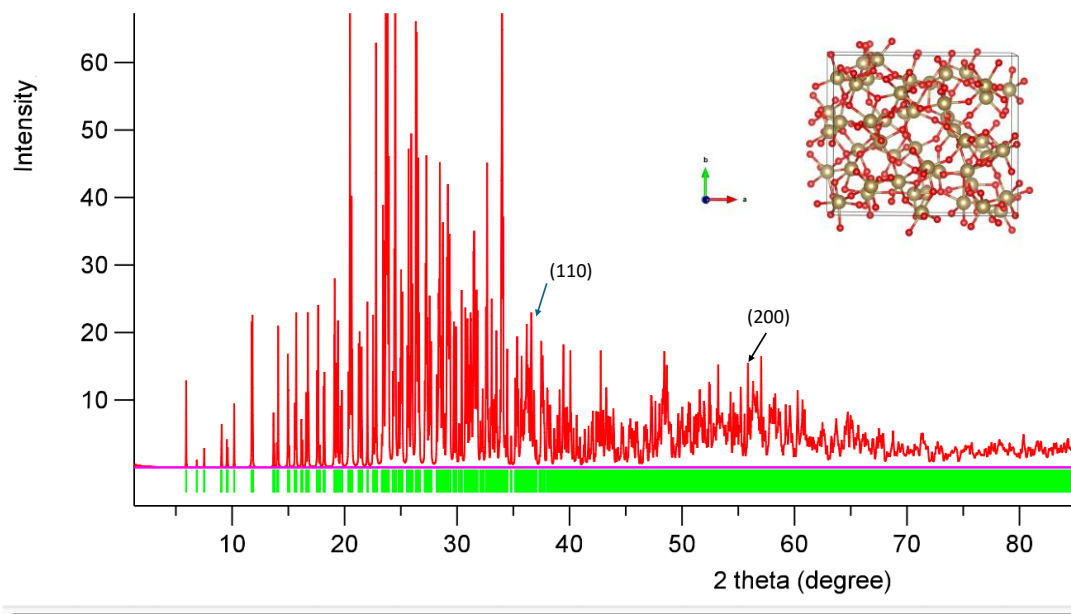


Figure 15. Amorphous Ta_2O_5 model (insert) and computed X-ray diffraction (XRD).

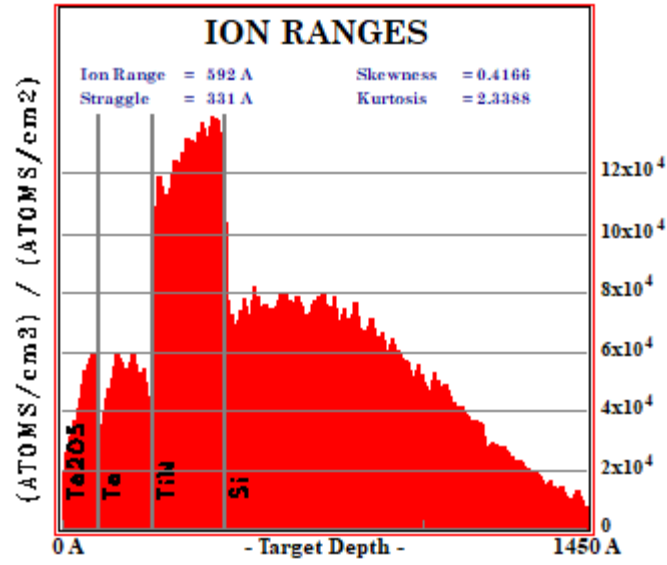


Figure 16. SRIM calculation of penetration depth for Si at 70Kev hitting a 10nm Ta₂O₅/15nm Ta/20nm TiN/100nm Si target. Thickness values were approximated from the XRR data shown in **Figure 31**. Densities of 8.2, 16.65, 5.4, and 2.329 g/cc were used for Ta₂O₅, Ta, TiN and Si, layers respectively

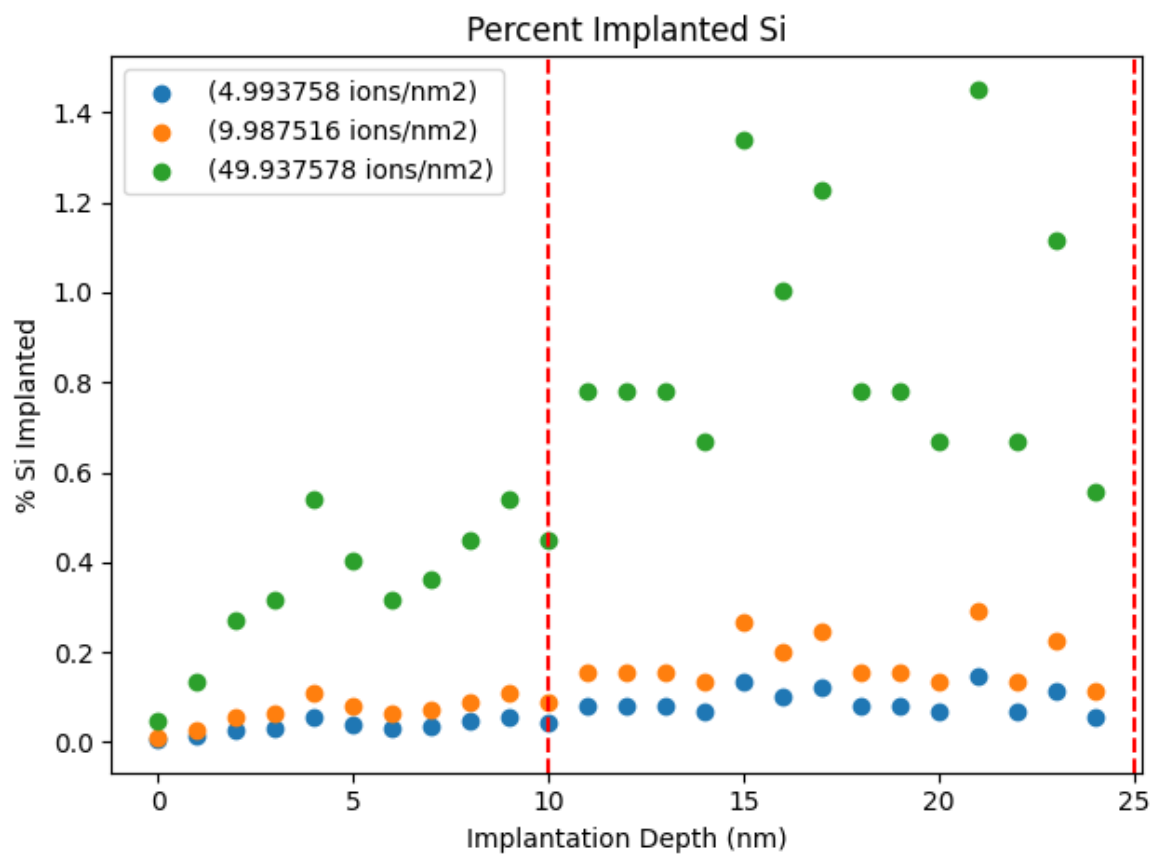


Figure 17. Shows implantation depth of Si in the two Ta₂O₅ and Ta active layers. Percent Si is calculated by the number of Si atoms normalized by the number of Ta atoms.

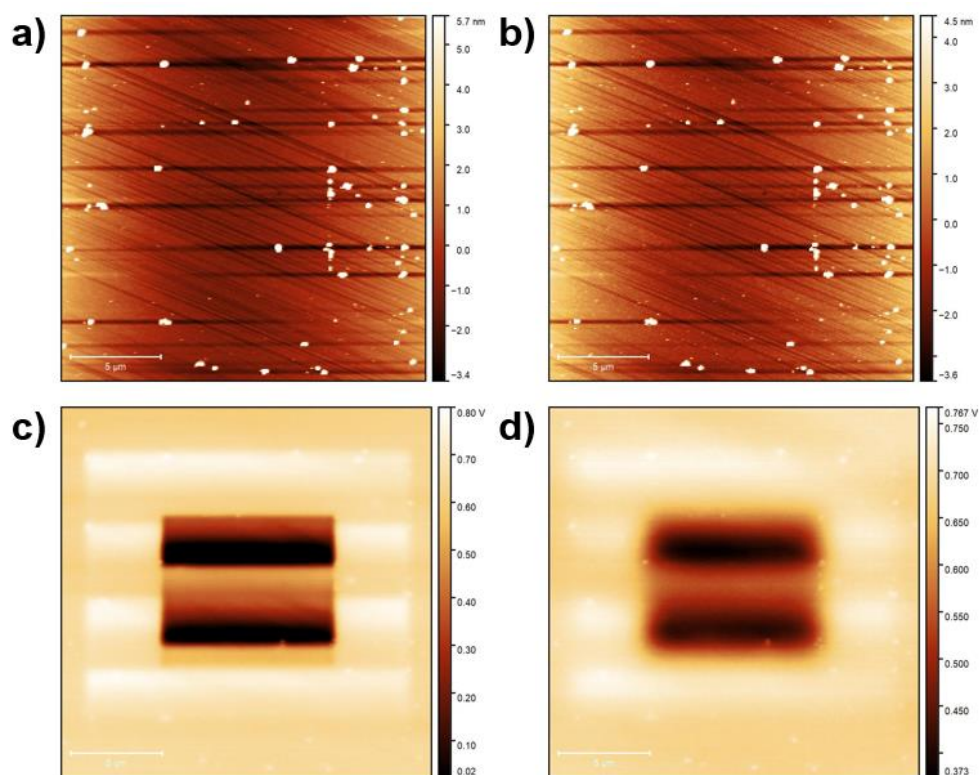


Figure 18. Shows topography (a, b) and CPD from two 20 μm KPFM scans. The initial scan (a, c) shows CPD differences after two C-AFM scans: one 15 μm C-AFM scan applying +3V to the tip and a second 8 μm C-AFM scan applying -3V to the tip. The second KPFM scan shows the same area after 14 hrs. A significantly reduced CPD change can be seen in the second scan due to charge trapping dissipation.

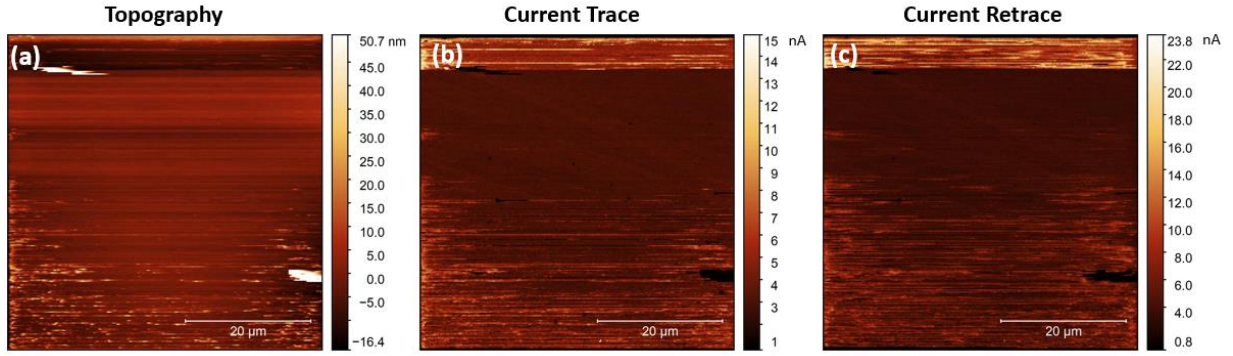


Figure 19. Shows topography (a), current during scan trace (first line scan) (b) and current during scan retrace (second line scan) (c) for the C-AFM/ToF-SIMS experiment 1. The C-AFM scan was started with an applied tip voltage of 750mV. The average current collected through the film increased from 1.61 to 3.16 nA for the trace and retrace of the scan, respectively, suggesting the film was undergoing a change in phase that promotes higher film conductivity. While scanning the surface with 750mV, the roughness increased from 4.07nm during the trace scan to 15.18nm during the retrace of the scan, so the voltage was decreased to 500 mV for the remainder of the scan (45 x 50 μm) in an attempt to reduce surface topography changes. The surface roughness was reduced to 1.49nm during the first pass of the scan (trace) and 8.95nm during the second pass (retrace). After decreasing the applied voltage to 500mV, the trace and retrace current were also reduced to 0.65 and 1.01nA respectively. This 55% increase in current suggests that the film is still undergoes a modest phase change under the 500mV applied field.

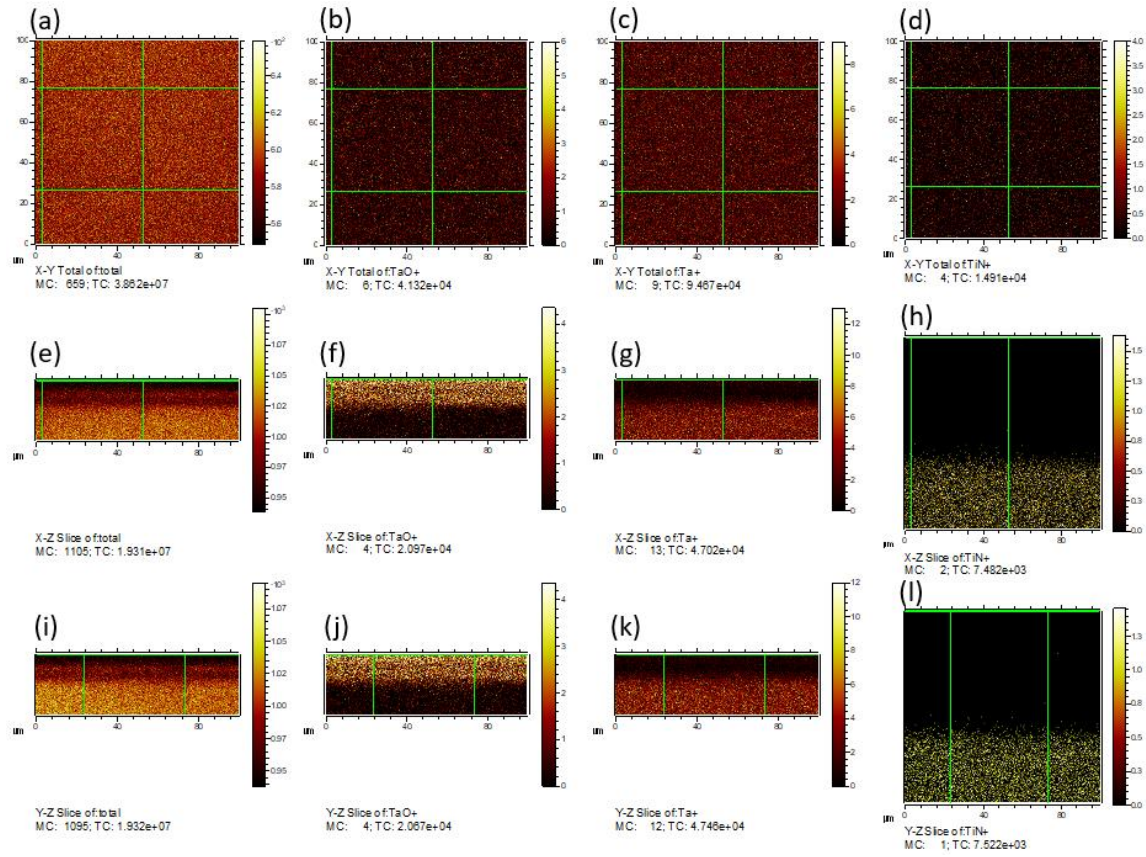


Figure 20. Shows Depth profiles of the 750mV/500mV C-AFM scan with oxygen buildup at the $\text{Ta}_2\text{O}_5/\text{Ta}$ interface. E-h show the data cubes looking at the x-plane, while i-l shows the data cubes from the y-planes.

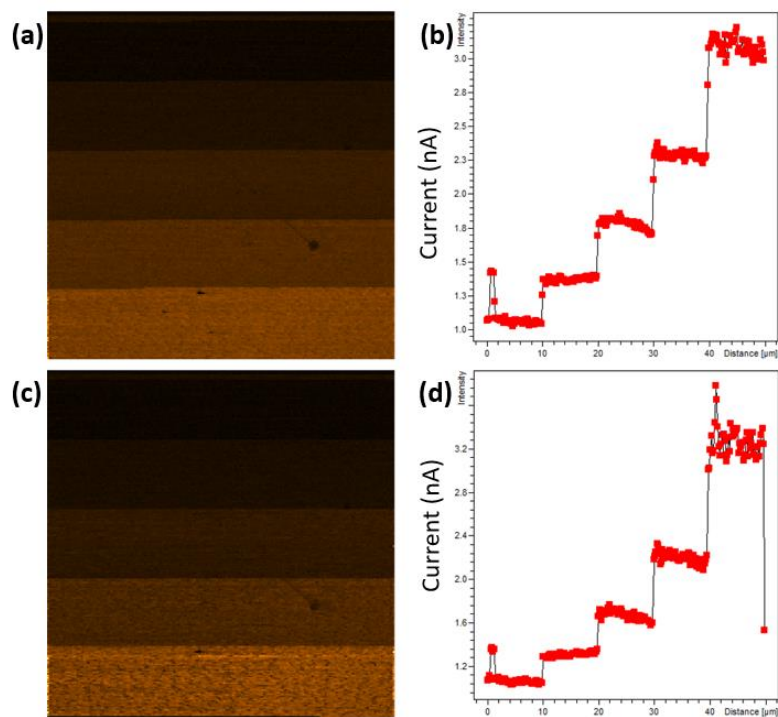


Figure 21. Current trace (a) and retrace (b) of the first 50 x 50 μm scan and the average current per line respectively (c and d). Correlates to **Figure 13**.

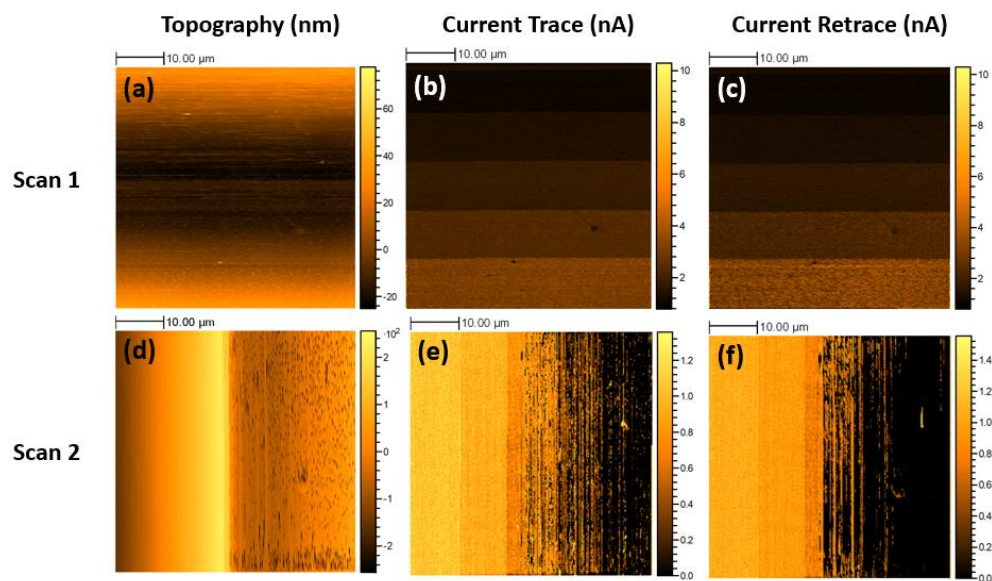


Figure 22. The topography, current trace and retrace for C-AFM scans 1 and 2. Correlates to **Figure 13**.

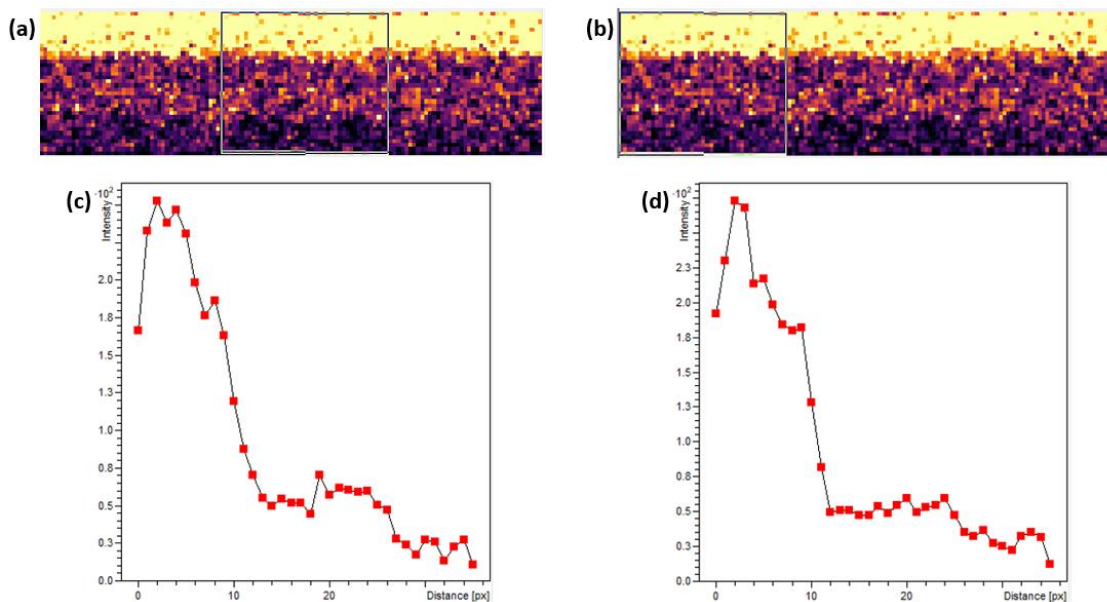


Figure 23. Shows YZ SIMS profiles of normalized oxygen counts from **Figure 13a** (**Figure 23a** and **Figure 23b**) and the corresponding area scans relative to the Y coordinate of the SIMS YZ profiles. (An increase in oxygen concentration correlating to the biased areas of: 0.5, 0.75 and 1V, can be seen in **Figure 23c**. This increase is not present in **Figure 23d** that correlates to pristine film as well as 0V and 0.25V regions)

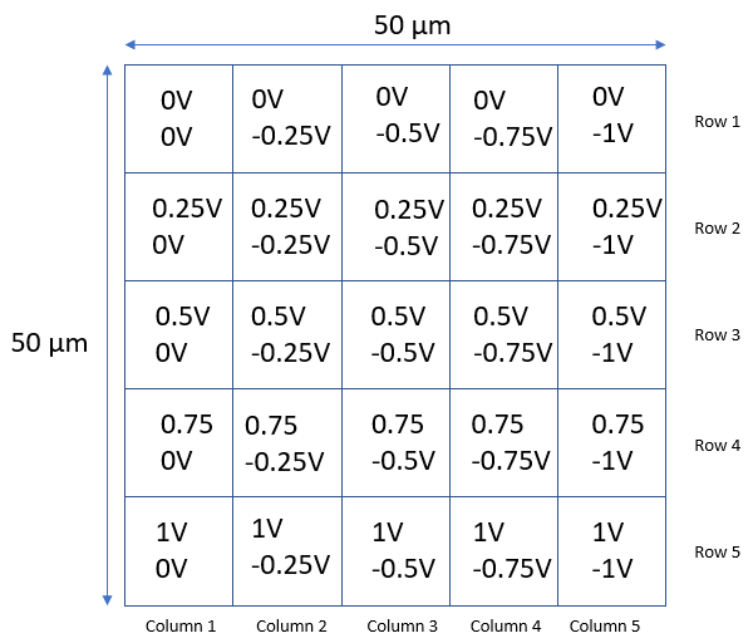


Figure 24. Bias pattern applied to the Ta₂O₅ surface by the AFM tip. The first value in each box is the voltage applied in the first scan, the second value in each box is the voltage applied during the second scan. Correlates to **Figure 13**.

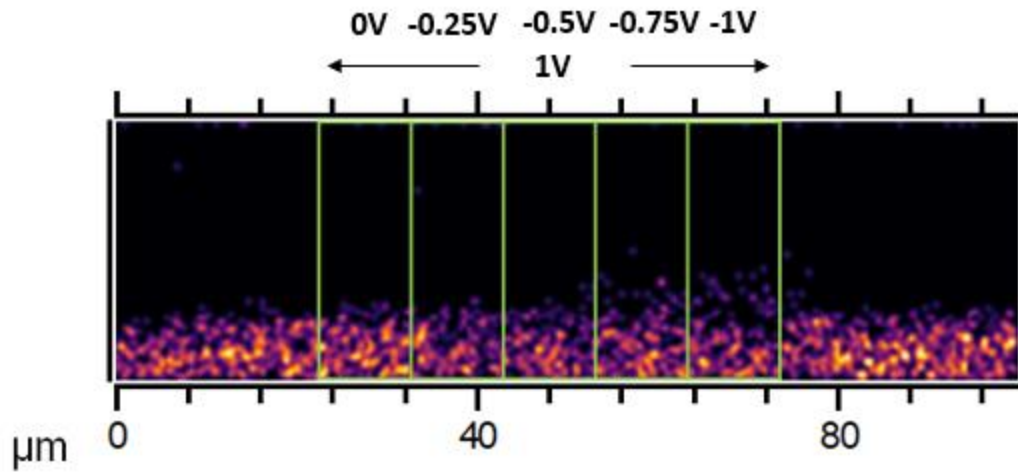


Figure 25. Shows TiO^+ XZ slice (corresponds to Row 1 in **Figure 24**). Breakdown occurs between -0.5 and -1 V but TiO^+ ion migration can be seen at -0.25V as well.

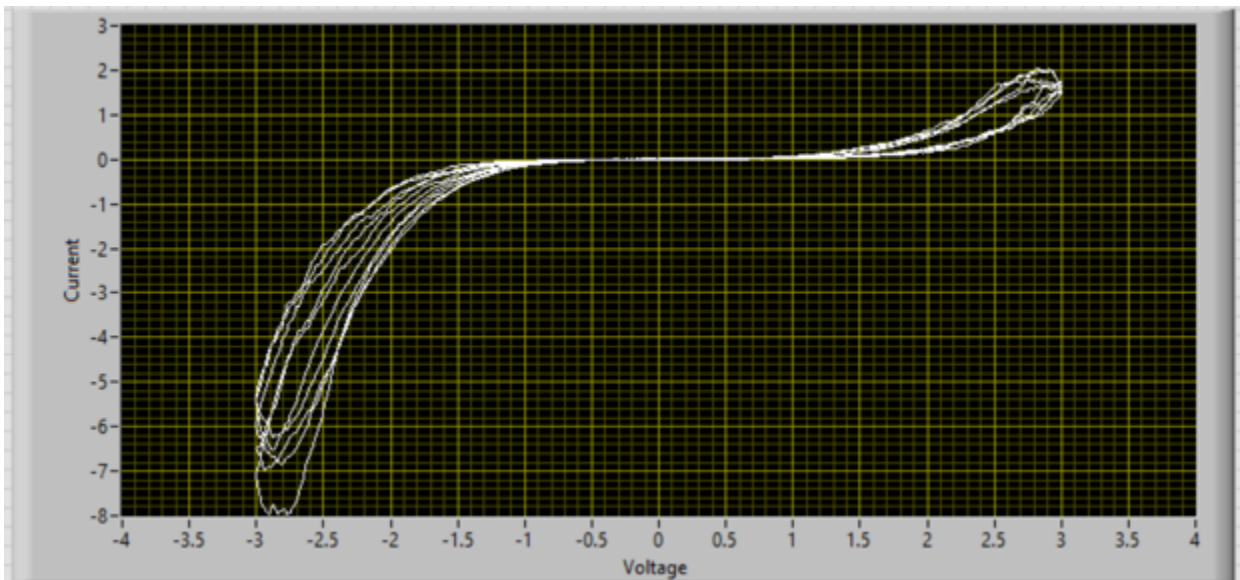


Figure 26. 5 consecutive IV sweeps in an oxygen cleaned area of the Ta_2O_5 film. The electric field was applied in 1 sec pulses at a rate of 1000 Hz. (Current in nA)

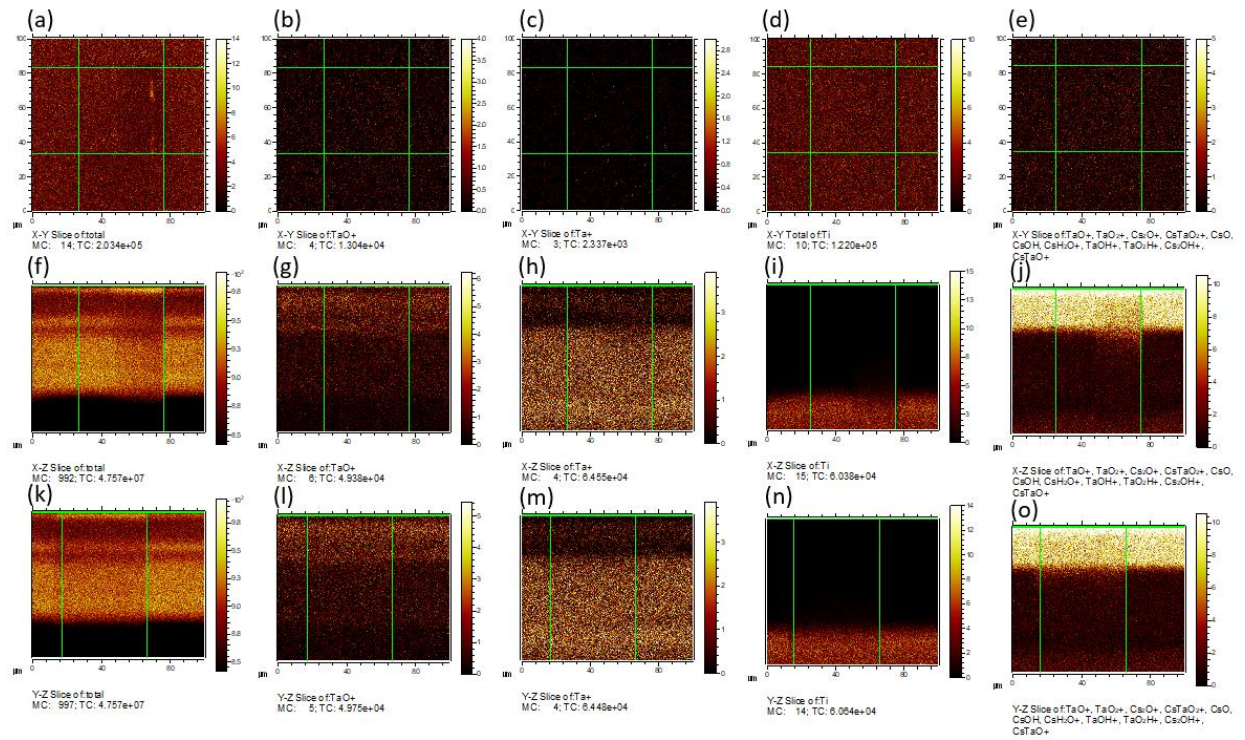


Figure 27. Depth profiles from the low voltage grid experiment (C-AFM/SIMS experiment 2)

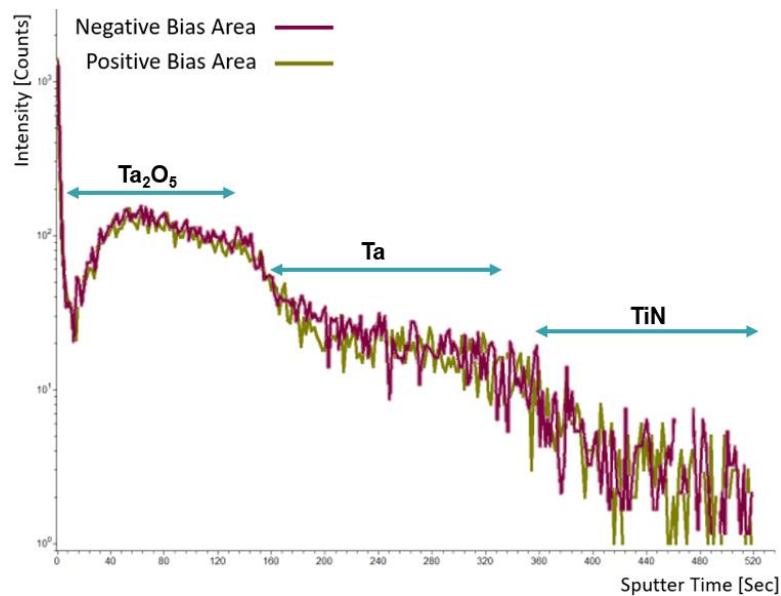


Figure 28. Shows the TaO^+ depth profile in the negative bias vs the positive bias area of film, poled at $\pm 4\text{V}$.

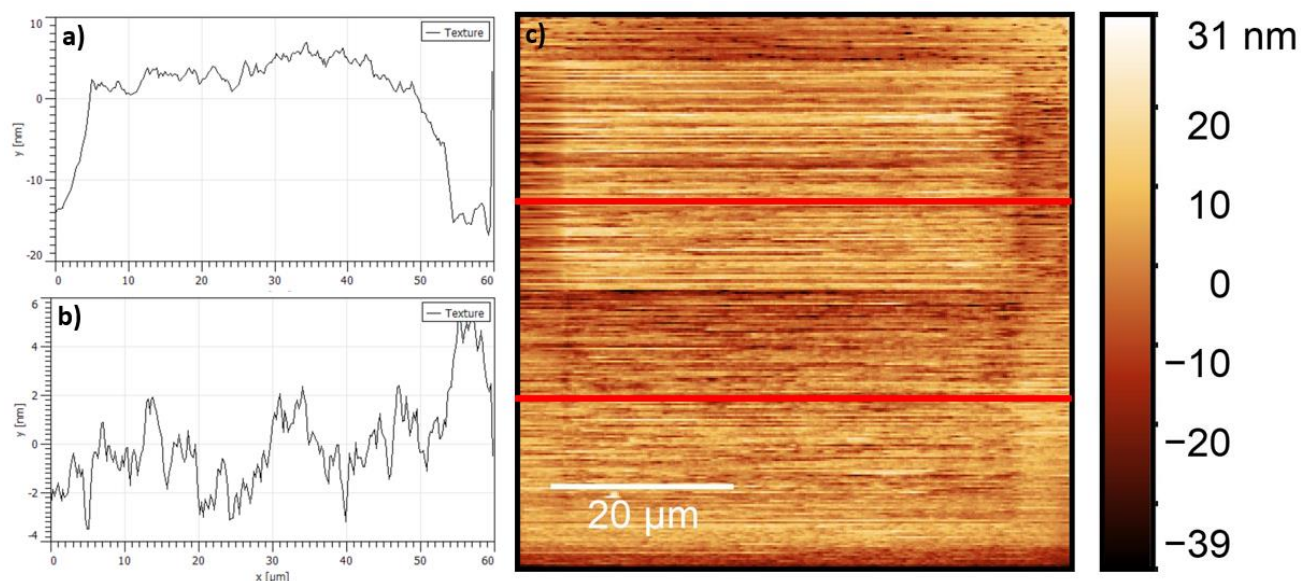


Figure 29. Shows 20 average topography line scans for the +4V region (a) and -4V region (b) taken from the 60μm pan out topography image. The topography image is the same data as the image in **Figure 14b**.

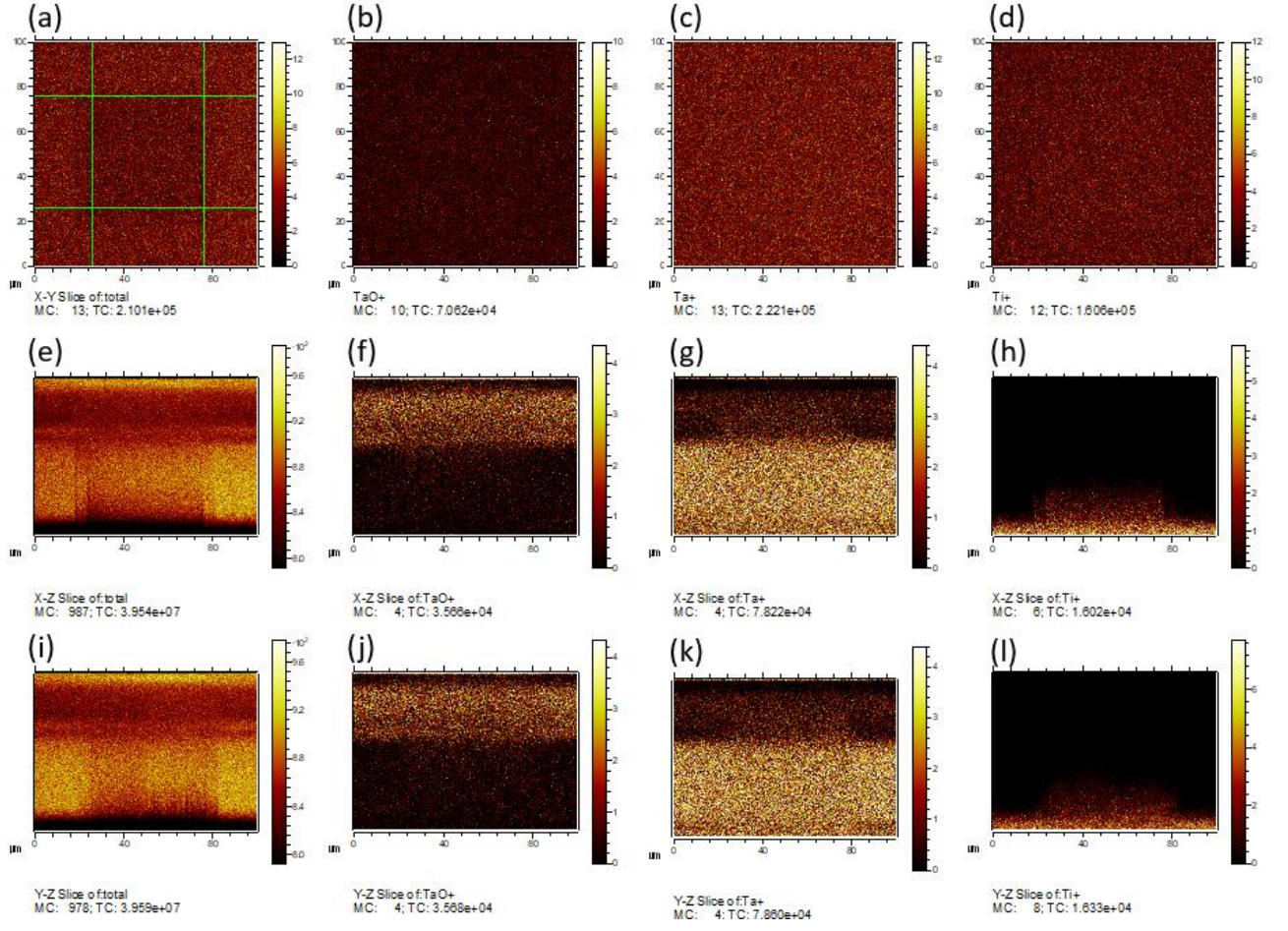


Figure 30. Ion count profiles of +/- 4V breakdown experiment. This correlates to the third C-AFM/ToF-SIMS experiment (**Figure 14** in main text).

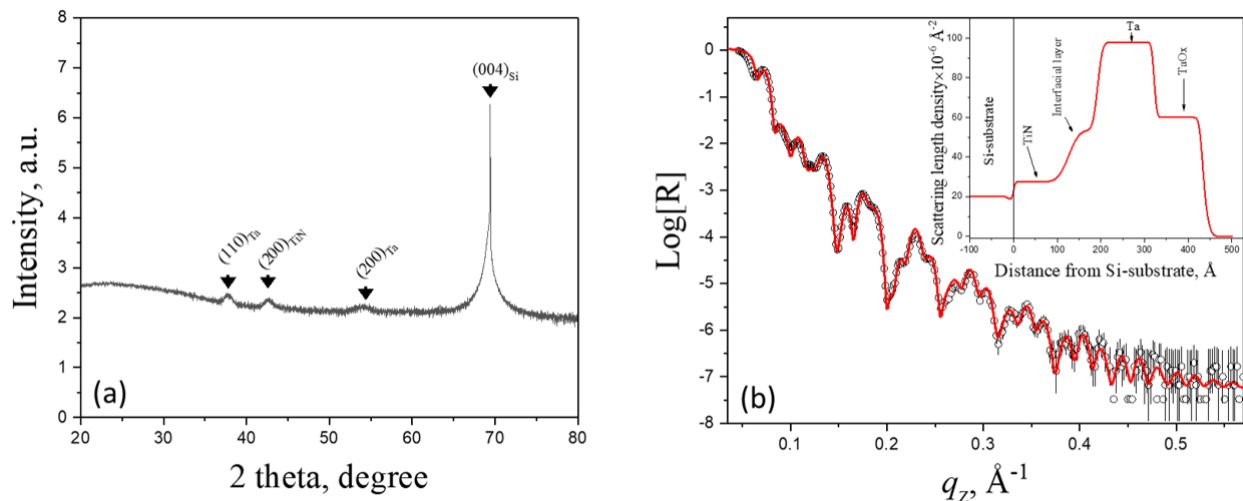


Figure 31. (a) θ - 2θ scan XRD and XRR patterns. XRD pattern indicates that the TaO_x layer is amorphous. The XRD pattern also indicates no crystalline reflection associated with Ta₂O₅ (TaO, TaO₂, Ta₂O₅), XRR (X-ray reflectivity) result in (b) shows the presence of multiple layers including top TaO_x layers, judging from both XRD and XRR, the Ta₂O₅/Ta bilayer is amorphous. The measure XRR curve (black circle) was fit (red curve) using the model in the inset in (b) based on the Parratt formalism.[1]

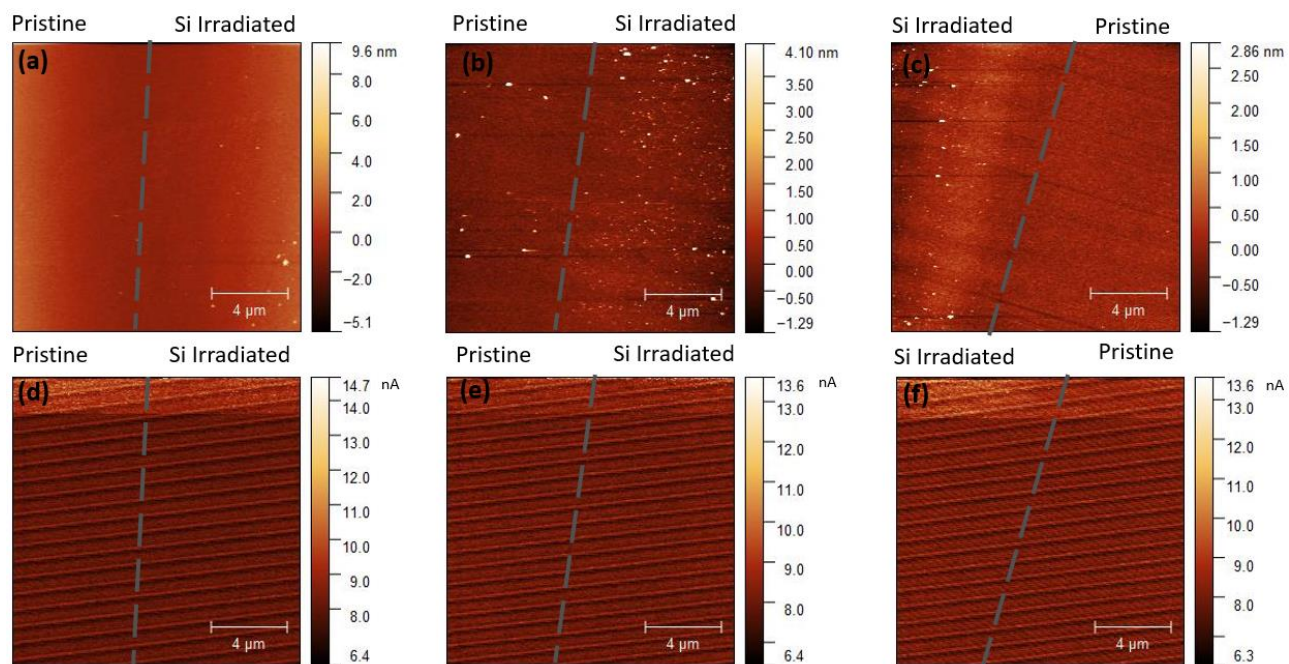


Figure 32. Shows topography (a-c) and corresponding current (d-f) of c-AFM scans. Correlates to **Figure 11**.

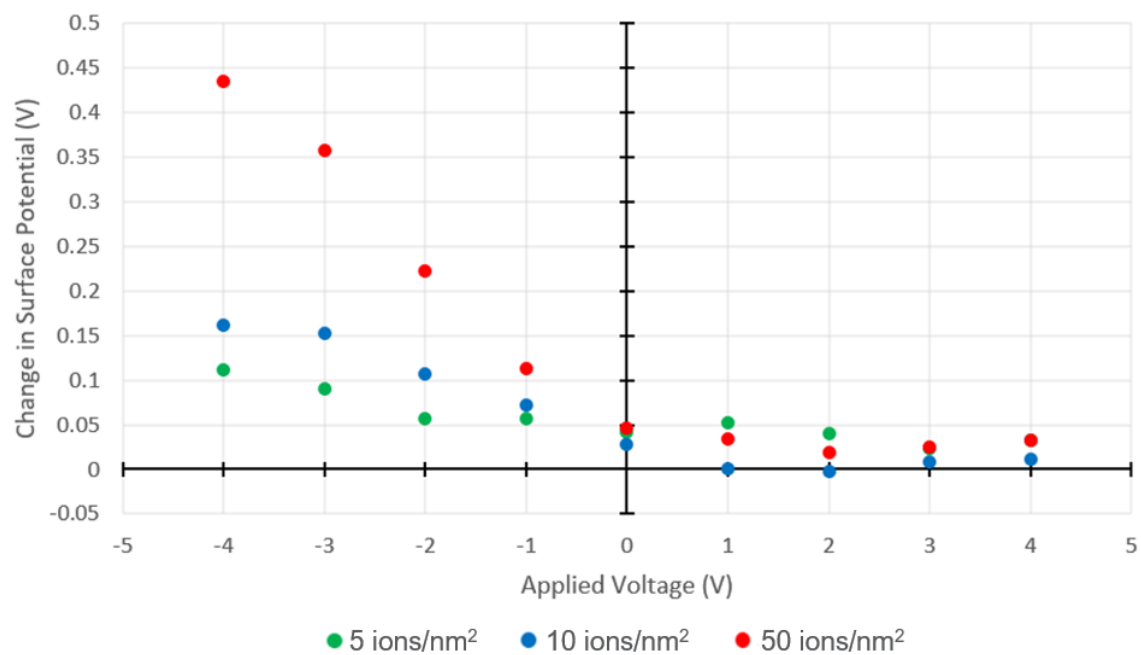


Figure 33. Change in CPD as a function of voltage applied to the surface. Areas where voltages were applied were averaged and normalized to the pristine region of the KPFM scan.

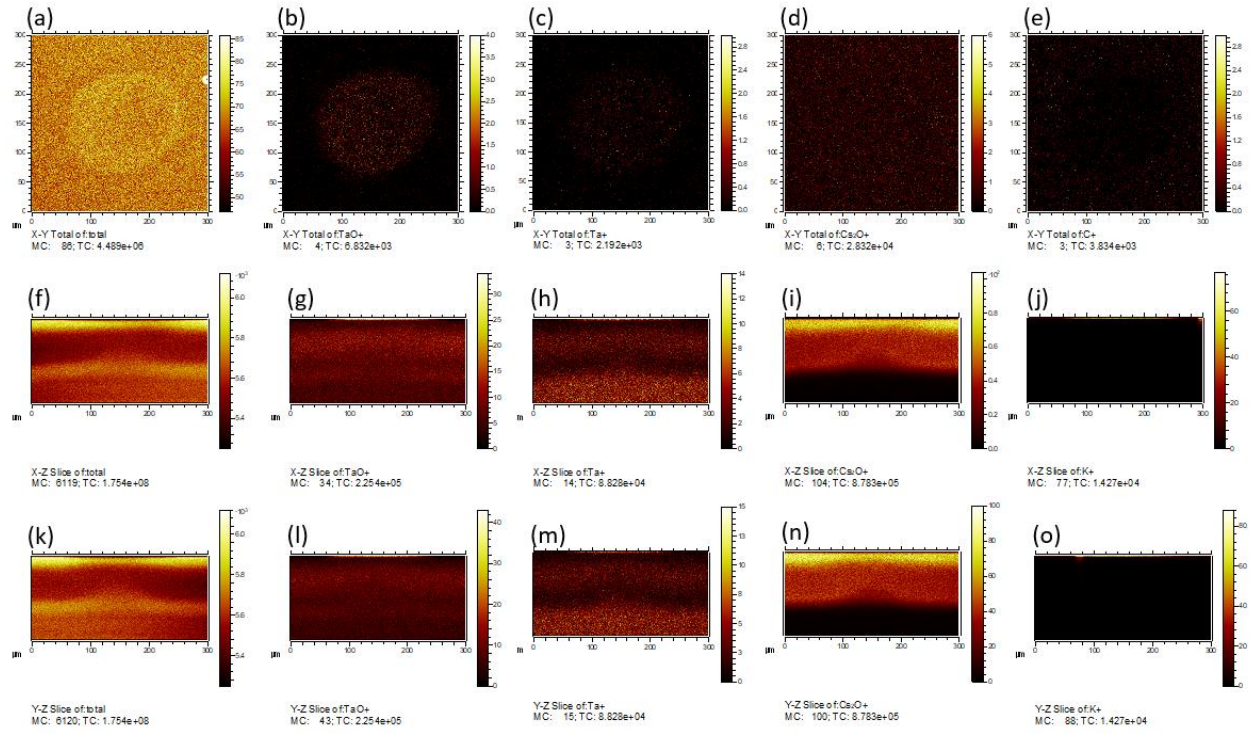


Figure 34. Shows X-Y, X-Z, and Y-Z slices of a ToF-SIMS depth profile of the Ta₂O₅/Ta film after sputtering a 50x50 μm area with a 1 keV oxygen sputter for 2 seconds. This is a comparable oxygen dose to what was used in the C-AFM/SIMS experiments (500um for 20 seconds).

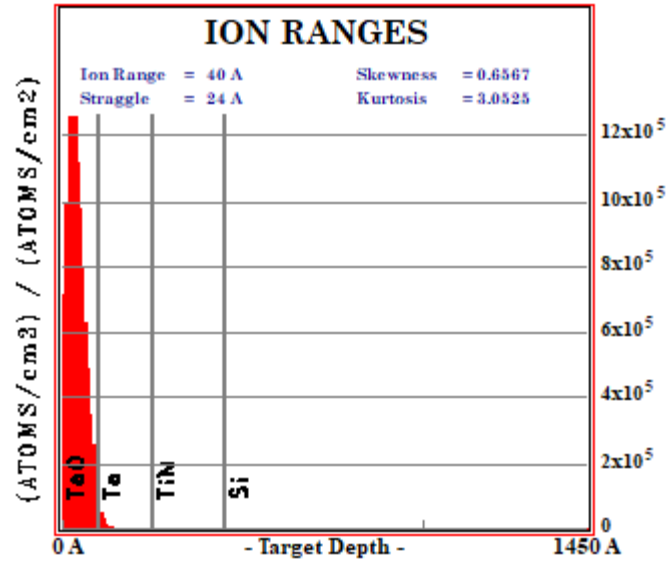


Figure 35. SRIM calculation of penetration depth for oxygen at 1Kev hitting a 10nm Ta₂O₅/15nm Ta/20nm TiN/100nm Si target. Thickness values were approximated from the XRR data shown in **Figure 31**. Densities of 8.2, 16.65, 5.4, and 2.329 g/cc were used for Ta₂O₅, Ta, TiN and Si, layers respectively

Reference

[1] L. G. Parratt *Phys. Rev.* **1954** 95 359

CHAPTER II

ELECTRICAL BEHAVIOR OF COMBINATORIAL THIN-FILM $ZR_xTA_{1-x}O_y$

Electrical Behavior of Combinatorial Thin-Film $\text{Zr}_x\text{Ta}_{1-x}\text{O}_y$

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Author Contributions

This work was originally published in Nanomaterials. Matthew Flynn-Hepford was the lead writer and experimentalist for this work. Matthew conducted the device fabrication, electrical characterization, XRD and ToF-SIMS experiments. Reece Emery did the XRR experiments. Steven Ranolph and Scott Retterer supervised device fabrication and assisted with editing. Gyula Eres did the XPS experiments. Bobby Sumpter did the molecular dynamics simulations and assisted on editing. Anton Ievlev supervised the ToF-SIMS experiments. Olga Ovchinnikova assisted on editing and funding acquisition.

Philip Rack acted as the primary editor, supervisor and was responsible for the project ideation.

Abstract

Combinatorial magnetron sputtering and electrical characterization were used to systematically study the impact of compositional changes in the resistive switching of transition metal oxides, specifically the $Zr_xTa_{1-x}O_y$ system. Current-voltage behavior across a range of temperatures provided insights into the mechanisms that contribute to differences in the electrical conductivity of the pristine Ta_2O_5 and ZrO_2 , and mixed $Zr_xTa_{1-x}O_y$ devices. The underlying conductive mechanism was found to be a mixture of charge trapping and ionic motion, where charge trapping/emission dictated the short-term cycling behavior while ion motion contributed to changes in the conduction with increased cycling number. ToF-SIMS was used to identify the origin of the “wake-up” behavior of the devices, revealing an ionic motion contribution. This understanding of how cation concentration affects conduction in mixed valence systems helps provide a foundation for a new approach toward manipulating resistive switching in these active layer materials.

Introduction

Amorphous oxides (TaO_x , ZrO_x) [1–5] and bulk phase change materials (VO_2/V_2O_5) [6] are showing tremendous potential as active layer materials for resistive random-access memory (ReRAM) materials. These oxides are compatible with existing complementary metal oxide semiconductor (CMOS) fabrication methods and have unique functional properties, such as the ability for in-memory analog computations, that could allow them to complement or replace conventional CMOS-based devices. For example, Ta_2O_5 has

shown subnanosecond switching [7], low switching voltage (~ 1 V), long state retention (>10 years), and high switching endurance ($>10^{10}$ cycles) [2]. Arrays of Pd/TaO_x/Ta/Pd cross bar devices have demonstrated complex computational tasks with improved energy efficiency and throughput compared to digital systems [8]. The resistive switching mechanisms in these materials are driven by oxygen migration and typically requires an initial electroforming step, wherein the film is switched from a high- resistance to a low-resistance state. This electroforming step is not fully understood and has not been thoroughly replicated in computational models [9], and is not always required for stable resistive switching [10]. However, it is generally considered important for initiating the onset of oxygen motion in highly insulating oxide films. This oxygen motion can be driven both in and out of the plane of the TaO_x layer, where the mechanism and the resulting resistive switching IV characteristics were shown by Lee et al. [2]. This mechanism shows a local movement of oxygen from the Ta₂O_{5-x} layer into a TaO_{2-x} layer, forming metallic filaments through the Ta₂O_{5-x} layer and a buildup of oxygen at the Ta₂O_{5-x}/TaO_{2-x} interface [2]. This process can be seen in the IV characteristics of the material and is typically seen as a sharp increase in current at the set voltage (V_{set}) where the metallic filaments are formed. Lee et al. subsequently demonstrated the effect that the active layers [2] and electrode materials have on the device characteristics [3]. In situ transmission electron microscopy (TEM) was used to image the oxygen motion in the active layers and showed that, by decreasing the inter-face roughness between the top electrode and the Ta₂O_{5-x} layer, the device behavior transitions from being dominated by

filament formation to behavior that is dictated by the buildup of interfacial oxygen [3]. This suggests that rough interfaces can enable localization of the electric field and drive filament formation. The effects of silicon doping of TaO_x was studied by Kim et. al., [11] where the doped devices showed higher on/off ratios, suggesting a larger depletion gap between the filament and electrode. This larger depletion gap was attributed to a higher oxygen mobility in the Si-doped tantalum oxide compared to the undoped oxide. This increase in oxygen motion was rationalized by the induction of oxygen mobility channels generated by stronger bonding in the Si-O bond relative to Ta-O.

Ta:ZrO systems, deposited by atomic layer deposition (ALD), have also been investigated by Kukli et al. [12], finding that the chemistry with a low zirconium concentration (Zr:Ta atomic ratio of 0.2) exhibited the largest hysteresis and most consistent switching. This chemistry showed the highest crystallization temperature (800 °C) forming a δ - Ta_2O_5 phase. Crystallization eliminated all hysteretic behavior for each chemistry studied, suggesting that the mechanism for resistive switching in these $\text{Zr}_x\text{Ta}_{1-x}\text{O}_y$ chemistries requires vacancy- driven ion movement, which requires less energy in amorphous systems. Kukli et al. [12] showed that hysteresis is dependent on the Zr:Ta ratio and that this hysteresis re-quires an amorphous structure, suggesting that modulating the Zr:Ta ratio has an effect on the vacancy concentration of the oxide layer.

Combinatorial synthesis of $\text{Y:Zr}_x\text{Ta}_{1-x}\text{O}_y$ by pulsed laser deposition (PLD) was conducted by Kiyota et al. [13]. The system consisted of a consistent 10 atomic % YO_x and a compositional gradient of Ta and Zr. A minimum in the dielectric constant (k) of 18 was

found at 30% ZrO_2 and then steadily increased to 22 with increasing Ta_2O_5 . However, the leakage current also steadily increased with increasing Ta_2O_5 . Zrinski et al. [14] investigated a combinatorial system of $\text{Ta}_x\text{Hf}_{1-x}\text{O}_y$ deposited by magnetron sputtering and a subsequent wet electrochemical anodization process to oxidize the topmost 20 nm of the film. Current-voltage measurements revealed that the high-Hf concentration zone exhibited poor resistive switching behavior, while the low-Hf zone did not show any improvements compared to Ta_2O_5 . Ratios between 50 and 70 atomic % Hf showed on/off ratios of 8 eight orders of magnitude with device endurance reaching one million cycles. This region exhibited unipolar switching compared to the high and low Hf regions, which exhibited bi-polar switching. This unipolar switching was driven by HfO_2 crystallites present in the otherwise amorphous oxide.

Doolittle et al. observed resistive switching that was attributed to charge trapping in defect states in $\text{Nb}_2\text{O}_{5-x}$ films [15]. These $\text{Nb}_2\text{O}_{5-x}$ devices generated current-voltage hysteresis at low frequencies by increasing voltage over the onset voltage needed to transition from Schottky emission to tunneling transport through the highly charged interface layer of the film. This topmost layer causes the turn on voltage to be dictated by the Schottky barrier height. Beyond the turn-on voltage, the devices transition to a Fowler–Nordheim (FN) tunneling/Poole–Frenkel (PF) mechanism that dictates the hysteretic behavior. Kim et al. also produced charge trapping- based $\text{Nb}_2\text{O}_{5-x}$ memristors, but in order to stabilize the high and low- resistance states, Ta_2O_5 and $\text{Al}_2\text{O}_{3-y}$ capping layers were inserted between the $\text{Nb}_2\text{O}_{5-x}$ active layer and Pt and Ti electrodes,

respectively [16]. The Ta_2O_5 layer pre-vented the discharge of energized trap states in the active layer to the Pt electrode, stabilizing the low- resistance state (LRS). The $\text{Al}_2\text{O}_{3-y}$ layer prevented charge migration from the Ti electrode to empty trap states in the active layer, thus stabilizing the high- resistance state (HRS). Similarly, electroforming-free hysteretic current-voltage behavior was shown by Yoon et al. [17] using a Pt/ Ta_2O_5 / HfO_{2-x} /TiN device stack that employed ALD to deposit the Ta_2O_5 and HfO_{2-x} active layers.

Reservoir computing (RC) has emerged as a powerful and energy-efficient paradigm for processing time-dependent information by utilizing the dynamics of nonlinear electrical systems. Unlike traditional recurrent neural networks, RC fixes the internal reservoir weights and trains only the output layer, greatly simplifying the training process while maintaining high computational capability for tasks such as pattern recognition, classification, and temporal prediction. Recent advances have demonstrated that volatile memristive devices are excellent candidates for physical reservoir computing because of their intrinsic short-term memory behavior and nonlinear, history-dependent conductance modulation. Ju et al. implemented an 8-bit reservoir computing system using volatile ITO/ZrOx/TaN memristors, exploiting gradual interface-type resistive switching and current decay phenomena to achieve high-dimensional temporal mapping and efficient multi-level data storage [18]. A similar approach has also been reported using Pt/BFO/SRO/STO ferroelectric devices [19], highlighting the critical role of volatile

resistive switching in constructing scalable, energy-efficient, and neuromorphic-compatible reservoir architectures.

This work leverages combinatorial thin-film sputtering to rapidly explore the ReRAM properties of mixed valence transition metal oxide active layers, where co-sputtering Ta and Zr metal targets in an Ar-O₂ ambient generates a compositional gradient of mixed oxidation states. Chemical composition and valence state were correlated to local current-voltage measurements via X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to elucidate the resistive switching mechanisms operative in the Zr_xTa_{1-x}O_y system.

Materials and Methods

Plane-wave density functional theory (DFT) calculations were carried out using Vienna Ab initio Simulation Package (VASP), version 6.5, and the projector-augmented wave (PAW) pseudopotentials for electron-ion interactions [20]. Exchange–correlation interactions were accounted for using the generalized gradient approximation (GGA) functional of Perdew–Burke–Ernzerhof (PBE) [21]. A previous model was used for amorphous tantalum oxide. That model was based on a super cell of crystalline Ta₂O₅, containing 168 atoms (Ta₄₈O₁₂₀ [22,23]) with optimized lattice constants of $x = 14.635 \text{ \AA}$, $y = 12.377 \text{ \AA}$, and $z = 11.761 \text{ \AA}$. During structural optimization, the atoms and cell volume re-laxed until the residual forces fell below $0.02 \text{ eV/\AA}$, with a cutoff energy of 520 eV and Gamma-point k-point sampling. To generate an amorphous structure, ab-initio molecular dynamics (AIMD) simulations were used in a melt-and-quench

approach. This model and its' oxygen vacancy derivatives has shown very good agreement with experimental cathode luminescence (CL), electron energy loss spectroscopy (EELS), and scanning microwave impedance microscopy (SMIM) [24]. In this study, starting with amorphous $\text{Ta}_{48}\text{O}_{119}$, AIMD was run using a Nose–Hoover thermostat at room temperature and used the mean square displacement (MSD) of O via Einstein's relation to find the respective diffusion coefficients. Following this simulation protocol, Zr was doped into the model following $\text{Zr}_x\text{Ta}_{1-x}\text{O}_y$; with $x = 5, 15, 20$ which corresponds to 10%, 31%, and 42% Zr doping. The largest MSD for oxygen and subsequently the highest diffusion coefficient was found to occur at a doping level of 31% Zr (see supplemental **Figure 43**).

A 5 nm Ti adhesion layer was deposited using DC magnetron sputtering onto a thermally grown SiO_2 (500 nm) coated silicon substrate. The bottom 40 nm Pt electrode was subsequently deposited on the Ti adhesion layer via magnetron sputtering. $\text{Ta}(20 \text{ nm})/\text{Zr}_x\text{Ta}_{1-x}\text{O}_y(10\text{--}15 \text{ nm})$ active layers were deposited on top of the Pt(40 nm) bottom electrode. The metallic Ta layer was deposited with an applied power of 100 W DC for 1 min 50 s with substrate rotation on to realize a uniform film thickness. The combinatorial $\text{Zr}_x\text{Ta}_{1-x}\text{O}_y$ layer was deposited with an applied power of 38 W DC on the Ta target and 100 W DC on the Zr target with a 25/5.2 sccm Ar/O_2 flow rate ratio and 5 mTorr pressure for 5 min and 50 s with the substrate stationary to realize the combinatorial gradient. X-ray reflectometry (XRR) was used to measure the center thickness of the deposited layers (see supplemental **Figure 44**) and energy dispersive spectroscopy (EDS) was used to

verify the composition gradient of the film across the 100 mm substrate. Grazing incidence X-ray diffraction (GIXRD) was used to confirm the amorphous structure of the film (see supplementary **Figure 45**). A PANalytical X'Pert Pro MRD equipped with a proportional Xenon counter was used for the XRR measurement and GIXRD, while a Zeiss Merlin SEM was used for the EDS measurement. XPS was also used to measure the composition and elucidate the bonding/valence characteristics in the films as the cation ratio varies across the sample. Films with pure Ta₂O₅ and ZrO₂ were also fabricated using the same parameters but with substrate rotation on to reduce thickness gradients.

Then, 100 mm diameter, 40 nm thick top Pt electrode pads were DC magnetron sputter-deposited via a photolithographically patterned lift-off process. Electrical cycling measurements were performed by biasing the Pt top electrodes with a Keithley 2400 source measure unit (SMU) while the continuous bottom Pt electrode was grounded. The electrical measurements were conducted along the Zr_xTa_{1-x}O_y composition gradient at various electrode positions representative of various stoichiometries. Each DC electrical cycle had a constant 1 min cycle time and consisted of 400 voltage increments where the voltage increment varied based on the voltage range studied. The leakage current behavior over time was measured using a Keithley 4200A-SCS parameter analyzer, manufactured by Tektronix (Beaverton, OR, USA). All electrical measurements utilized a Form Factor Cascade CM300xi probe station. A diagram of the film stack along with the corresponding band diagram is illustrated in **Figure 36**. Also shown in **Figure 36** is the

estimated cation composition gradient and thickness across the 100 mm diameter substrate.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) system, ToF.SIMS 5 by iONTOF (Münster, Germany), was used to profile pristine and cycled devices. An alternating sputter of Cs^{++} and Bi^{3++} was used to profile and image the device. A 1 keV Cs^{++} ion beam was rastered in a $500 \times 500 \mu\text{m}^2$ area to form a sputtered crater for 20 frames. Four frames of a 30 keV Bi^{3++} ion beam were used to raster a $100 \times 100 \mu\text{m}^2$ area. An electron flood gun was used to mitigate charging during profiling. **Figures 46a,c,e,f** shows an images of the CsPt^+ ion count in order to show the relative position of the device centered in the ion beam raster. **Figures 46b,d,f,h** show the areas of interest that was were used for the depth profiles to isolate ions from the device and exclude ions from the native film in the corners of the $100 \times 100 \mu\text{m}^2$ scan.

Results and Discussion

The device film stack geometry can be found below in **Figure 36a**, alongside the theoretical band diagram (**Figure 36b**). The band diagram of the film stack illustrates the large barrier to charge injection from the top Pt electrode as compared to injection from the bottom Pt/Ta electrode. The predicted cation concentration (**Figure 36c**) and thickness (**Figure 36d**) of the memristive oxide layers were simulated across the wafer; many of the parameters that are relevant for the sputtering system were experimentally determined in the previous work [25].

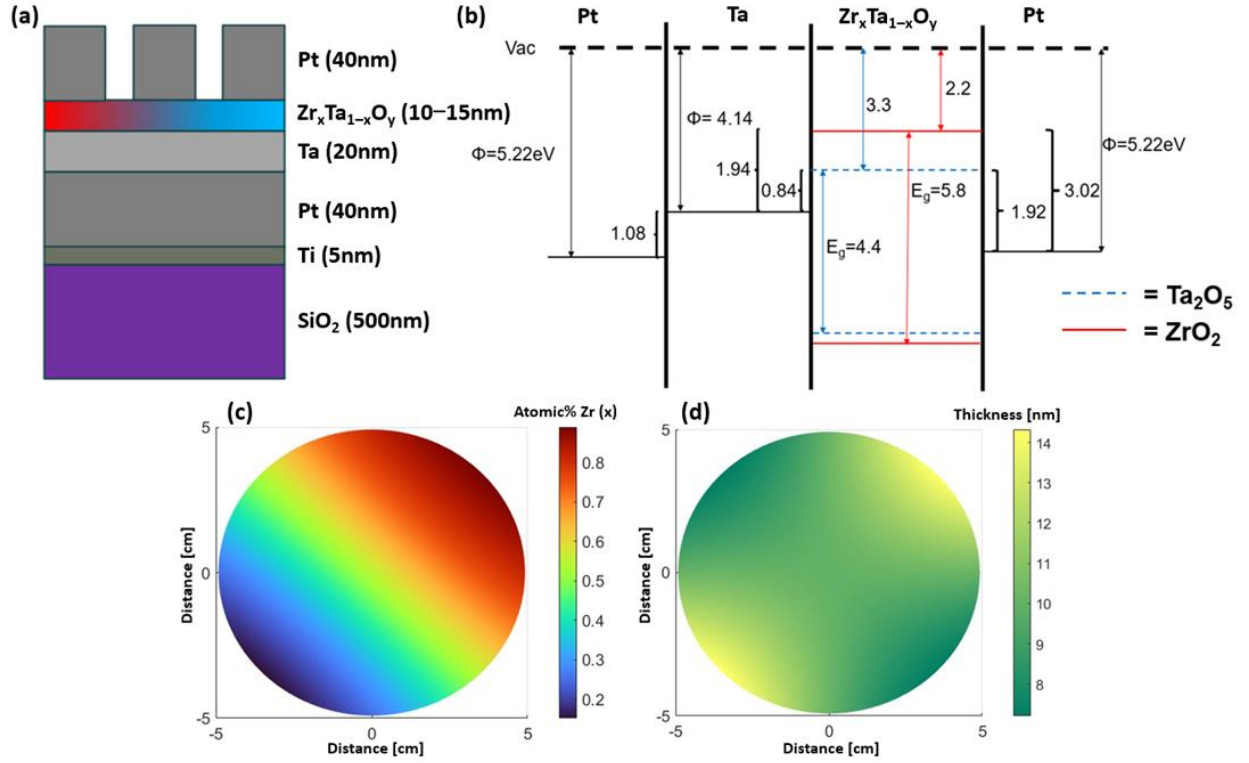


Figure 36. Schematic of the (a) thin film stack and (b) the expected band diagram of the devices. Schematic of (c) simulated cation atomic % Zr (note that atomic % Ta is 1–atomic % Zr), and (d) thickness of the combinatorial $Zr_xTa_{1-x}O_y$ layer. The ZrO_2 bandgap was taken from Li et al. [26], Ta_2O_5 bandgap from Zhuo et al. [27], while Pt and Ta work functions were taken from Mechtly [28].

Figure 44 shows a XRR thickness as a measurement at the center of the combinatorial wafer, while **Figure 47** compares the measured (EDS) and simulated [25] Ta and Zr cation atomic % percentage measured along the centerline of the substrate, which are in good agreement. For the results presented below, the cation compositions were estimated from the simulated sputtering model. Calculated mean square displacement (MSD) values were determined at various Ta/Zr ratios and showed an increase in oxygen mobility around 30% Zr. The MSD plot of oxygen for three different Zr doping concentrations is shown in **Figure 43**.

Figures 37a–d are XPS spectra for the Ta 4f (and Zr 4p), Ta 3d, O 1s, and the valence band energy regions, respectively. As can be observed, all of the spectra shift to lower binding energy with increasing Zr content. The shifts in the Ta, Zr, and O core levels (b–d) are consistent with observations of Tewg et al. that were attributed to charge transfer mechanisms affecting all three elements in the film [29]. Namely, as Zr concentration is increased, the positive charge of the cation Ta and Zr decreases and the negative anion charge on the oxygen increases. As noted in the Ta 4f spectra, the Ta^{4+} peak increases with increasing Zr, which affirms the decrease in the overall charge on the Ta cations. Interestingly, the valence band also shifts to lower binding energy with increasing Zr content, which is not consistent with the band diagram pictured in **Figure 36**.

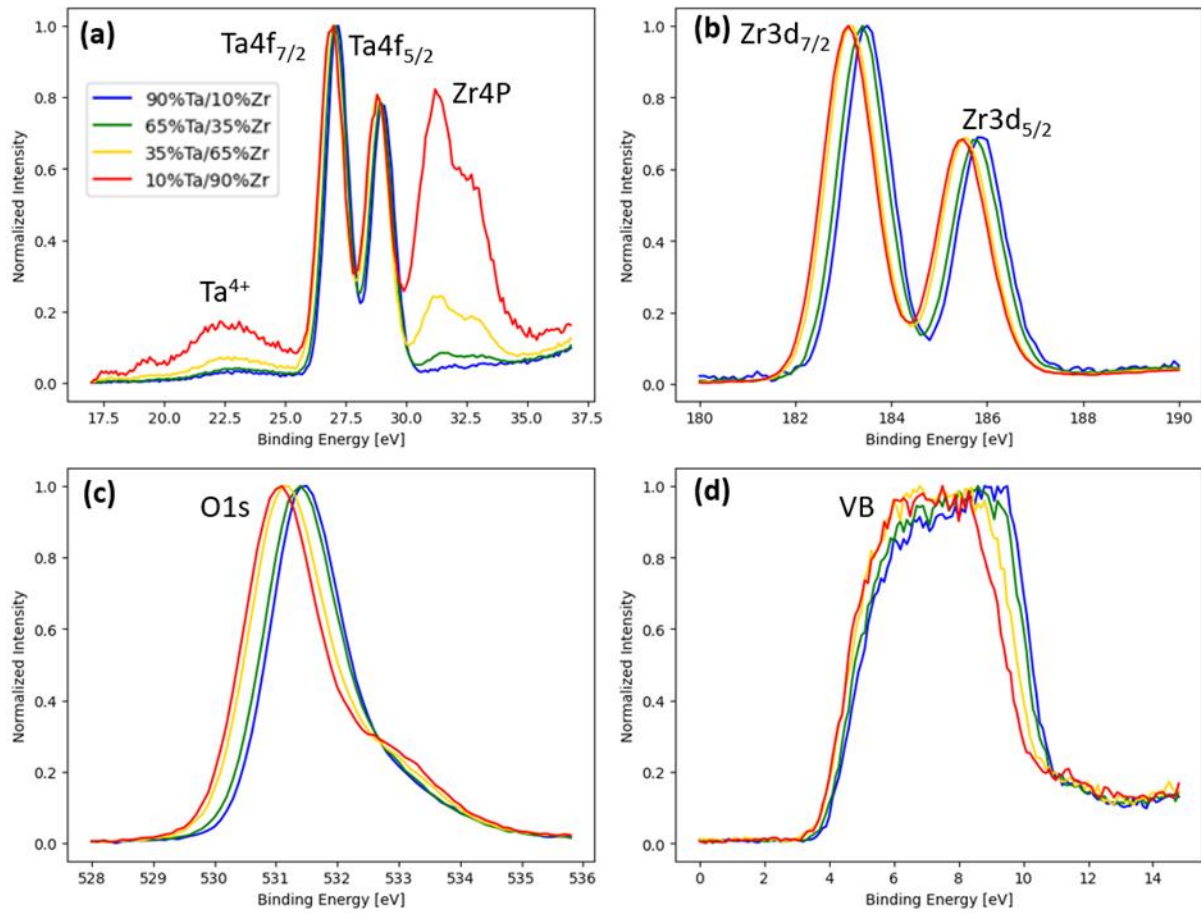


Figure 37. Comparison of normalized binding energy for (a) the Ta 4f peaks, (b) the Zr 3d peaks, (c) the O 1s peak, and (d) valence band across the combinatorial $Zr_xTa_{1-x}O_y$ film.

This suggests that perhaps the electron affinity of the Ta_2O_5 is slightly larger or the ZrO_2 is slightly smaller than the diagram suggests; in either case, the conduction band barrier height difference between the ZrO_2 and Ta_2O_5 would be larger than the 1.1 eV represented in **Figure 36**.

Figure 38a,b illustrate the current density-electric field measurements of the pure Ta_2O_5 devices, which revealed a “wake-up” behavior of about five cycles at ± 0.2 V/nm. After these wakeup cycles, cycles 6–25 showed consistent resistive switching where the devices switch from the HRS to the LRS upon the forward and reverse positive voltage cycle. The post wake-up behavior of both devices shows a distinct turn-on voltage. Arrangement of the probes indicates that the positive voltage cycle is due to electron injection from the Ta interlayer bottom electrode of the device, which is consistent with the lower work function and barrier height for the Ta/ Ta_2O_5 interface. The negative voltage sweep for injection from the Pt/ Ta_2O_5 top electrode has a much higher barrier height and consequently higher turn-on field and, thus, rectifying behavior. In contrast to the Ta_2O_5 devices, **Figure 38c,d** show that the pure ZrO_2 devices exhibit a longer wake up period of about 15 cycles, after which, the ZrO_2 devices also exhibit resistive switching from HRS to LRS. Plots showing cycles 6–10, 11–15, 16–20, and 21–25 for a pristine ZrO_2 device can be seen in **Figure 48**. During the initial cycling, the ZrO_2 devices exhibit switching from an LRS to an HRS, before slowly transitioning to high-to-low resistance state switching.

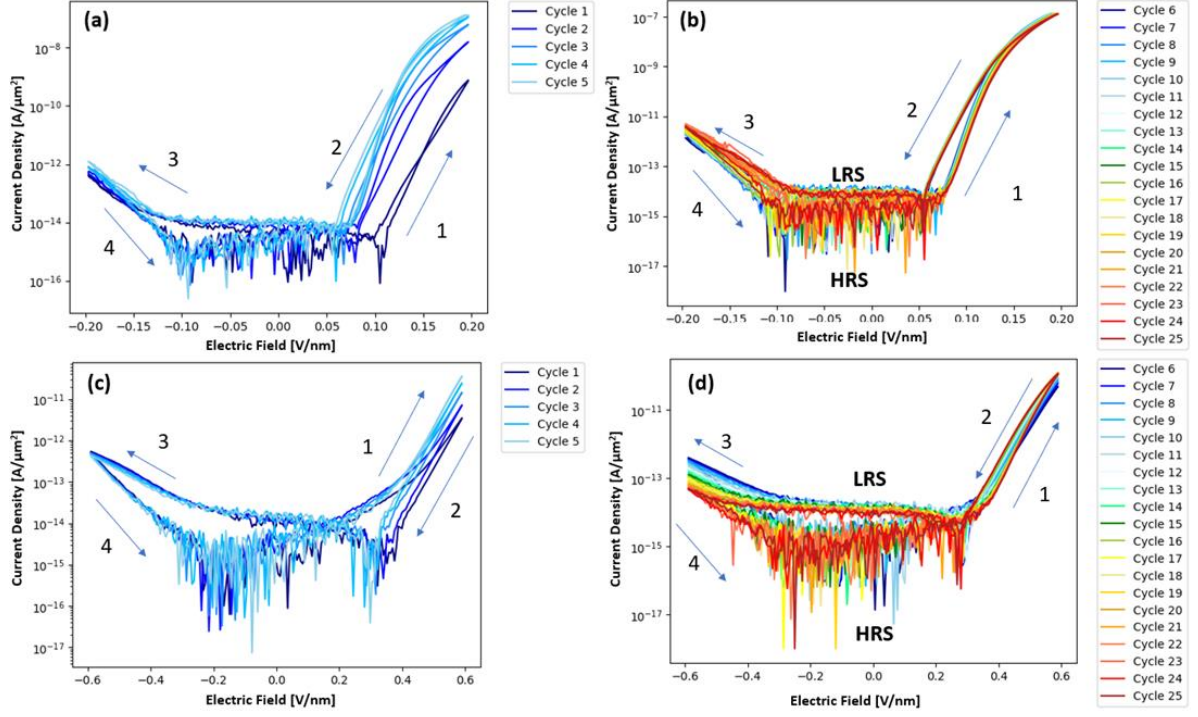


Figure 38. Current density vs. electric field characteristics of a Pt/Ta/Ta₂O₅/Ta device for (a) first 5 cycles and (b) cycles 6–25. Current density -electric field behavior of Pt/Ta/ZrO₂/Pt device for (c) the first 5 cycles illustrating the wake-up cycles, and (d) cycled 6–25 where smaller shifts are observed. HRS and LRS signify the low-resistance state and high-resistance state, respectively. Note that the arrows in the figures show the order of the cycling.

This transition from LRS/HRS switching to HRS/LRS switching is attributed to a shift from charge capture-controlled PF conduction, where charge capture rate is above the charge emission rate, to emission-controlled PF conduction. This shift is caused by a decrease in trap depth with increased cycling, effectively increasing the charge emission rate. The ZrO_2 devices also show decreasing current (higher resistance) during subsequent negative sweeps and this negative polarity switching did not saturate up to 25 sweeps. When measuring $\text{Zr}_x\text{Ta}_{1-x}\text{O}_y$ combinatorial devices, the wakeup period is not as pronounced compared to the pure Ta_2O_5 or ZrO_2 devices. The current density versus electric field for $\text{Zr}_x\text{Ta}_{1-x}\text{O}_y$ is plotted as a function of the composition (normalized by the thickness gradient from **Figure 36d**) in **Figure 39a,b** for cycle 1 and 5, respectively, where a composition range of $0.133 < x < 0.878$ was measured. The turn-on field was defined as the field where the current begins to increase above the low voltage noise. **Figure 39c** shows the expected trend, that the turn-on field increases linearly with the theoretical bandgap. The theoretical bandgap was calculated assuming the bandgap scales linearly with Zr content. **Figure 39d** shows that the hysteresis increases up to about 30% Zr then steadily decreases with increasing Zr. This maximum hysteresis at 30% Zr matches the concentration (30% Zr) found by Kiyota et al. to have the minimum dielectric constant in a $\text{Y:Zr}_x\text{Ta}_{1-x}\text{O}_y$ system [13]. This maximum hysteresis concentration is also closest to the concentration (Zr:Ta atomic ratio of 0.2) found by Kukli et al. [12] to have the largest hysteresis and most consistent switching behavior.

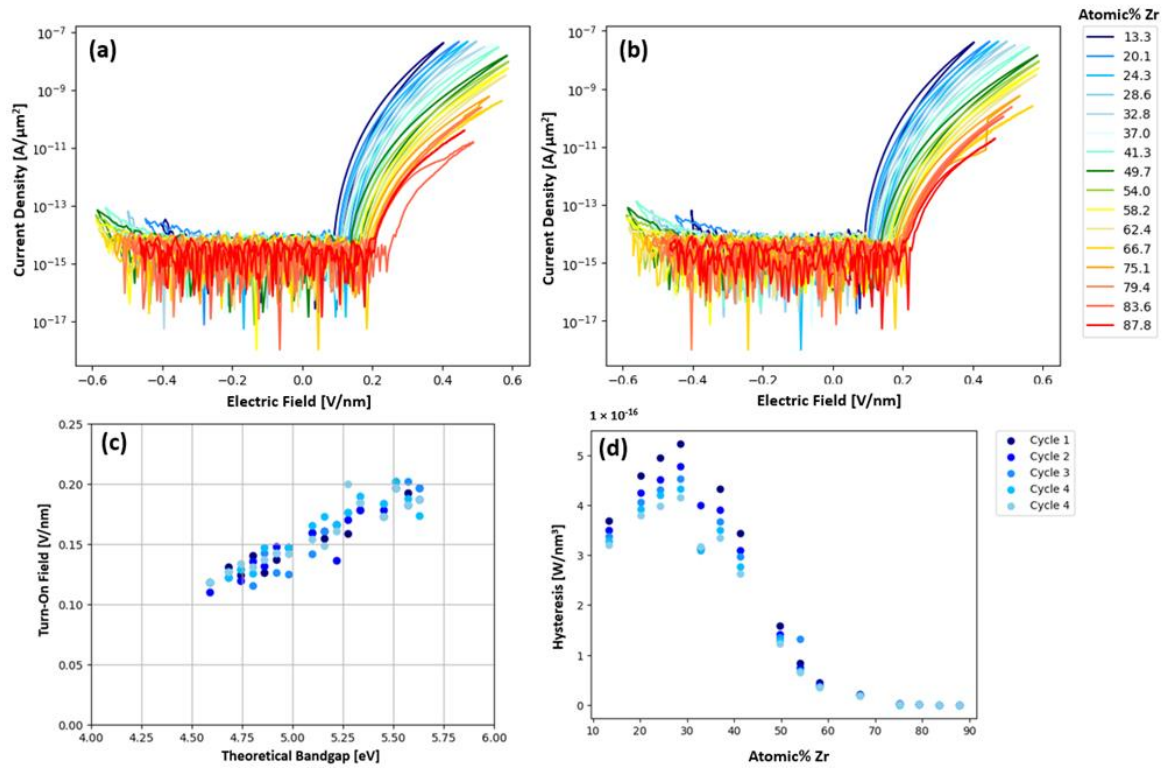


Figure 39. Current density versus electric field for (a) cycle 1 and (b) cycle 5 as a function of composition across the combinatorial $\text{Zr}_x\text{Ta}_{1-x}\text{O}_y$ wafer. The relationship of (c) turn-on field and theoretical bandgap (composition), and (d) hysteresis versus Zr concentration.

The AIMD simulations presented in **Figure 43** also show the highest MSD for oxygen at a Zr concentration of 30 atomic percent. This result suggests that ionic motion could also be contributing to the increased hysteresis around 30% Zr region.

To understand the mechanisms responsible for the hysteresis observed in the $Zr_xTa_{1-x}O_y$ system, various current injection mechanisms that can be operative in metal--insulator--metal (MIM) devices were explored. The current density -electric field behavior is similar to what was observed by Doolittle et al. for memristive Nb_2O_5 devices, where Schottky emission was determined to be the primary conduction mechanism prior to the turn-on voltage [15]. This is supported by **Figure 39c**, showing the linear increase in the turn-on field with increasing zirconium content. After current onset, trap- assisted Fowler--Nordheim (FN) tunneling dominates current injection through the highly charged layer at the electrode/ $Zr_xTa_{1-x}O_y$ interface, while Poole--Frankel (PF) charge trapping and emission is responsible for conduction through the remainder of the amorphous $Zr_xTa_{1-x}O_y$ film. During the reverse sweeps, hysteresis occurs because the emission rate is higher than the charge capture rate, which allows for higher conductivity in the reverse sweep relative to the forward sweep. It is also suspected that a portion of the trap states remain filled during the reverse sweep, effectively increasing the charge emission/capture ratio. This current limited electron capture process is dependent on the emission rate by trap states (e_e),

$$e_e = v_{th}\sigma_n N_C N_t \exp \left(-\frac{E_C - E_t}{k_B T} \right) \quad (1)$$

and charge capture rates (c_e),

$$c_e = v_{th} \sigma_n n N_t \quad (2)$$

where v_{th} is the carrier thermal velocity, σ_n is the electron capture cross section, n is the density of available electrons, N_t is density of traps, N_c is the effective density of states and $E_c - E_t$ is the trap depth. In this case, the primary charge carrier for this mechanism is electron motion.

This temperature- driven inequality of emission and capture of charge is confirmed in **Figure 40a**, where measurements were conducted across a range of temperatures and show that the calculated hysteresis (**Figure 49a**) increases with increasing temperature for the five cycles measured. An increase in the maximum current density with temperature is demonstrated in **Figure 40a**, which could be explained by an increase in thermal carrier velocity and the number of trap states. This increase in current and hysteresis with temperature also suggests a possible ionic motion contribution to the conduction mechanism. A similar combination of Schottky emission at low voltages and tunneling/PF conduction at higher voltages was observed by Doolittle et al. [15]. PF conduction is observed at voltages above the turn on voltage while Schottky emission is driven by a highly charged layer at the electrode/active layer interface. Poole–Frankel conduction is described by

$$J_{PF} = q\mu N_0 E \exp\left(-\frac{q}{k_B T} \left(\Phi_D - \sqrt{\frac{qE}{\pi\epsilon}}\right)\right) \quad (3)$$

where q is elemental charge, μ is electron mobility, N_0 is defect concentration, E is electric field, Φ_D is defect trap energy, ϵ is the high- frequency dielectric constant. As shown in **Figure 49b**, the defect trap energy (Φ_D) of a device with $Zr_3Ta_7O_y$ was

determined to be 1.16 eV from the intercept of a plot of the activation energy versus the square root of electric field (**Figure 40b**). This trap energy is significantly higher compared to the trap energy found by Doolittle et al. in Nb₂O₅ (0.22 eV) [15]. These values for Nb₂O₅ and Zr_xTa_{1-x}O_y are qualitatively consistent considering Zr_xTa_{1-x}O_y exhibited a higher onset field (0.125 V/nm versus 0.005–0.09 V/nm in Nb₂O₅). The negative bias portion of the IV cycling shows significantly lower current due to a higher Schottky barrier height at the Pt/oxide interface.

Similar plots for the Ta₂O₅ devices are shown in **Figure 50**. The Ta₂O₅ injection shows a decrease in PF trap activation energy with increasing field with a zero-field trap depth of 0.93 eV. The increased trap depth of the Zr₃Ta₇O_y film compared to the pure Ta₂O₅ and ZrO₂ films is attributed to the increasing bandgap with the addition of ZrO₂ to Ta₂O₅ and thus deeper trap states. The increased trap depth also suggests that the conduction mechanism of the mixed Ta/Zr cation film exhibits a similar conduction mechanism to the Ta₂O₅ devices, at least at modest amounts of Zr. **Figure 51** shows the current voltage behavior for the ZrO₂ injection along with the PF activation energy and trap depth calculations. Counter to the Ta₂O₅ injection, the ZrO₂ devices show an increasing PF trap activation energy with increasing field, generating a zero-field trap depth of 0.05 eV. The low trap depth of the ZrO₂ devices suggests that the PF trap-emission mechanism is not the dominate current transport mechanism in the pure ZrO₂ film.

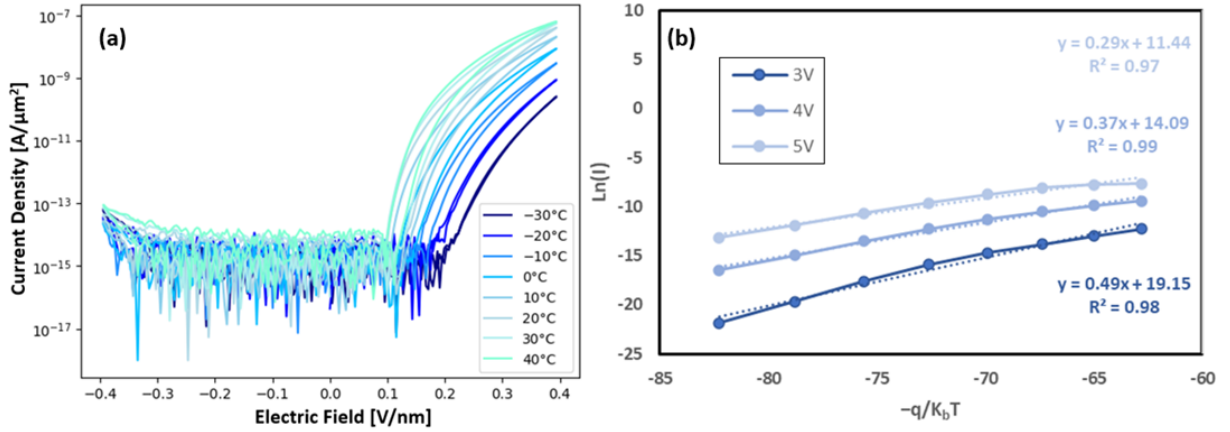


Figure 40. Electronic behavior of $\text{Zr}_3\text{Ta}_7\text{O}_y$ device at various temperatures. Shows (a) current density and electric field relationship and (b) $\text{Ln}(I)$ versus $-q/K_bT$ plot for various voltages which are used to determine the PF activation energy (slope) for each temperature.

Following Doolittle et al., **Figure 41** shows normalized current versus time as a function of bias voltage for Ta₂O₅ (**Figure 41a**), ZrO₂ (**Figure 41b**), and Zr₃Ta₇O_y (**Figure 41c**), all poled such that electron injection is from the bottom Pt/Ta electrode (or positive voltage applied to the top Pt contact). See **Figure 52** and **Figure 53** for the corresponding absolute values of the current-time plots and initial current density values versus field for each active layer, respectively. The Ta₂O₅ injection shows a decrease in current versus time below the turn-on field (~ 0.11 V/nm) and a current increase above the turn-on field. This signature is consistent with a transition in the mechanism from Schottky emission below the turn-on field to trap-assisted tunneling and Poole–Frenkel trap hopping above the turn-on field. Similarly, the ZrO₂ device exhibits a shift from decreasing current versus time to increasing current versus time at the turn-on field around ~ 0.5 V/nm. The higher turn-on field is due to an increase in barrier height of the Ta/ZrO₂ interface. While the exact current transport mechanism above turn-on is not clear due to the temperature-dependent behavior observed in **Figure 51**, it is interesting that the device also demonstrates a similar change in the current versus time below and above the turn-on field. The Zr₃Ta₇O_y device also demonstrated a rise in current above the turn-on field, similar to the Ta₂O₅ and ZrO₂ devices, and has a threshold in the behavior between 0.08 and 0.12 V/nm. While the rise in the normalized current in the Zr₃Ta₇O_y device above the turn-on field decreases in magnitude with increasing field, the absolute values of current are higher (see **Figure 52**). Also note that the Zr₃Ta₇O_y device broke down (and reached 1 mA compliance) after 30 s at a field of 0.41 V/nm.

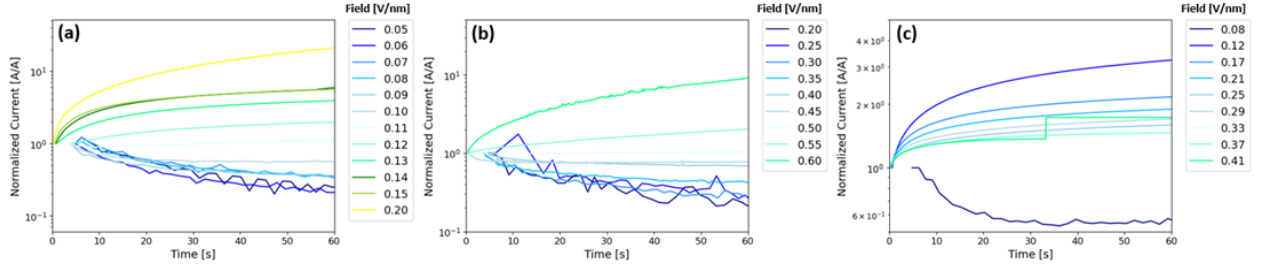


Figure 41. Normalized leakage current versus time for (a) Ta₂O₅ devices (b), ZrO₂ devices, and (c) Zr₃Ta₇O_y devices at various electric fields.

While the mechanisms proposed for the observed hysteresis are attributed to the PF conduction and trap-assisted tunneling, to elucidate whether ionic motion was participating in the observed wake-up behavior observed in the ZrO_2 and Ta_2O_5 devices, TOF-SIMS depth profiles were performed on pristine devices and compared to devices after 25 measurement cycles. The ToF-SIMS depth profiles, shown in **Figure 42a**, show shifts in Cs_2O^+ (surrogate for oxygen), Ta^+ and Zr^+ signals at the top Pt/ ZrO_2 and Ta/ ZrO_2 interfaces after cycling the device $25\times$. This suggests that there is some oxygen motion within the active layer during this wake-up period. The corresponding current-voltage cycling can be found in **Figure 54**. The relevant signals normalized to the total signal are shown in **Figure 55** and **Figure 56** for the ZrO_2 and Ta_2O_5 devices, respectively. In the ZrO_2 device, oxygen can be seen to migrate in the ZrO_2 layer toward the bottom Ta layer. This migration is tracked using the Cs_2O^+ signal. As Doolittle et al. [15] suggests, a highly charged layer generated at the electrode/active layer interface, can result in increased tunnel injection during the during the positive sweep. Thus, the observed oxygen buildup observed at the ZrO_2/Ta interface, could be inducing a highly charged layer or oxidizing the interface and thus locally increasing the electric field, which is consistent with the observed maximum current increase observed with increasing cycle number during positive poling. Tracking the Zr^+ signal shows a concomitant migration of Zr^+ at the Ta interface. This could be due to slight densification during the wake-up or demixing at the ZrO_2/Ta interface. In the Ta_2O_5 devices shown in **Figure 42b**, minimal change is observed in the Cs_2O^+ signal and the Ta^+ signal.

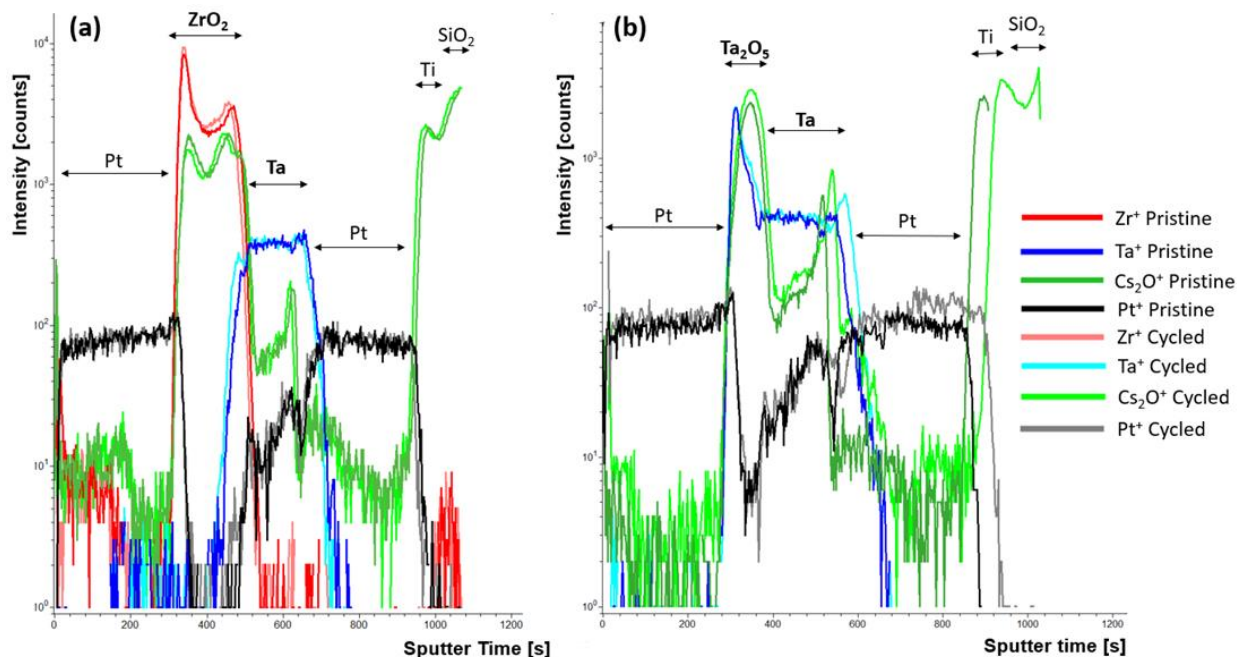


Figure 42. Ta^+ , Zr^+ , Cs_2O^+ , and Pt^+ signals of pristine and cycled (a) ZrO_2 devices and (b) Ta_2O_5 devices. The labels indicating the device active layers are in bold font. The profiles were aligned to the top Pt/oxide interface to account for any ion current or thickness variations in the surface or top Pt electrode layers.

This is likely due to the smaller fields required to operate and wake-up the device up. The spike in Ta^+ count at the Pt/ Ta_2O_5 interface is attributed to the matrix effect generating increased ionization rates at interfaces due to variation in bonding compared to the bulk of the film [30,31]. It is interesting that there is a slight expansion of the Ta layer observed, along with a buildup of oxygen bottom Ta/Pt interface (though note that the scale is logarithmic, so a low concentration relative the Ta_2O_5 layer concentration). These changes at the Ta/Pt interface are not expected to substantially change the conduction mechanism in the Ta_2O_5 devices as a majority of the voltage drop should be across the Ta_2O_5 layer. The shift in Pt^+ at in the Ta_2O_5 device is attributed to thickness variation across the sample in the bottom Pt layer and is not expected to affect device performance.

Conclusions

A combinatorial thin film synthesis process was used to rapidly investigate the memristive properties of a $\text{Zr}_x\text{Ta}_{1-x}\text{O}_y$ system. Varying the Zr concentration systematically increased the bandgap while also increasing the trap depth due to the formation of more complex defect states. The underlying conductive mechanism of the $\text{Zr}_x\text{Ta}_{1-x}\text{O}_y$ was found to be a combination of charge trapping and ionic motion, where charge trapping/emission dictated the short-term cycling behavior while, over time, ion motion contributed to changes in the conduction with increased cycling number. EDS was used to characterize the composition gradient and device characteristics were measured as a function of the cation concentration. XPS showed that all of the core level Ta 4f, Zr 3d, and O 1s spectra shift to lower binding energy with increasing Zr content,

consistent with energy transfer among the ions. The $\text{Zr}_x\text{Ta}_{1-x}\text{O}_y$ system showed volatile resistive switching, consistent with PF charge trapping behavior, induced by a transition from Schottky emission to trap-assisted tunneling through the highly charged layer at the electrode/active layer interface. The devices exhibited hysteretic diode behavior with a defined turn-on voltage and two distinct resistance states. The hysteresis area peaks around 30% Zr (relative to the total cation concentration of $\text{Ta} + \text{Zr} = 100\%$), which correlates well with ab initio molecular dynamics (AIMD) simulations which showed maximum mobility at $\sim 31\%$ Zr doping. An increase in current and hysteresis with increasing temperature suggests an increase in thermal carrier velocity and trap states along with a possible ionic motion component. Trap activation energy was highest for the $\text{Zr}_3\text{Ta}_7\text{O}_y$ active layer (1.16 eV) since the mixed valences of Ta^{5+} and Zr^{4+} generate deeper trap states compared to pure Ta_2O_5 and ZrO_2 . Slight ionic motion was observed in the ToF-SIMS depth profiles of cycled compared to pristine ZrO_2 and Ta_2O_5 devices. In the ZrO_2 devices, the ZrO_2 layer width decreased with increased cycling along. The Ta_2O_5 devices only showed an increase in the Ta layer thickness after cycling, along with a buildup of oxygen at the bottom Ta/Pt interface. Future studies will work toward increasing the long-term stability and increasing the HRS/LRS ratio of the devices to elucidate the temporal charging/discharging response of the non-volatile device.

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Appendix

Supporting Information

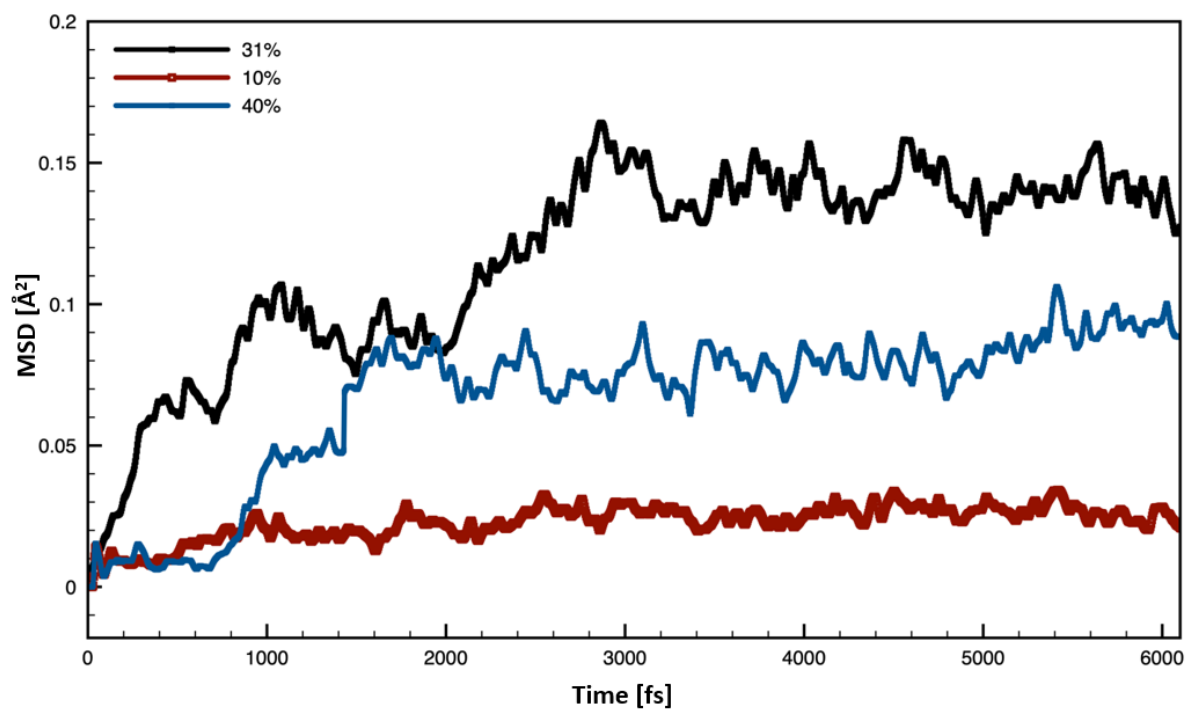


Figure 43. Mean square displacement of oxygen for 10%, 31%, and 40% Zr doped tantalum.

XRR results (measured prior to adding Pt caps)

Layer	Layer Description	Density (g/cm ³)	Thickness (nm)	Roughness (nm)	Delta, e-7	Beta, e-7
5, 0	ZincBlende, Ta ₂ O ₅ 0.500 ZrO _{0.500}	9	10.349	1.342	232.47339	14.91413
4, 0	DensityOnly, Ta	10.077	20.01	0.861	237.93819	20.50842
3, 0	DensityOnly, Pt	22.781	42.797	0.398	544.69691	55.85802
2, 0	DensityOnly, Ti	4.101	4.928	0.599	121.76695	10.4566
1, 0	DensityOnly, SiO ₂	2.64	513.079	0.017	85.44901	1.11502
Substrate	Diamond, Si	2.328	600000	0.139	75.68502	1.72955

Blue= data, Red = model fit.

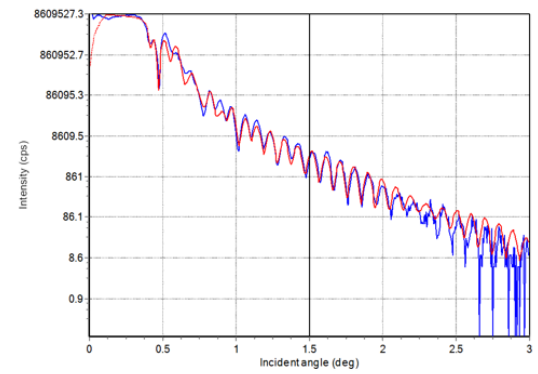


Figure 44. Shows XRR results of a measurement taken in the middle of the $\text{Zr}_x\text{Ta}_{1-x}\text{O}_y$ combinatorial wafer.

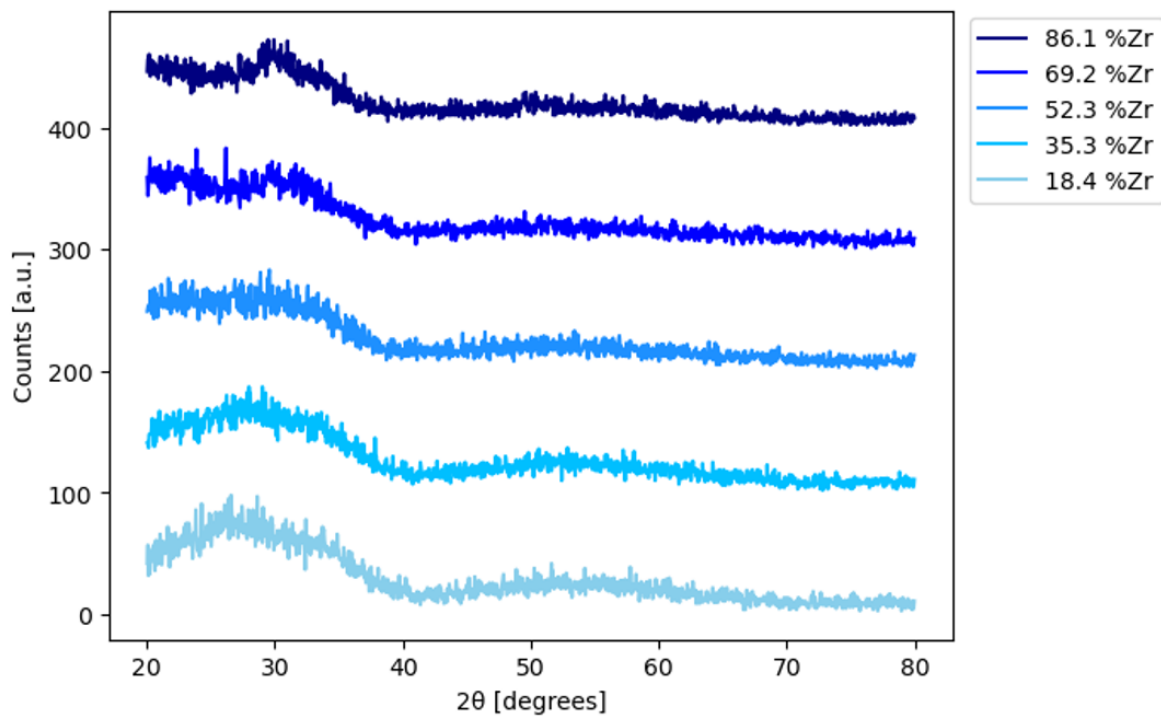
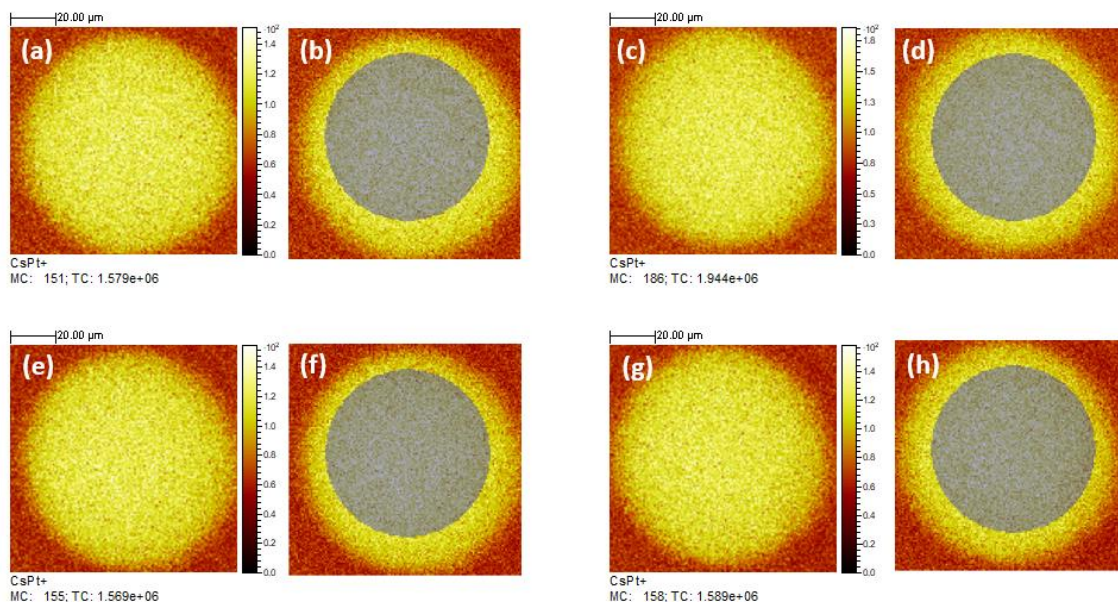


Figure 45. Grazing incidence x-ray diffraction (GIXRD) of the combinatorial film confirming the amorphous structure. The measurements at 86.1%, 69.2%, 52.3% and 35.3% Zr were offset by +400, +300, +200 and +100, respectively.



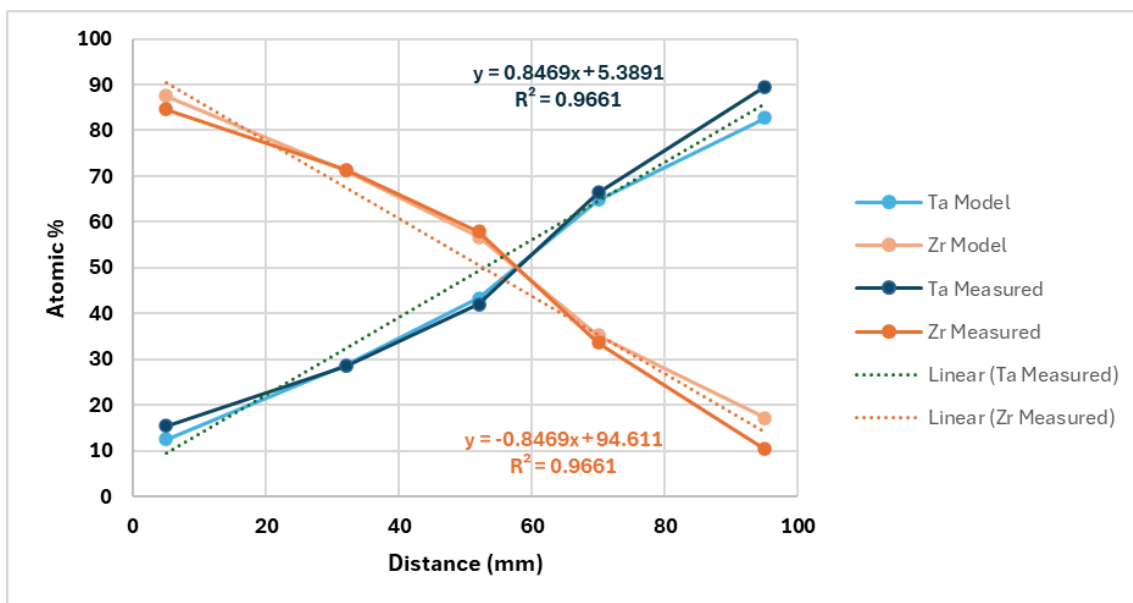


Figure 47. Shows comparison of chemistry model compared to EDS measurements across the $Zr_xTa_{1-x}O_y$ film

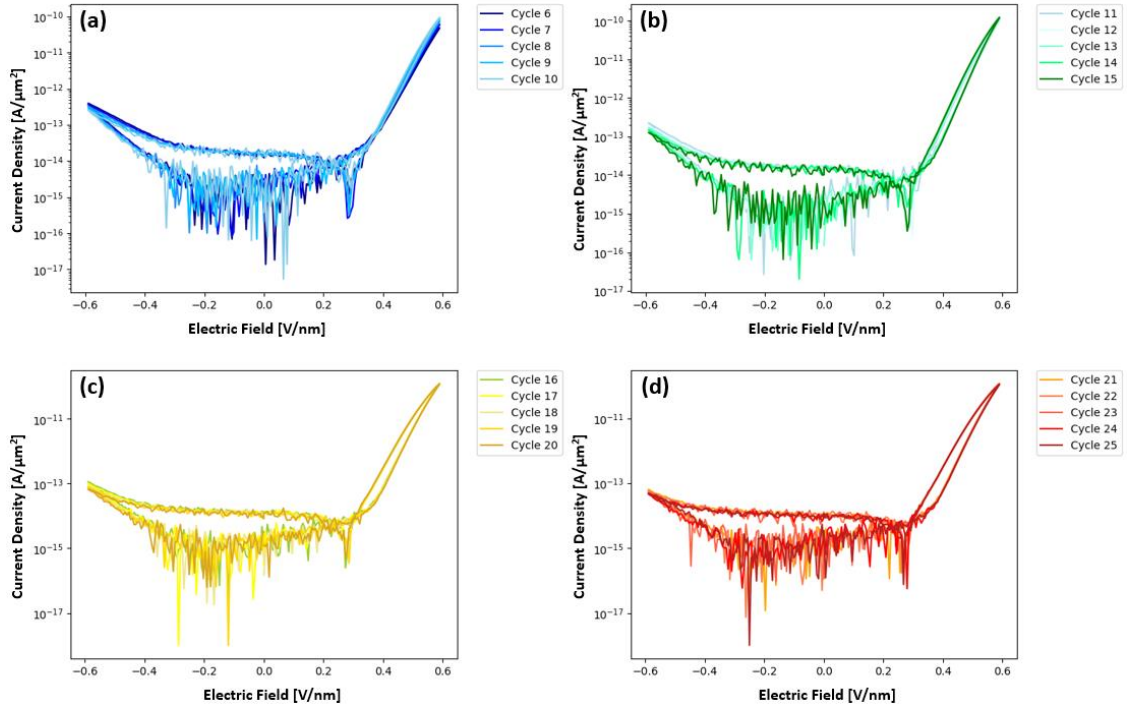


Figure 48. Shows current density and electric field relationship of ZrO₂ device before (a-b) and after (c-d) positive polarity is stabilized.

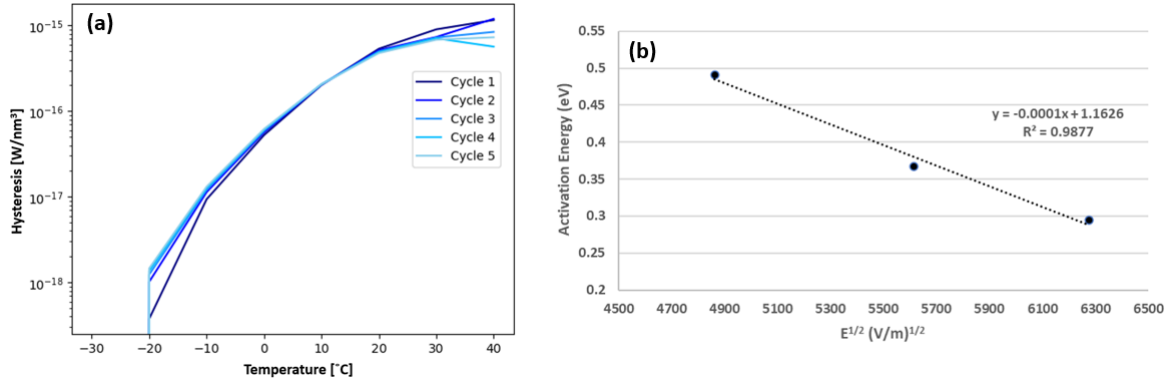


Figure 49. Shows hysteresis (a) and activation energy (b) curves for a $\text{Zr}_3\text{Ta}_7\text{O}_y$ device. Note the hysteresis increases of the for each cycle number as a function of increasing temperature a). (b) shows the plot of the activation energy versus the square root of electric field, where the y-intercept is the PF trap energy depth.

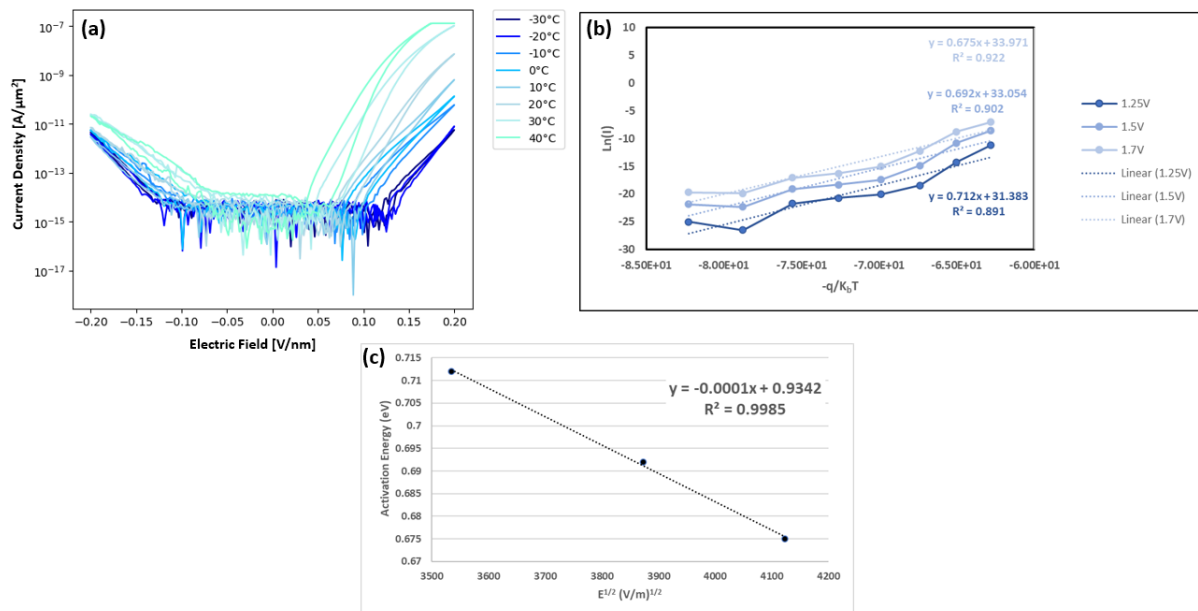


Figure 50. Current-Voltage behavior (a), PF activation energy (b) and trap depth (c) for Ta_2O_5 devices

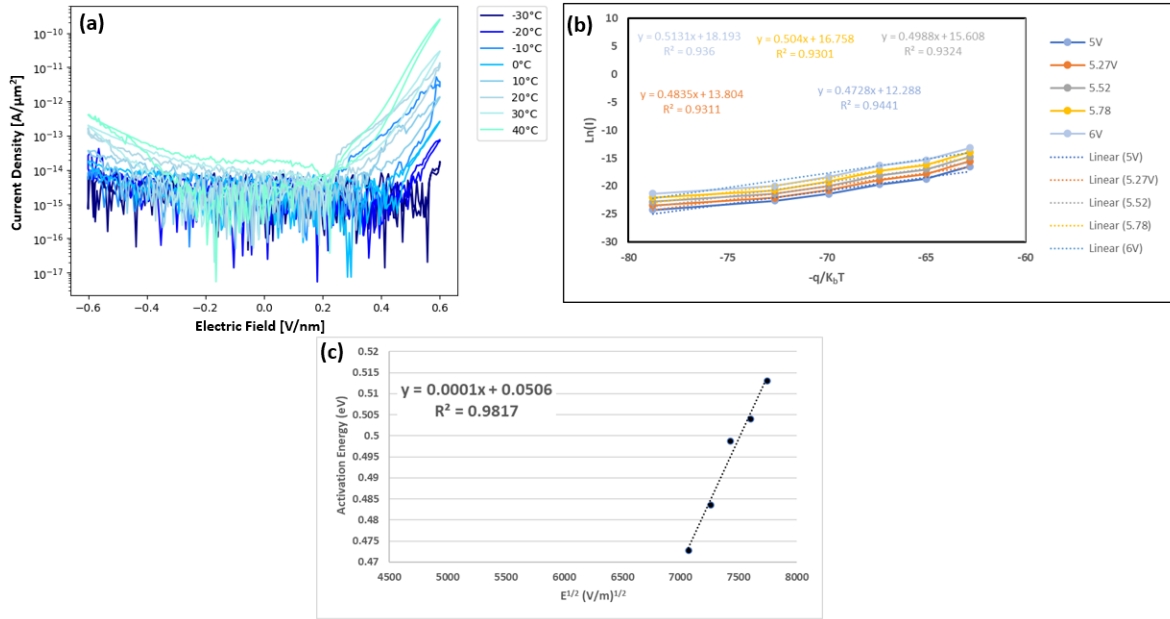


Figure 51. Current-Voltage behavior (a), PF activation energy (b) and trap depth (c) for ZrO₂ devices

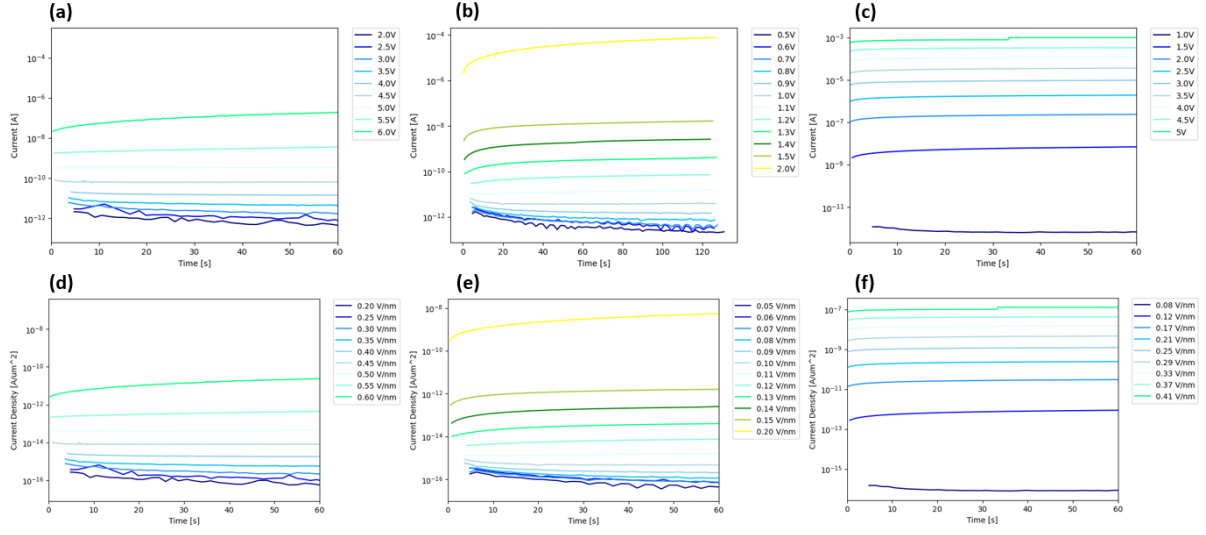


Figure 52. Leakage current for ZrO_2 devices (a), Ta_2O_5 devices (b) and $\text{Zr}_3\text{Ta}_7\text{O}_y$ devices (c) at various voltages over time. **Figures 52 (d-f)** show current density vs time at the equivalent electric fields to **Figures 52 (a-c)**, respectively

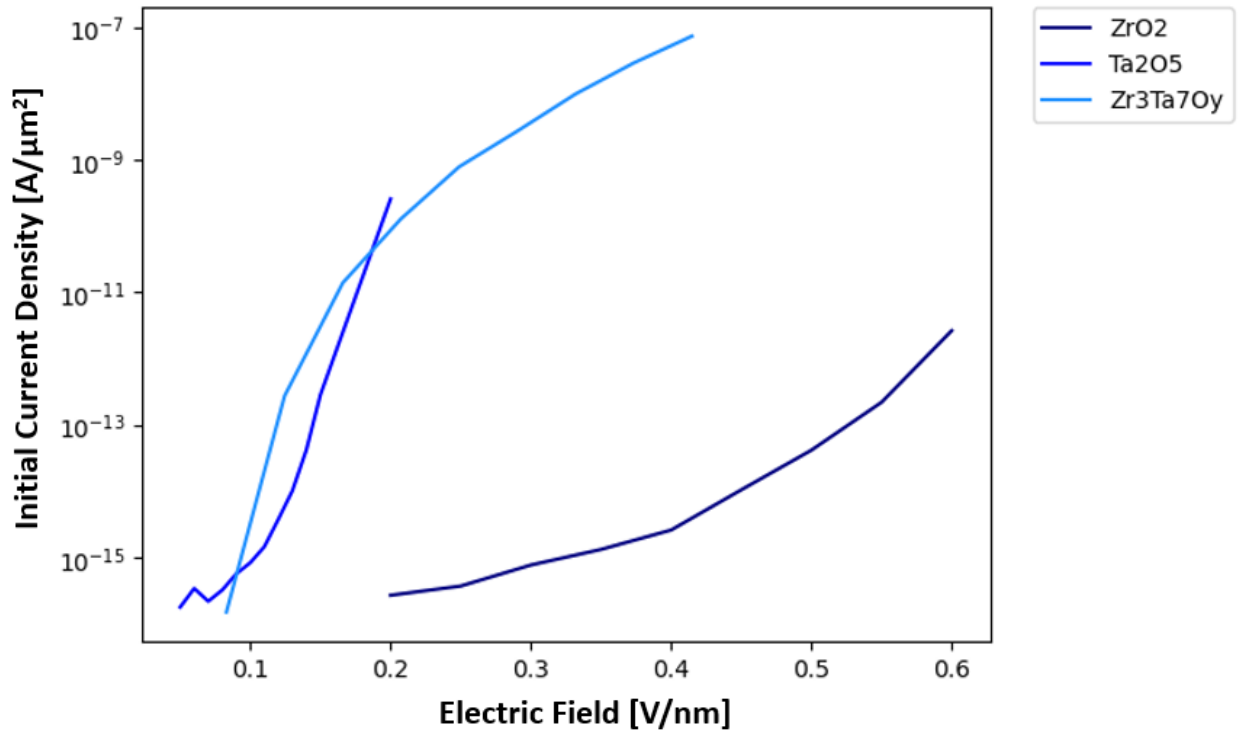


Figure 53. Initial current density of leakage current measurements for Ta₂O₅, ZrO₂ and Zr₃Ta₇O_y devices.

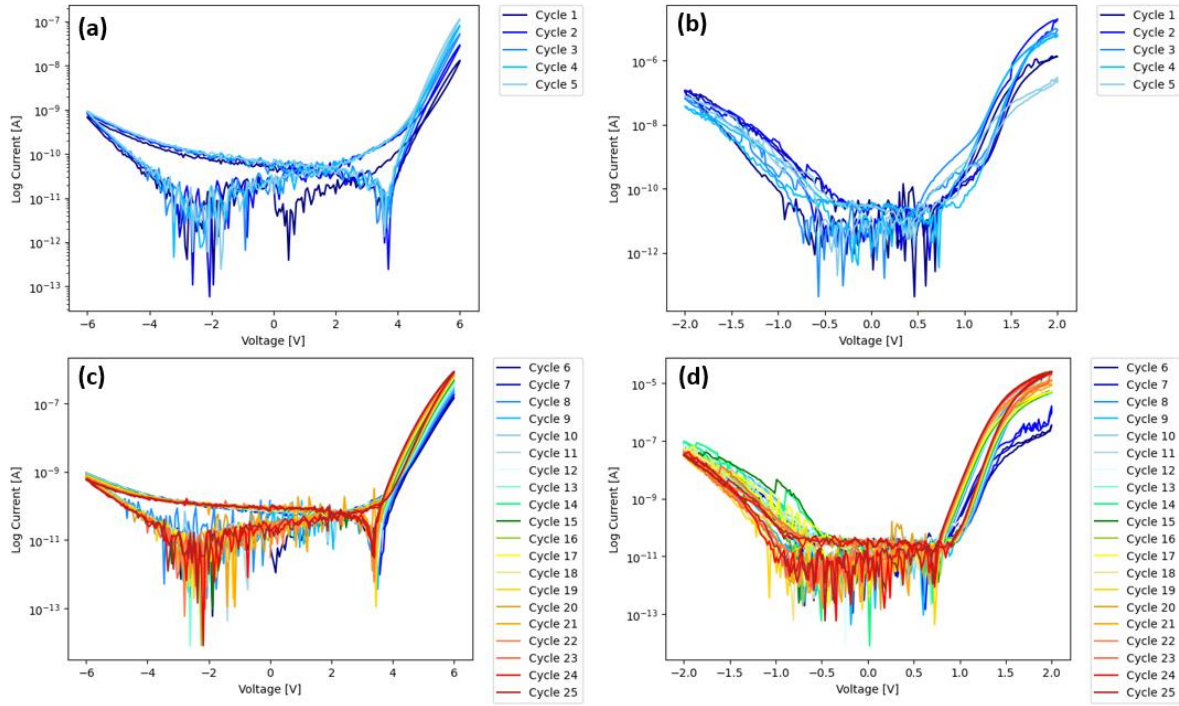


Figure 54. Current-voltage cycling that corresponds to cycled SIMS devices. ZrO₂ devices cycled 25x, (a) and (c), and Ta₂O₅ devices cycled 25x, (b) and (d). Ta₂O₅ cycled device was 9mm away from pristine Ta₂O₅ device while ZrO₂ cycled device was 1mm away from pristine ZrO₂ device. The increased noise in these cycles compared to **Figure 38** is attributed to the addition of silver paint to the circuit that, that was used in order to ground the devices.

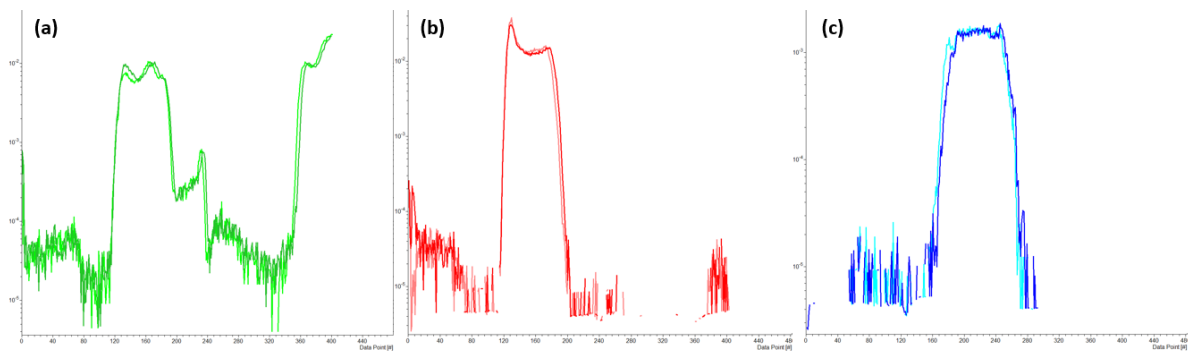


Figure 55. Shows the Cs_2O^+ (a), Zr^+ (b) and Ta^+ (c) normalized to the total signal. Corresponds to **Figure 42(a)**.

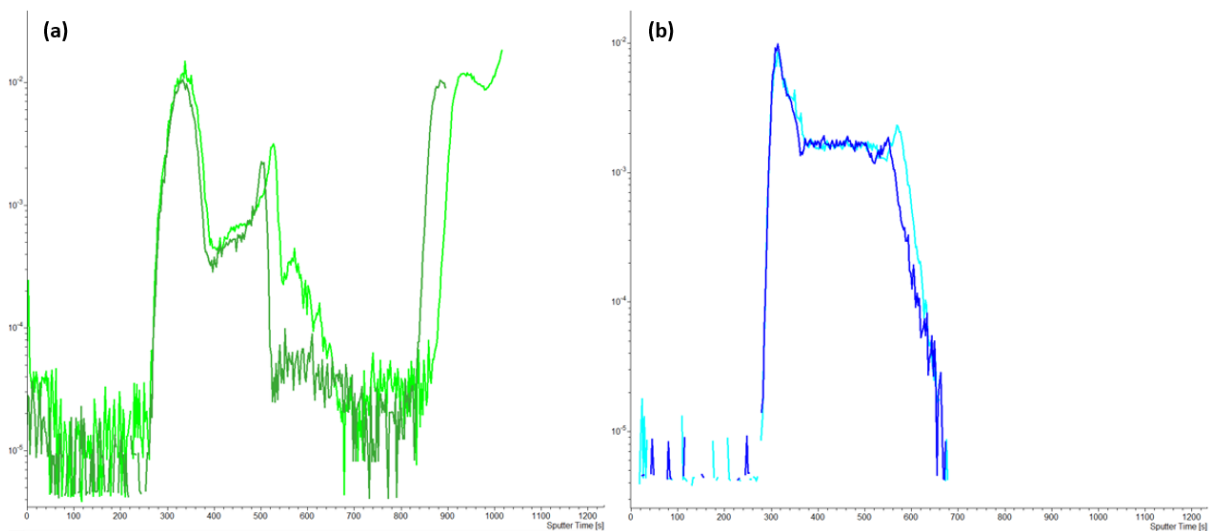


Figure 56. Shows Cs_2O^+ (a) and Ta^+ (b) signals normalized to the total signal. Corresponds to **Figure 42(b)**.

CHAPTER III

LEVERAGING COMBINATORIAL SPUTTERING TO INVESTIGATE

ELECTRICAL PROPERTIES OF $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ COMPOSITIONS

Leveraging Combinatorial Sputtering to Investigate Electrical Properties of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ Compositions

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Autor Contributions

This work is in preparation for submission. Matthew was the primary writer and primary experimentalist for this work. Matthew fabricated the devices, did the electrical measurements and analysis, along with the XRR and XRD experiments. Kyle Specker did the EDS measurements, Steven Randolph and Scott Retterer supervised the device fabrication. Kyle Kelley supervised device fabrication and experimental setup. Philip Rack acted as the primary editor, supervisor and was responsible for the project ideation.

Abstract

Combinatorial magnetron sputtering was used to generate a library of devices with a wide range of Hf:Zr ratios. The electrical properties of these devices were systematically investigated and correlated to the crystal structure. XRD, XRR, EDS were used to measure film structure, thickness and chemistry across the sample, respectively. Time resolved PUND measurements were used to confirm ferroelectric behavior in devices ranging from 49 to 22 atomic % Hf. The switching current and polarization were extracted from the PUND measurements. Ferroelectric is shown to increase from 49 to 36% Hf, then further decreasing Hf decreases the switching polarization while also generating peak splitting behavior. Device endurance properties were measured and showed consistent switching while enduring cycling from 1×10^5 to 1×10^4 cycles. Increased cycling of bimodal switching unified the peak splitting while increasing the overall switching polarization. XRD structural measurements showed high orthorhombic/tetragonal peaks in the regions exhibiting ferroelectricity, suggesting that the primary phase driving the ferroelectric behavior is orthorhombic.

Introduction

The resurgence of interest in ferroelectric materials for next-generation microelectronics has been largely driven by the discovery of robust ferroelectricity in doped hafnium oxide (HfO₂) thin films. Unlike traditional perovskite ferroelectrics, hafnia-based ferroelectrics exhibit scalable ferroelectricity even in ultrathin films (<10 nm), compatibility with CMOS integration, and resilience to high-temperature processing. These attributes

position hafnium oxide derivatives as front-runners for use in ferroelectric field-effect transistors (FeFETs), non-volatile memories (FeRAM), and emerging neuromorphic and logic-in-memory technologies.

The $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ (HZO) system has been a particular focus of investigation due to the Zr-induced stabilization of the polar orthorhombic ($\text{Pca}2_1$) phase responsible for ferroelectric behavior. Early work by Schroeder et al. [1] mapped out the temperature-dependent phase transitions in $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ and identified a compositional window around $x \approx 0.5$ where the orthorhombic phase is most stable. Their findings provided direct evidence that HZO can exhibit proper ferroelectricity, not merely as a result of defect-induced symmetry breaking but as a genuine structural phase transition. This orthorhombic phase competes with the monoclinic, tetragonal, and cubic polymorphs, and its stability is highly sensitive to composition, thermal treatment, and processing conditions.

Wu et al. [2] expanded upon this by analyzing how the Hf:Zr atomic ratio influences switching dynamics and endurance. They reported that intermediate compositions (especially $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$) balance remanent polarization and cycling stability, minimizing common failure modes such as fatigue and imprint. These results underscore the need for precise control over film stoichiometry to optimize device performance.

Zr-rich compositions, such as $\text{Hf}_{0.2}\text{Zr}_{0.8}\text{O}_2$, are typically viewed as antiferroelectric, but Dahlberg et al. [3] showed that integration with III–V substrates such as InAs could enhance ferroelectric behavior, likely due to strain-induced phase stabilization at the interface. Their results emphasize the importance of substrate effects and interfacial

energy in tuning ferroelectric phase stability, especially in heterostructures and low-dimensional systems.

Deposition conditions also play a critical role. Oh et al. [4] investigated as-grown crystalline HZO films using $\text{Hf}[\text{Cp}(\text{NMe}_2)_3]$ and $\text{Zr}[\text{Cp}(\text{NMe}_2)_3]$ precursors via atomic layer deposition (ALD). Their results highlight how Zr content and post-deposition annealing strongly influence phase formation and ferroelectric performance. Importantly, they showed that crystalline HZO can be obtained directly during growth—rather than relying solely on post-deposition thermal treatments, if precursor chemistry and process parameters are carefully optimized. This insight offers promising routes toward low-temperature processing of ferroelectric layers, enabling 3D integration and back-end-of-line (BEOL) compatibility.

Similarly, Mittmann et al. [5] explored the impact of ambient oxygen during the sputtering process and demonstrated that carefully controlling oxygen partial pressure can stabilize the ferroelectric phase even when using ceramic $\text{HfO}_2\text{-ZrO}_2$ targets. Their work suggests that, beyond alloying chemistry and annealing, ambient gas environment during deposition can directly affect defect densities and grain boundary evolution.

Demonstrating these two key parameters influence phase formation and polarization fatigue.

These findings are complemented by the work of Kelley et al. [6], that emphasized the influence of the surface electrochemical state on ferroelectric switching. Results showed that the environment and electrode interface chemistry can modulate ferroelectric

behavior by altering surface defect states, particularly oxygen vacancies, which are known to influence internal fields and domain dynamics. Xi et al. [7] also found that variations in oxygen flow during magnetron sputtering significantly impact crystallinity and ferroelectric performance in Zr-doped HfO₂ films. Oxygen-rich conditions tend to suppress vacancy-mediated degradation, leading to better retention and reduced leakage. Finally, Wang et al. [8] proposed a low-temperature optical annealing strategy for wake-up-free Hf_{0.5}Zr_{0.5}O₂ capacitors. Their results illustrate that by carefully controlling the thermal budget and energy delivery, one can suppress common wake-up phenomena attributed to defect redistribution, thereby enhancing long-term device stability and reducing power consumption.

Doped HfO₂ or ZrO₂ materials can exhibit a range of phases such as, cubic (Fm $\bar{3}$ m), rhombohedral (R3m), monoclinic (P2₁/c) and tetragonal (P4₂/nmc). There are also multiple orthorhombic phases that can form, including the orthorhombic polar (Pca2₁), nonpolar (Pnma), nonpolar (Pbca) and antipolar (Pbca).[1], [9], [10] The rhombohedral phase of ZrO₂ (R3m) has shown ferroelectric behavior,[11], [12] while the tetragonal (P4₂/nmc) phase has shown antiferroelectric behavior.[4], [13] The orthorhombic (Pca2₁) doped HfO₂ phases can also exhibit ferroelectric behavior.[14]

These studies reveal that the ferroelectric response of Hf_xZr_{1-x}O₂ is governed by a complex interplay of factors: composition, interfacial strain, defect chemistry, ambient deposition environment, and thermal processing. While the orthorhombic phase is central

to ferroelectricity in HZO, its stabilization depends critically on not only the Hf:Zr ratio but also the synthesis method and subsequent thermal history.

In this work, combinatorial magnetron sputtering is leveraged to generate HZO devices with a range of chemical compositions. The materials and devices are systematically analyzed and compared in order to provide insights into how the HZO composition and processing parameters influence crystallographic phase formation, electrical behavior, and device reliability. Using characterization tools such as X-ray diffraction (XRD), piezoresponse force microscopy (PFM), and polarization–electric field (P–E) measurements, we aim to clarify the mechanisms underlying phase selection and switching stability in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ (HZO) films across a wide composition range.

Experimental

Magnetron sputtering was used to deposit the bottom W electrode by applying 100 W RF power to a W target in a 5 mTorr Ar environment. The HZO combinatorial device film was deposited by applying 62W DC and 114W DC to metallic Hf and Zr targets, respectively, with 5/25 O_2 /Ar standard cubic centimeters per minute flow rates, respectively, with a total pressure of 6 mTorr. A top W layer was similarly sputter deposited and photolithography was used to pattern 100 μm diameter W electrodes across the Hf:Zr gradient. Devices were spaced 1 mm apart. The fully fabricated devices were annealed in a 50 mTorr Ar atmosphere with an applied temperature ramp up to 670°C over 26 min and then cooled under 50 mTorr Ar to room temperature. The wafer used for XRD was fabricated in a similar matter to the device sample, but with 55W DC power for

the Hf target and 114W DC for the Zr target. This adjustment was made due to system drift. Electrical measurements were conducted with a Form Factor Cascade CM300xi probe station along with a Keithley 4200 electrical source. PUND measurements used electrical pulses with 5×10^{-5} sec rise and fall times, 5×10^{-5} sec delay time and 1×10^{-6} sec hold. Pulse parameters for the endurance measurements for 42% Hf were 1×10^{-4} sec rise and fall time, 1×10^{-4} pulse delay and 1×10^{-5} pulse width. X-ray reflection and diffraction (XRR and XRD) measurements were conducted using a X'Pert³ MRD from Malvern Panalytical. Beam size was adjusted to 2mm along the chemistry gradient and 9.5 mm perpendicular to the HZO gradient.

Results and Discussion

The devices formed from the HZO chemistry gradient produced different switching characteristics. The wafer and device geometry are shown in **Figure 57(a)**, along with the thickness profile (**Figure 57(b)**) and the atomic cation % (**Figure 57(c)**). These thickness and cation %, measured by XRR and EDS, respectively, show a large chemistry and thickness range. The range of the cation atomic % Hf ranges from 3 to 85%, (with the balance cation atomic % Zr ranging from 15 to 97%). Slight thickness gradients emerge in the magnetron combinatorial co-sputtering system, in this case the thickness gradient ranges from ~15 to 25 nm. These types of samples allow systematic investigation of switching mechanics as a function of cation composition without batch-to-batch errors. Device measurements were conducted across the wafer to investigate the ferroelectric properties as a function of the Hf:Zr gradient.

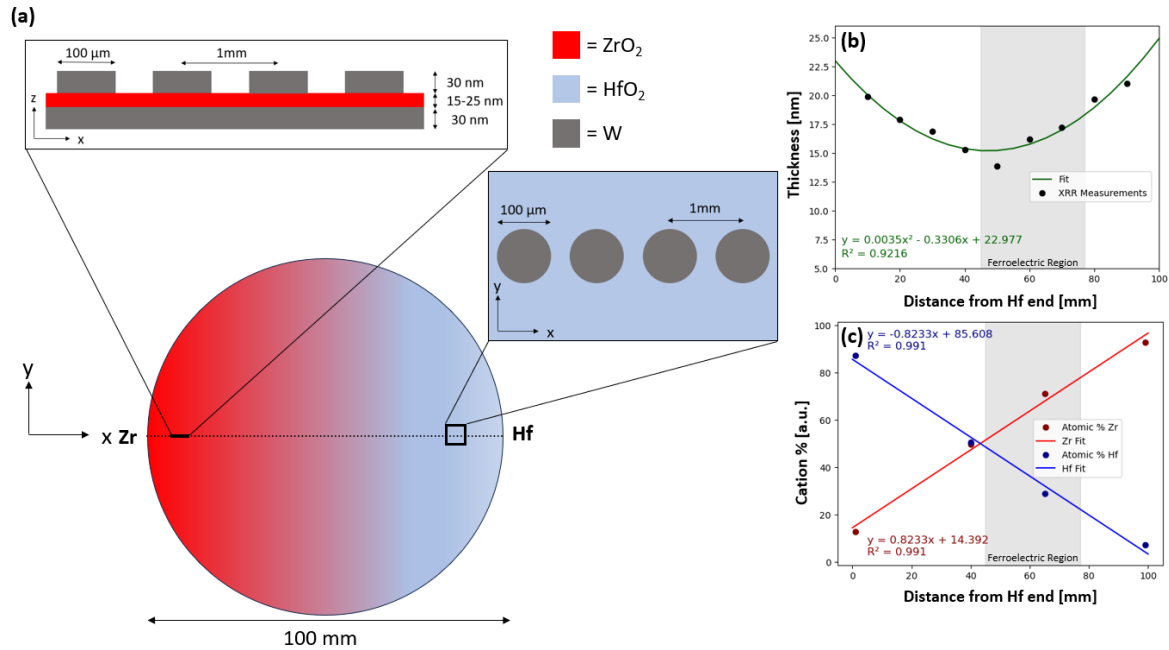


Figure 57. Shows (a) wafer and device geometry along with corresponding (b) XRR thickness measurements and (c) EDS cation atomic % measurements as a function of position on the sample, respectively. Note that the grey region in (b) and (c) corresponds to the ferroelectric region of the sample.

The time-resolved PUND measurements are shown in **Figure 58(a)**. These PUND measurements confirm ferroelectric switching behavior between 49 to 22 atomic % Hf. At 49% Hf, the ferroelectric response increases with decreasing Hf content and peaks at 35 % Hf. The polarization normalized with device active layer thickness can be found in **Figure 63**. As noted, the increase in polarization is not just due to the slight increase in thickness in this range and thus has chemical origins. Structural changes are seen in the XRD data (Figure 62), showing an increased orthorhombic/tetragonal phase peak in the ferroelectric region. The approximant remnant polarization is shown in **Figure 64**. The switching current and switching polarization for Hf concentrations from 49 to 36% Hf can be seen in **Figure 58(b)** and **Figure 58(c)**, respectively. This switching current density was found by subtracting the U from the P pulse and the D from the N pulse. The switching polarity was found by integrating this switching current with respect to time to determine switching charge and normalizing with pad area. The switching current density (**Figure 58 (b-c)**) corroborates the findings of the time-resolved PUND data. At concentrations lower than 36% Hf, further decreasing of the Hf concentration decreases the overall ferroelectric response and yields a bimodal switching mechanism. This trend is observed in **Figure 59**, which illustrates the (a) time resolved PUND measurements, (b) switching current density and (c) switching polarization. Similar peak splitting behavior was seen by Dahlberg et. al. [3] in ALD deposited $\text{Hf}_{0.34}\text{Zr}_{0.66}\text{O}_2$ and $\text{Hf}_{0.2}\text{Zr}_{0.8}\text{O}_2$ chemistries and was attributed to internal fields generated by charge trapping of oxygen vacancy states.[15]

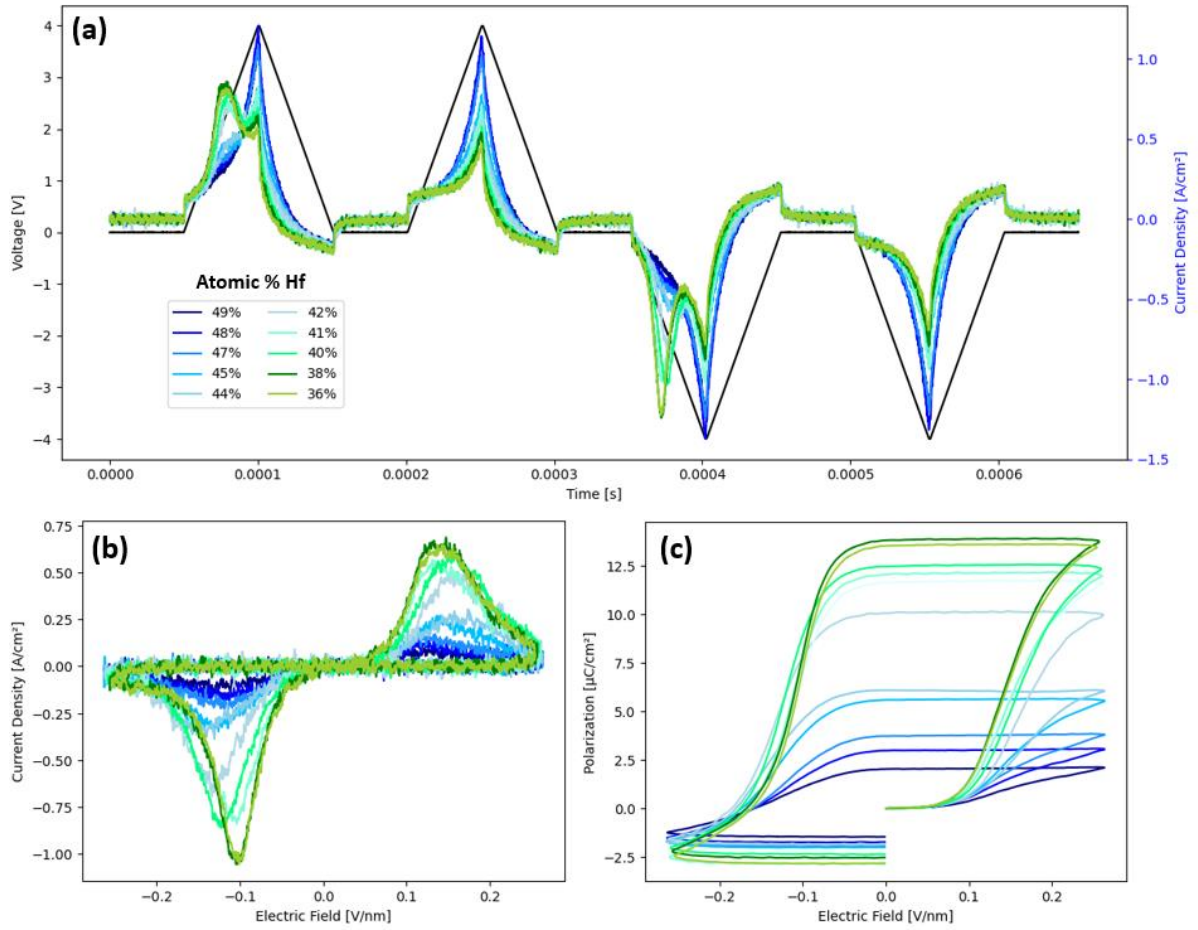


Figure 58. Switching current of high Hf concentration devices. (a) shows the time resolved PUND measurements and (b) the extracted switching current density and (c) polarization for Hf cation compositions ranging from 49 to 36% Hf.

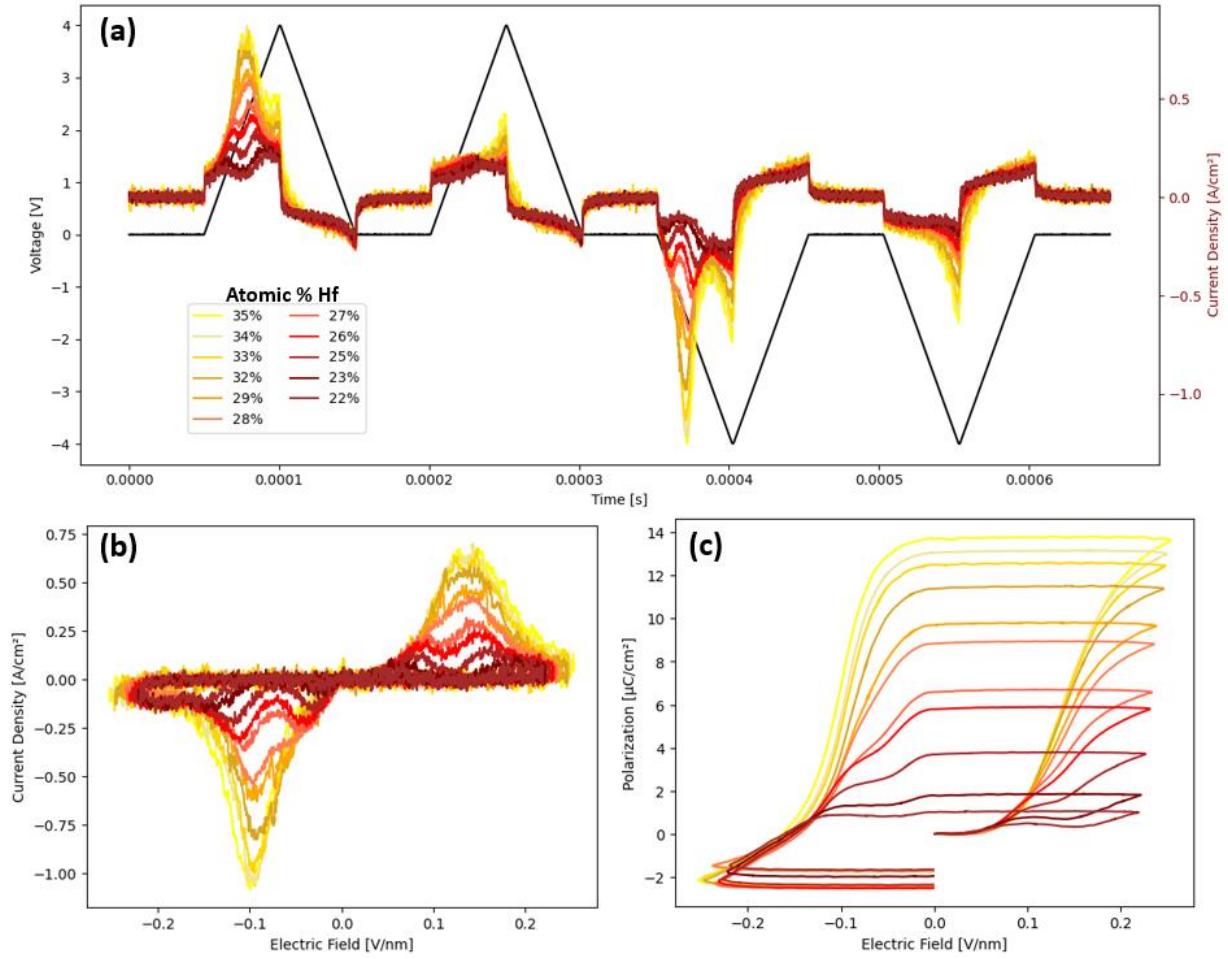


Figure 59. Shows (a) PUND measurement with respect to time along with (b) the switching current and (c) the switching polarization for Hf chemistries of 35 to 22% Hf.

These defects can be generated at the HZO/W interface due to mismatching of the cubic W lattice. **Figure 59** illustrates the bimodal switch that starts to occur around 27 % Hf. It should be noted that the remnant polarization is about half that of the switching polarization since the measurements are started with devices switched to a negative polarization state. Outside of the ferroelectric region of the sample, the high Hf% region (>49%) exhibits high conductivity while the lowest Hf region (<22%) exhibits very insulating behavior. Additional measurements of the high and low Hf % extremes can be found in **Figure 65**.

The total polarization from each PUND pulse along with the switching polarization is shown in **Figure 60**. This summarizes the trend of switching polarization across the HZO gradient. Note that the positive switching polarization (P_{sw}) is consistently lower compared to the average switching polarization (Q_{sw}). This increased negative polarization is caused by reduced switching when the devices are driven from the top W electrode compared to the bottom sheet W electrode. It seems that driving the HZO film from the bottom electrode switches slightly more of the HZO film due to leakage of the field since the bottom electrode is not patterned and thus, not sharply defined.

In order to further investigate the peak splitting in the low Hf composition devices, a series of PUND/endurance measurements were conducted on a device with 23% Hf. Cycling 10,000 cycles while taking PUND measurements 4 times per decade, shows a merging of the split peaks.

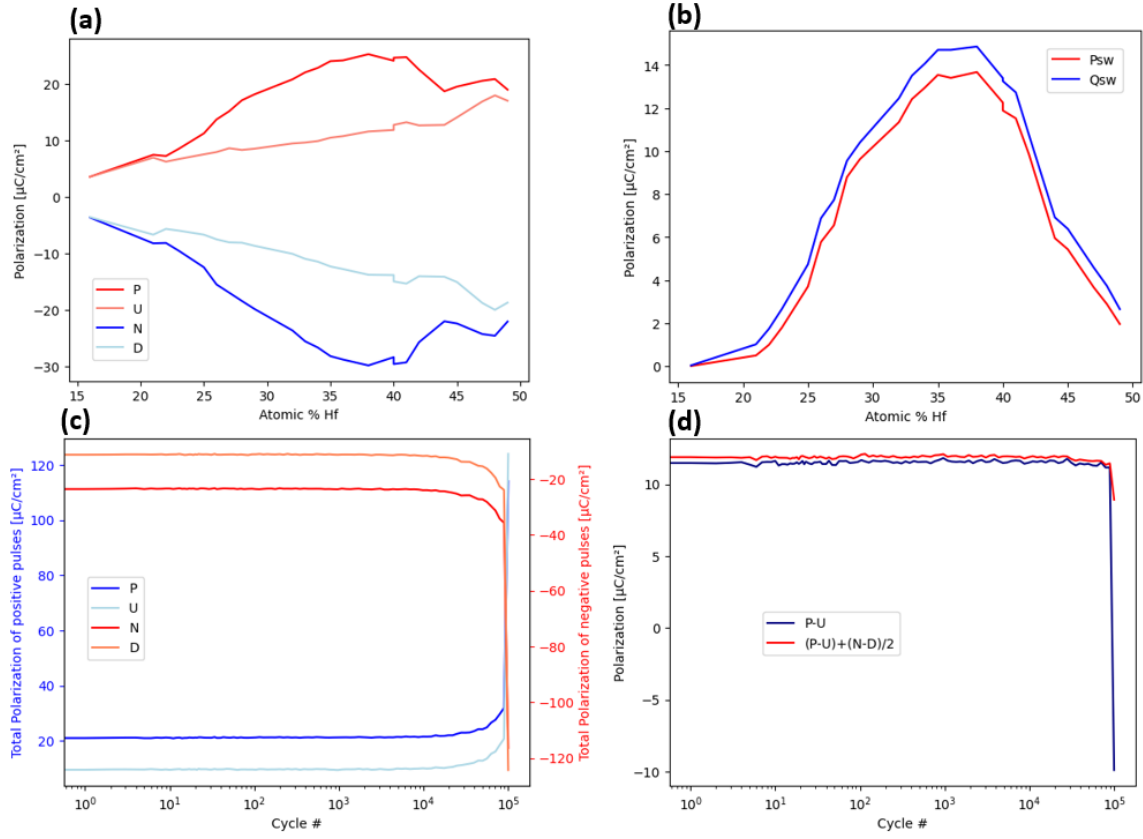


Figure 60. Plot of the (a) total polarization for each pulse in the PUND measurements as a function of atomic % Hf and (b) the switching polarization of the P pulse (P_{sw}) and the average switching polarization of the P and N pulses (Q_{sw}). Also shown are (c,d) the endurance behavior for a device with 41% Hf.

Figure 61 shows the current density/voltage behavior with time (**Figures 61a-b**) as well as the switching current density and switching polarization (**Figures 61c-d**) as a function of cycle number. If the peak splitting is driven by internal fields from charge trapping in defect states,[15], [16] then the merging of these peaks would be from recombination/annihilation of oxygen vacancies. It is also possible that there is a tetragonal antiferroelectric phase present along with the ferroelectric phase, these phases would switch at different fields and appear as a peak split. Though, the antiferroelectric current-voltage behavior seen previously, show peaks in all 4 quadrants of the scan[3]. The behavior seen in the high Zr concentration devices in this work only show peaks in quadrant 1 and 3, where the voltage ramps up. According to the trend in **Figure 61**, the ferroelectric phase dominates with increased cycling, suggesting if the antiferroelectric tetragonal phase was participating in the peak splitting behavior, it would need to transform into the orthorhombic ferroelectric with increased cycling. An *in-situ* experiment with atomic structure resolution, such as STEM or synchrotron x-ray microdiffraction, during cycling could be performed to confirm the defect or phase change mechanisms. This device started to fail after 10,000 cycles and fully failed after 100,000 cycles. The data included in **Figure 61** along with the failure cycles can be found in **Figure 66** and **Figure 67**.

A second sample was made to investigate the effects of the W electrode on HZO film structure.

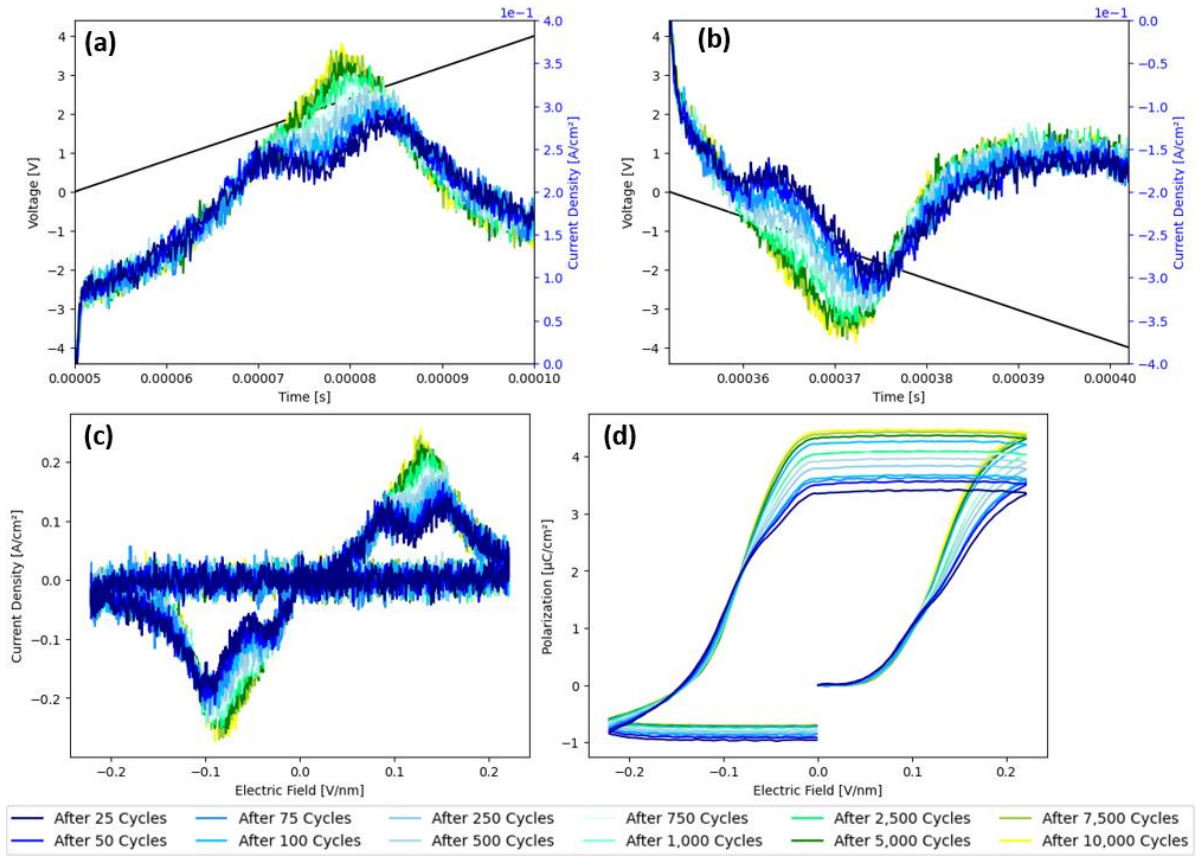


Figure 61. Shows the (a) evolution of a bimodal switching device (23 atomic % Hf) as a function of cycle number, specifically the P pulse response, (b) the N pulse response, (c) the switching current response and (d) the polarization response all as a function of the cycle number.

The bottom W and HZO layer were deposited similarly to the device wafer, but instead of patterning W top electrode caps, half of the sample was covered in a top W layer and the other half uncovered. The orientation of the deposited top W is shown in **Figure 62(a)**. The corresponding EDS and XRR measurements for thickness and chemistry trends are shown in **Figure 62 (b)** and **62(c)**, respectively. The XRD scans across the sample on the W/HZO/W and W/HZO are shown in **Figure 62 (d)** and **Figure 62(e)**, respectively. HfO₂ and ZrO₂ form a solid solution because the Zr⁺⁴ and Hf⁺⁴ ions have very similar size and thus the phases and lattice spacing of the oxides are very similar; for instance, the monoclinic (P2₁/c) ZrO₂ lattice parameter $a = 0.51454\text{nm}$ and the HfO₂ $a = 0.51156\text{nm}$. [16] Thus as ZrO₂ is added to HfO₂ a slight decrease in the associated lattice parameters is expected. As shown in **Figure 62(d)** and **Figure 62(e)**, the peak positions shift to slightly lower 2θ values with increasing ZrO₂. The peaks observed in this work correspond to the orthorhombic (111) and tetragonal (011) (30.7°) planes, along with the monoclinic (111) (31.8°) and (-111) (28.5°). The 2θ values are similar to those observed in previous HZO thin films. [4], [6], [17] These peaks can be seen in **Figure 62(d)** and **Figure 62(e)** along with labels correlating to the expected bulk ZrO₂ peak positions, calculated from the t, o and m phase lattice parameters [16], [18], [19]. The discrepancy between the measured XRD peaks and the referenced ZrO₂ peak locations is attributed to compressive stress in the film, resulting in a decrease in interplanar distance. Correlating the XRD scans to the Hf composition shows an increase in the o(111)/t(011) peak with increasing Zr content concomitant with a decrease in the m-phase.

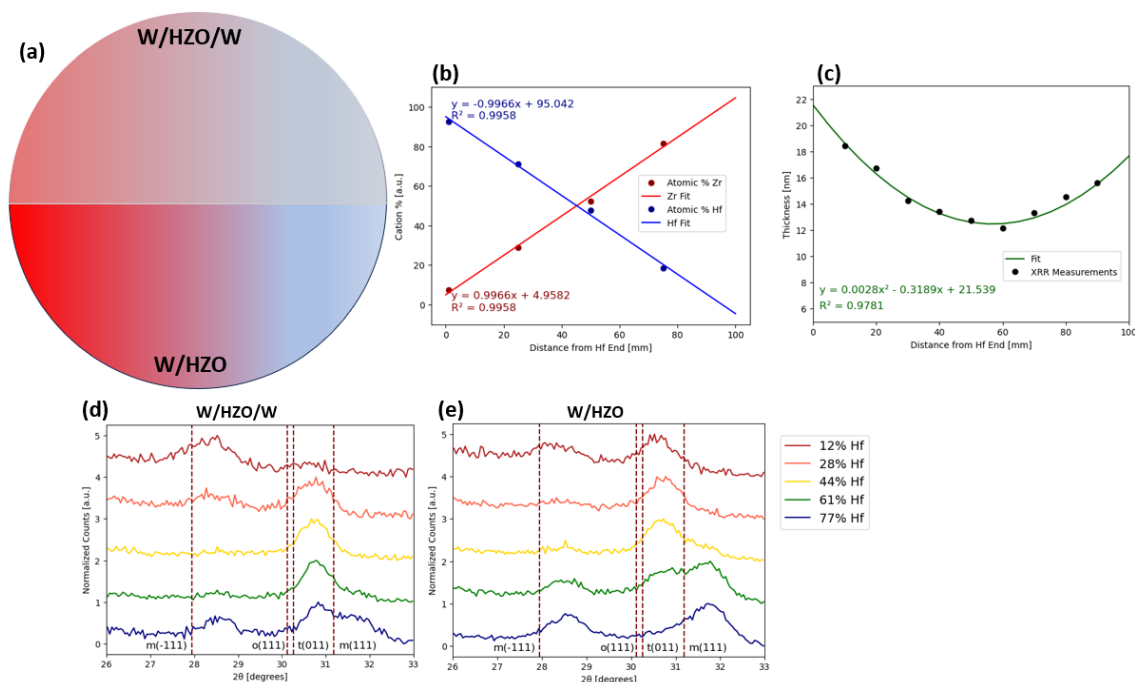


Figure 62. Shows a diagram the second film that was synthesized with half the sample having a W/HZO stack and half a W/HZO/W stack (a), along with the corresponding EDS (b) and XRR (c) measurements. XRD measurements along the center of the wafer on the W/HZO/W half (d) and the W/HZO half (e) are also shown. Peaks correlating to the orthorhombic (o), tetragonal (t), and monoclinic (m) phases are assigned with dashed lines. Note that the XRD scans are offset by +1 normalized count each. The unnormalized plots can be found in **Figure 68**.

At low Hf (< 28% Hf) concentration the m-phase appears re-emerge, specifically on the W/HZO/W geometry. Adding a top W layer appears to decrease the monoclinic phase overall, and specifically decreases the crystallization of the (111) plane at high Hf concentrations. The 1.7% Hf concentration in the W/HZO/W stack shows a peak similar to the m-phase (-111) but does not show its sister m-phase (111) peak. This suggests the HZO film has a preferred orientation likely caused by the thermal stress induced by the W layers due to the difference in coefficient of thermal expansion between the HZO and W during the anneal. Based on **Figure 57**, the XRD scans at 44 and 28% Hf concentrations are within the expected ferroelectric region and these scans show high o(111)/t(011) peaks. The ferroelectric behavior of the 28% Hf region exhibits low ferroelectric polarization and is close to the transition point between the classic ferroelectric and peak splitting behavior. The 44% Hf concentration region also shows low ferroelectric switching. It is expected that the maximum ferroelectric response (35% Hf) would be between these two measurements and exhibit the highest o(111)/t(011) peak. The 61% Hf region in the W/HZO/W geometry is an outlier, in that it exhibits a large o(111)/t(011) peak but is outside the measured ferroelectric region, suggesting that the non-ferroelectric t-phase is the primary contributor to this peak. The 77% Hf peak is dominated by the monoclinic phase and is thus consistent with the electrical measurements that had no ferroelectric behavior.

Conclusions

This work leverages combinatorial sputtering to generate a wide range of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$

chemistries ($\sim 3 < x < 85$) for rapid device property investigation. Magnetron sputtered films demonstrate a cost effective, CMOS compatible method for generating ferroelectric devices. This systematic study of cation composition changes shows a kickoff of ferroelectric behavior at 22% Hf with increasing ferroelectric response and peaks at 38% and disappears at 49%. At lower Hf concentrations ($22 < x < 28\%$), the conventional ferroelectric switching transitions into bimodal peak splitting behavior. The peak splitting originates from either oxygen vacancy driven charge trapping at the active layer interfaces or from an electrically driven tetragonal-orthorhombic phase change. Increased cycling reduces the peak splitting behavior and increases the classic ferroelectric response, suggesting the unifying of the two peaks originates from an increase in the ferroelectric phase from the destruction of oxygen vacancies or from a persisting change from tetragonal to orthorhombic phase. The structure of the HZO in the W/HZO/W system shows decreased monoclinic phase overall compared to W/HZO. The peaks associated with the o, t, and m phase are seen at higher 2θ values compared to referenced ZrO_2 values. This is attributed to compressive strain from the W electrode, reducing the interplanar spacing. The measured ferroelectric region correlates to a high orthorhombic/tetragonal XRD peak. It is expected that the orthorhombic phase is the primary contributor to the ferroelectric response.

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Appendix

Supporting Information

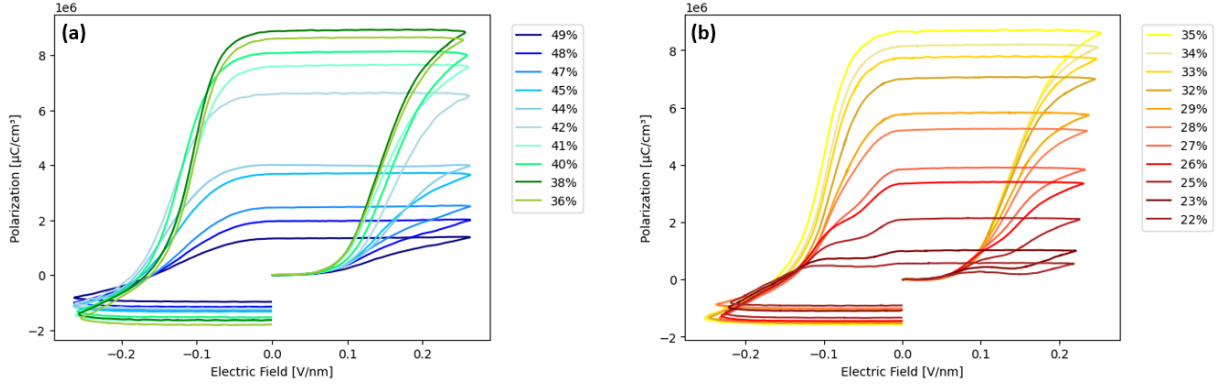


Figure 63. Shows the polarization normalized to thickness for (a) 49-36% Hf and (b) 35-22% Hf devices

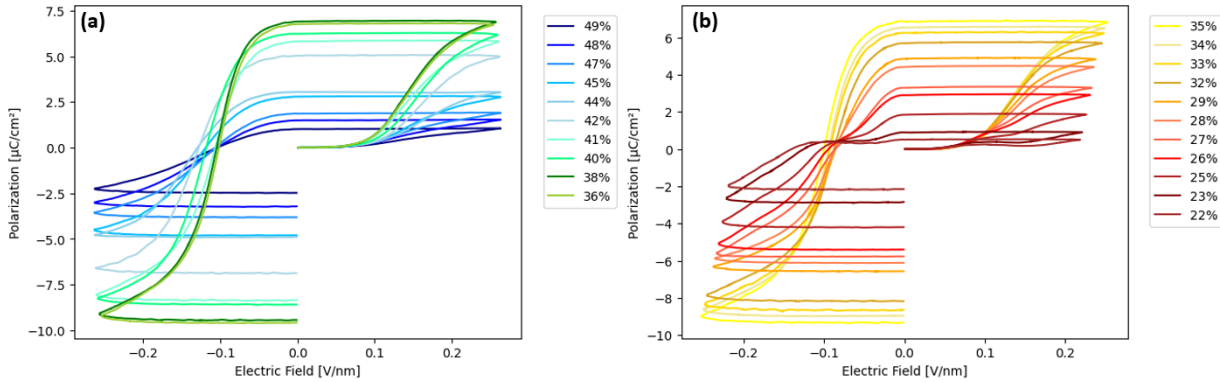


Figure 64. Shows approximate remnant polarization of the (a) 49-36% Hf and (b) 35-22% Hf devices by dividing the initial positive switch by 2.

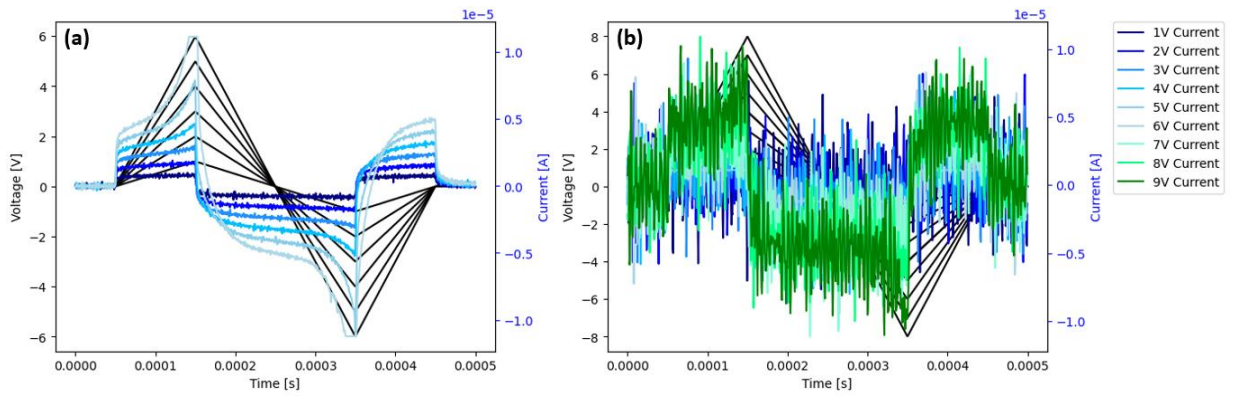


Figure 65. Shows the electrical properties of HZO devices with (a) 81% Hf and (b) 9% Hf

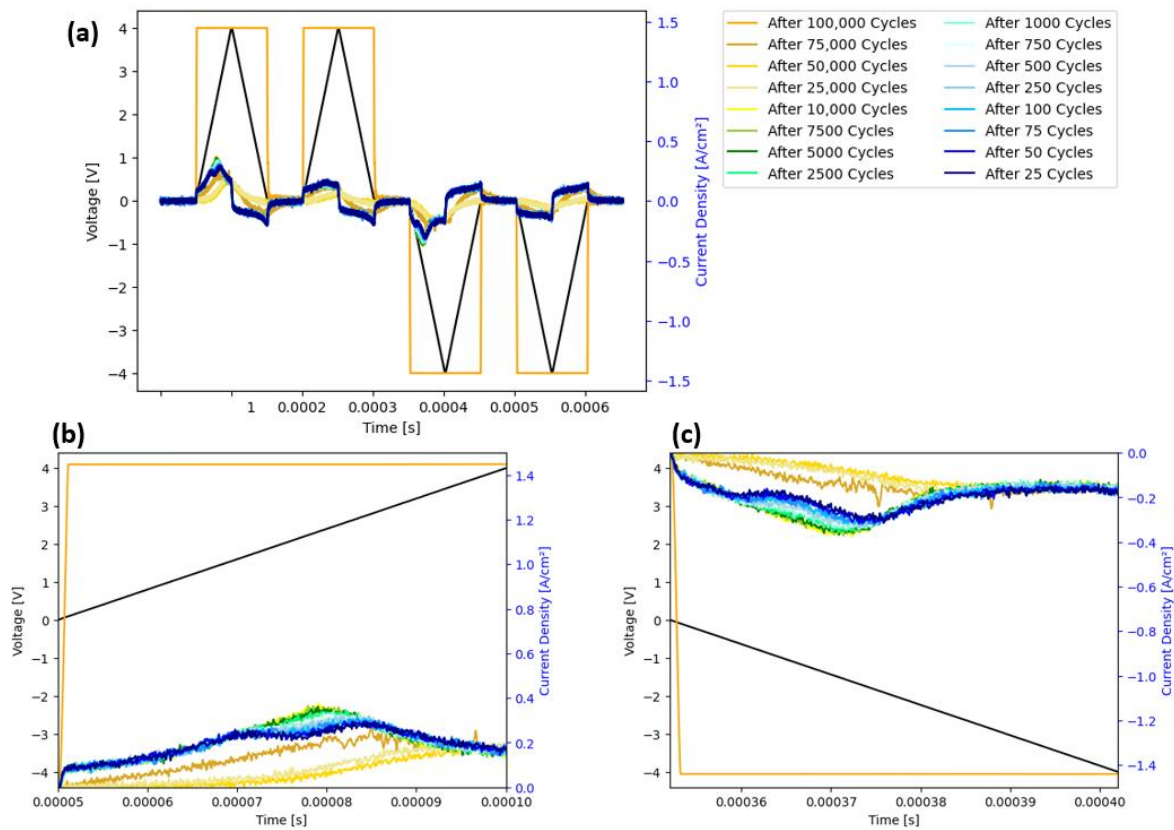


Figure 66. Shows data from **Figure 61** from paper along with breakdown. Time resolved PUND data (a) along with zoomed in plots of the P and N pulse, (b) and (c), respectively.

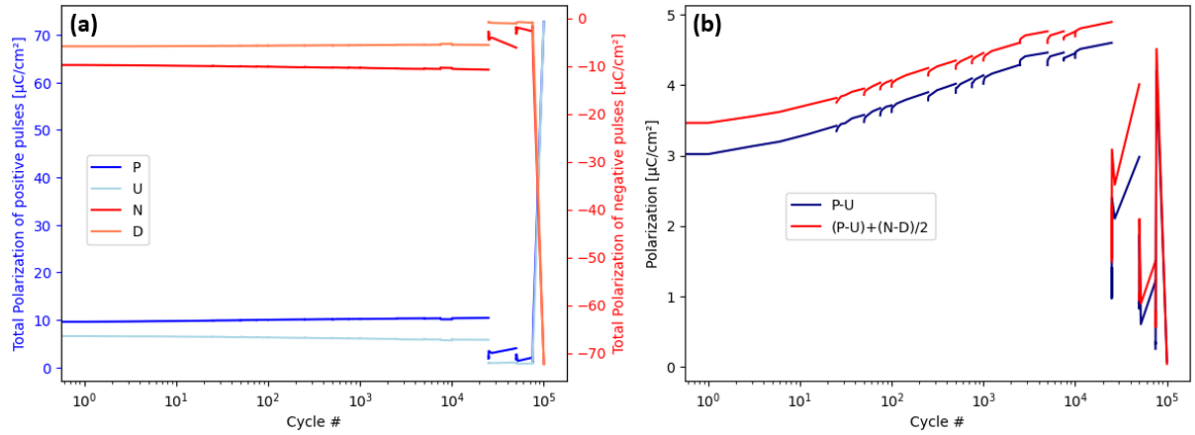


Figure 67. Show polarization from positive and negative pulses calculated from **Figure 61(a)**, along with the average polarization from **Figure 61(b)**

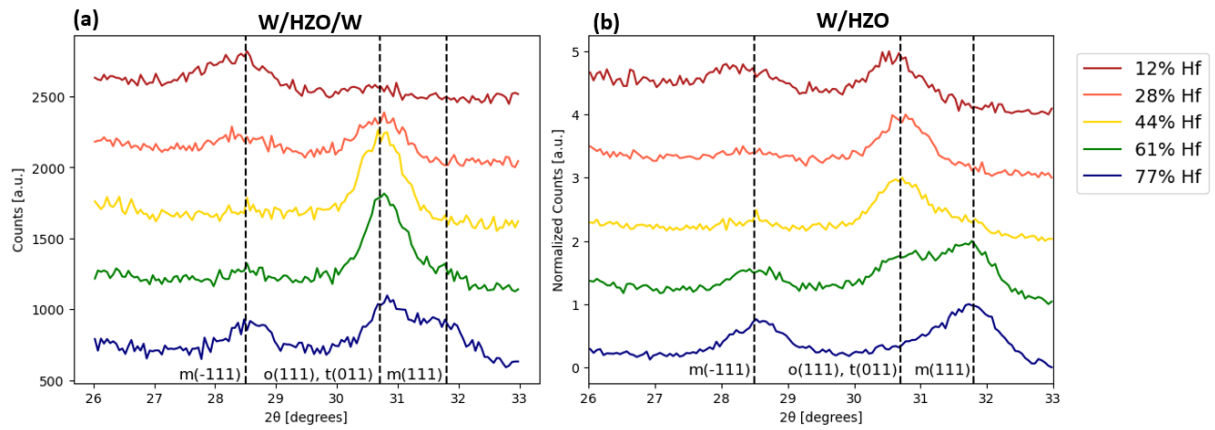


Figure 68. Shows XRD across the HZO chemistry gradient for (a) W/HZO/W film stack and (b) W/HZO film stack.

CONCLUSION

The continued scaling of semiconductor technology, long governed by Moore's Law, is facing fundamental limitations as device dimensions approach atomic scales.

Simultaneously, the global demand for data processing is growing rapidly, with information technology emerging as the fastest-growing consumer of electricity worldwide. These challenges necessitate the development of alternative computing paradigms and novel materials capable of delivering high performance at significantly reduced energy costs. This work explores material innovations in memristive and ferroelectric oxide systems, with a focus on understanding the mechanisms that govern their switching behavior and identifying pathways toward stable, energy-efficient operation.

The switching mechanisms in tantalum oxide (Ta_2O_5) memristive thin films were investigated through a combined experimental approach utilizing Conductive Atomic Force Microscopy (C-AFM) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Kelvin probe force microscopy (KPFM) was also used in tandem with C-AFM to measure the surface potential effects. These techniques enabled direct visualization of ion migration under applied electric fields, revealing three distinct regimes of behavior: (1) charge trapping at low current levels, (2) field-assisted oxygen vacancy migration at moderate bias, and (3) irreversible breakdown due to Joule heating at high current densities. These observations underscore the importance of carefully balancing electric field strength and current in order to access reversible, stable switching mechanisms.

Future optimization of these films will involve tuning the film thickness and chemical composition to decouple field-driven effects from current-induced degradation. In addition, molecular dynamics simulations are proposed to identify the energy thresholds for oxygen and tantalum ion migration, thereby defining the safe operational window for device function.

A combinatorial library of $\text{Zr}_x\text{Ta}_{1-x}\text{O}_y$ was synthesized via combinatorial magnetron sputtering. Systematic variation of the Zr concentration revealed an increase in the bandgap and the formation of deeper electronic trap states due to the mixed valence states of Ta^{5+} and Zr^{4+} . Electrical measurements and depth profiling indicated that switching behavior in this system arises from a combination of charge trapping and gradual ionic migration. At intermediate Zr concentrations ($\sim 30\%$), the devices exhibited maximum ionic mobility, as confirmed by ab initio molecular dynamics simulations, along with pronounced hysteresis and diode-like behavior. These findings suggest that short-term device response is dominated by fast electronic processes, while longer-term cycling induces subtle ionic redistribution that impacts device stability and endurance.

Ferroelectric $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ (HZO) thin films, which were fabricated using a combinatorial sputtering process. These films demonstrated behavior consistent with those produced via atomic layer deposition (ALD), but with significantly reduced processing time and cost. By systematically varying the Hf:Zr ratio and analyzing the resulting phase assemblage, it was shown that increasing Zr content promotes transitions from the monoclinic to orthorhombic and tetragonal phases. In some compositions, bimodal switching behavior

emerged, likely arising from either interfacial charge trapping at oxygen-deficient sites or electric-field-induced structural phase transitions. Device performance was also found to be influenced by stress imposed by metal electrodes, particularly at high Zr concentrations where preferential monoclinic orientation was observed in W/HZO/W stacks.

These investigations demonstrate the critical role of compositional tuning, defect engineering, and interfacial control in optimizing oxide-based resistive and ferroelectric switching devices. By combining experimental characterization with computational modeling, this work provides a framework for designing next-generation memory technologies that are scalable, reliable, and energy efficient. These findings not only contribute to the fundamental understanding of ion-electron interactions in oxide thin films but also support the broader effort to develop alternative computing architectures capable of sustaining technological growth in the post-Moore era.

VITA

Matthew Flynn-Hepford is a doctoral candidate in the Department of Materials Science and Engineering at the University of Tennessee, Knoxville. Matthew is originally from Newport, Pennsylvania. He is the only child of Patricia Flynn and Gary Hepford.

He earned his Bachelor of Science in Materials Science and Engineering from the Pennsylvania State University in 2016, where he also completed a minor in Polymer Science. Following his undergraduate studies, he received a Master of Engineering in Plastics Engineering from the University of Massachusetts Lowell in 2019.

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Matthew has authored and co-authored multiple peer-reviewed publications in journals such as *Macromolecules*, *Journal of Solid-State Chemistry*, *Advanced Electronic Materials* and *Nanomaterials*, with one of his recent works selected for the front cover. He has presented his research at national conferences, including the Materials Research Society meetings. His diverse background in polymers, metals, and electronic materials reflects a multidisciplinary approach to solving complex materials challenges.