Impacts of ion irradiation on HfO2-based resistive random access memory devices

Xiaoli He

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Impacts of Ion Irradiation on HfO$_2$-based Resistive Random Access Memory Devices

by

Xiaoli He

A Dissertation
Submitted to the University at Albany, State University of New York
in Partial Fulfillment of
the Requirements for the Degree of
Doctor of Philosophy

College of Nanoscale Science and Engineering
2013
Abstract

The impacts of ion irradiation on so-called vacancy-change mechanism (VCM) and electrochemical-metallization mechanism (ECM) ReRAM devices based on HfO$_2$ are investigated using various ion sources: H$^+$ (1 MeV), He$^+$ (1 MeV), N$^+$ (1 MeV), Ne$^+$ (1.6 MeV) and Ar$^+$ (2.75 MeV) over a range of total doses ($10^5$ – $10^{11}$ rad(Si)) and fluences ($10^{12}$ – $10^{15}$ cm$^{-2}$). VCM-ReRAM devices show robust resistive switching function after all irradiation experiments. VCM resistive switching parameters including set voltage ($V_{\text{set}}$), reset voltage ($V_{\text{reset}}$), $on$-state resistance ($R_{\text{on}}$) and $off$-state resistance ($R_{\text{off}}$) exhibited, in most cases, modest changes after irradiation. Decreases in forming voltage ($V_f$) and initial resistance ($R_{\text{fresh}}$) of fresh devices were observed after all irradiation experiments on VCM-ReRAM devices with the exception of Ar$^+$ irradiation at the highest fluence ($10^{15}$ cm$^{-2}$). In that case $R_{\text{fresh}}$ increased by an order of magnitude. For VCM-ReRAM devices it was also observed that irradiation beyond a dose threshold of approximately 5 Grad(Si) could induce $off$-$to$-$on$ state transition events. This behavior could lead to errors in a VCM-ReRAM memory system. ECM-ReRAM devices (based on HfO$_2$) were also subjected to ion irradiation. Under proton irradiation ECM-ReRAM devices remained functional, but with relatively large positive variations (20-40%) in $V_{\text{set}}$, $V_{\text{reset}}$ and $R_{\text{on}}$, and large negative variations (~ -60%) in $R_{\text{off}}$. In contrast to VCM HfO$_2$-ReRAMs, ECM-based devices exhibited increased $V_f$ after irradiation, and no $off$-$to$-$on$ transitions were observed. Interestingly, for ECM-ReRAM devices, high-fluence Ar irradiation resulted in a transition of the electrical conduction mechanism associated with the conductive filament forming process from a Poole-Frenkel conduction mechanism (pre-irradiation) to ionic conduction (post-Ar irradiation). ECM-ReRAM
devices irradiated with lighter ions did not exhibit this effect. The different ion irradiation responses of the two types of HfO$_2$-ReRAMs studied originate from their distinct switching mechanisms – vacancy filament switching for VCM-ReRAMs and metal filament switching for ECM-ReRAMs – which respond differently to the irradiation-induced changes in the vacancy/defect densities and crystallite structures in HfO$_2$. SRIM (Stopping and Range of Ions in Matter) modeling was used to roughly estimate the density of irradiation-induced vacancies. These model results correlated well with experimental observations in terms of vacancy defect density thresholds sufficient to impact ReRAM switching behavior. Physical characterization of pre- and post-irradiation ReRAM devices using techniques including XRD, AES, SEM, EDS, and SIMS were also employed to support the modeling and electrical measurements. This work suggests that HfO$_2$-based ReRAM devices are a promising candidate for space and nuclear applications requiring a ‘radiation-hard’ memory technology.
Acknowledgements

I would like to express my deepest appreciation to my research adviser Dr. Robert E. Geer for his continuous support and the considerable efforts he made to make it possible for me to complete my PhD degree. It would certainly have been impossible to succeed without Dr. Geer's tremendous encouragement and invaluable guidance during my thesis research. His strong scientific insight and proficiency in solid-state materials and device physics has guided me in conducting my research in a more professional way. I am also sincerely grateful that Dr. Geer made every effort to support and encourage me to present my work in conferences. Moreover, Dr. Geer has been considerate and supportive personally, and his sense of humor always lightens the dull days. I feel extremely fortunate to have him as my adviser and cannot thank him enough both personally and professionally.

I am truly indebted to my former adviser Dr. Wei Wang, who initially brought me the ReRAM project. His numerous ideas on ReRAM devices stimulated my curiosity. I am grateful to him for opening the door for me to explore the resistive switching mechanism and the radiation effects on ReRAM devices. I would also like to thank my committee members: Dr. Nathaniel Cady, Dr. Mengbing Huang, Dr. Shadi Shahedipour-Sandvik, and Dr. Rebecca Cortez (from Union College) for their support and assistance with this thesis work.

A special thanks goes to SEMATECH who kindly provided the TiN/HfO$_2$/TiN(W) devices, and Dr. Cady along with his research group members – Benjamin Briggs, Jihan Caplong, and Dr. Seann Bishop – for kindly providing the Cu/HfO$_2$/Ni ReRAM devices. Without their support, this project would have not have been complete. I am also
indebted to Dr. Ming Liu and Dr. Yan Wang from the Chinese Academy of Sciences, who provided Pt/HfO$_2$:Cu/Cu ReRAM devices for my proton irradiation study. I am grateful to Dr. Natalya Tokranova for the help of e-beam deposition of HfO$_2$, Dr. Magnus Bergkvist for the deposition of Au nanoparticles, and Dr. Harry Efthathiadis as well as Dr. Sean Teehan for ZnO deposition assistance.

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Finally, I express greatest gratitude and thanks to my family for supporting me through this journey, and I wish them a long, healthy and happy life.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>BCA</td>
<td>Binary Collision Approximation</td>
</tr>
<tr>
<td>BE</td>
<td>Bottom Electrode</td>
</tr>
<tr>
<td>CC</td>
<td>Current Compliance</td>
</tr>
<tr>
<td>CF</td>
<td>Conducting Filament</td>
</tr>
<tr>
<td>CMP</td>
<td>Chemical Mechanical Planarization</td>
</tr>
<tr>
<td>ECM</td>
<td>Electrochemical Metallization</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>FeRAM</td>
<td>Ferroelectric Random Access Memory</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width Half Maximum</td>
</tr>
<tr>
<td>HRS</td>
<td>High Resistant State</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>IL</td>
<td>Insertion Layer</td>
</tr>
<tr>
<td>LET</td>
<td>Linear Energy Transfer</td>
</tr>
<tr>
<td>LRS</td>
<td>Low Resistant State</td>
</tr>
<tr>
<td>MIM</td>
<td>Metal-Insulator-Metal</td>
</tr>
<tr>
<td>MOS</td>
<td>Metal-Oxide-Semiconductor</td>
</tr>
<tr>
<td>MRAM</td>
<td>Magnetoresistive Random Access Memory</td>
</tr>
<tr>
<td>NIEL</td>
<td>Nonionizing Energy Loss</td>
</tr>
<tr>
<td>NVM</td>
<td>Nonvolatile Memory</td>
</tr>
<tr>
<td>PCRAM</td>
<td>Phase Change Random Access Memory</td>
</tr>
<tr>
<td>PKA</td>
<td>Primary Knock-on Atom</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>ReRAM</td>
<td>Resistive Random Access Memory</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>SCLC</td>
<td>Space Charge Limited Current</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SRIM</td>
<td>Stopping Range of Ions in Matter</td>
</tr>
<tr>
<td>TAT</td>
<td>Trap-assistated Tunneling</td>
</tr>
<tr>
<td>TCM</td>
<td>Thermochemical Memory</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TID</td>
<td>Total Ionizing Dose</td>
</tr>
<tr>
<td>VCM</td>
<td>Valence Change Memory</td>
</tr>
<tr>
<td>WKB</td>
<td>Wentzel-Kramers-Brillouin</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-rad Diffraction</td>
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<tr>
<td>XRF</td>
<td>X-ray Fluorescence</td>
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1. Introduction

Si-based flash memory currently dominates nonvolatile memory (NVM) technology, due to its high density and low fabrication cost. However, flash memory devices also suffer from several serious limitations, such as (for NAND flash memories) low endurance ($10^4$ – $10^5$ cycles), long erase time (~ ms), and high operating voltage (~ 15 V) [1, 2]. In addition, the scalability of flash memory technology is also limited [1]. Therefore, new NVM concepts are actively explored to potentially replace flash memory devices [1, 2]. These include ferroelectric random access memory (FeRAM) [3, 4, 5], magnetoresistive random access memory (MRAM) [6, 7], and phase change random access memory (PCRAM) [8, 9, 10]. Recently, resistive random access memory (ReRAM) devices based on electrically switchable resistance have attracted much attention and become one of the more promising NVM candidates [11, 12, 13, 14], and are also the topic of this dissertation.

A ReRAM cell generally consists of a capacitor-like metal-insulator-metal (MIM) structure, as shown in Figure 1.1. In general, the 'M' layers are comprised of conventional metals or conducting non-metals; the 'I' layer is comprised of insulating or resistive materials, including a large variety of transition metal oxides, chalcogenides or organic compounds. ReRAM devices can be electrically switched between at least 2 different resistance states: a high resistance state (HRS or off-state, with a high resistance $R_{\text{off}}$) and a low resistance state (LRS or on-state, with a low resistance $R_{\text{on}}$). In other words, a ReRAM device in its off-state can be set to an on-state by applying a programming (or set) voltage. Conversely, it can be reset from an on-state to an off-state when an erase (or reset) voltage is applied. The resistance of the cell is measured by a small bias voltage
which does not perturb the state. Multi-level switching with more than 2 resistance states has been realized for storage of multiple bits per cell [15, 16, 17] when using appropriate voltage pulses or current compliances, which is one of the tempting properties of ReRAMs. Excellent and reliable resistive switching performance has been reported in the literature for ReRAM devices. High $R_{\text{off}}/R_{\text{on}}$ ratios (~$10^7$), ultrafast programming speeds (5 ns), long retention times (> 10 years) and good endurance ($10^{15}$ cycles) have been reported [16, 18, 19]. These performance parameters, taken together with an attractive potential for device scaling and a high compatibility with CMOS technologies, make ReRAM devices a promising candidate for next generation NVMs.

![Schematic view of the MIM structure of a ReRAM cell.](image)

**Figure 1.1 Schematic view of the MIM structure of a ReRAM cell.**

One important application of NVM is for on-board memory for the aerospace and nuclear industries, which demand robust operation under various harsh radiation environments. Thus, it is critical to investigate the impact of radiation, such as energetic charged particles and photons, on ReRAM devices. It is well known that radiated particles deposit kinetic energy (including ionizing energy and nonionizing energy [20]) into the target material as it is traversed. The energy deposited in the target material can induce a variety of effects such as irradiation-induced changes in defect concentrations and/or microstructure of the target material. Such changes can substantially impact the resistive switching mechanisms of ReRAM devices and, hence, eventually affect the
resistive switching performance. The purpose of this work is to investigate the impacts of ion irradiation on two types of HfO$_2$-based ReRAM devices with distinct switching mechanisms so as to compare the relative sensitivity of those switching mechanisms as a function of ion mass, fluence, and dose. This understanding will also address questions of ReRAM radiation hardness for future aerospace space applications.

1.1 Introduction to resistive random access memories

1.1.1 ReRAM unipolar and bipolar resistive switching

The resistive switching behavior of a ReRAM device involves SET and RESET processes. During the SET process, the current is limited to a preset current compliance (CC) and the ReRAM device is set from its off-state to an on-state when the initial low current approaches the current compliance at the set voltage ($V_{set}$). The device then remains in the on-state until a RESET process is performed. During the RESET process, the device is reset to its off-state at a reset voltage ($V_{reset}$) at which point the high current drops back to a low current value. Figure 1.2 shows the resistive switching schemes of the SET and RESET processes for a prototypical ReRAM device. In terms of resistive switching with respect to the applied electrical polarity, ReRAM devices have 2 main switching modes. One is unipolar resistive switching wherein the SET and RESET processes are performed with the same voltage polarity (Figure 1.2(a)). The other is bipolar resistive switching, in which SET is accomplished at one voltage polarity and RESET occurs with a reversed voltage polarity (Figure 1.2(b)). It should be noted that, for an as-fabricated ReRAM device, a 'forming' process is typically required to switch the pristine off-state into a switchable on-state by applying a high voltage stress, the so-called
forming voltage \( V_f \). After the forming process, ReRAM devices can be set and reset repeatedly at a much lower threshold voltage, respectively.

![Diagram of I-V schemes](image)

**Figure 1.2** The basic I-V schemes of unipolar switching (a), and bipolar switching (b). "CC" is the current compliance, which is a fixed current for the SET process.

Nonpolar resistive switching has also been reported wherein resistive switching of ReRAM devices can be alternated between unipolar and bipolar. Note that Figure 1.2 only describes the resistive switching schemes with respect to the current and switching direction.

These resistive switching phenomena have been observed in various types of materials, such as transition metal oxides \([2, 12]\), chalcogenides \([21, 22, 23, 24]\), and organic compounds \([25, 26, 27]\). Depending on the specific ReRAM system, the I-V curves may vary significantly and the switching may be unipolar, bipolar or nonpolar. Reference [28] presents a summary of ReRAM devices with a wide variety of oxides and electrode materials, which exhibit either unipolar or bipolar resistive switching behavior.

### 1.1.2 ReRAM switching mechanisms

The resistive switching mechanism associated with ReRAM devices is strongly dependent on the specific oxide and electrode materials utilized in its fabrication and remains an active area of research. Various resistive switching mechanisms have been
proposed. These include space charge limited current (SCLC) [29, 30], trap charging/discharging [31], and the redox-based formation and rupture of conducting filaments [14, 32]. In particular, the redox-related filamentary switching mechanism has gained considerable attention and it is reviewed in detail by R. Waser and coworkers [11, 13, 32]. In their taxonomy, resistive switching is classified into three main categories based on the switching mechanism: thermochemical mechanism (TCM); electrochemical metallization mechanism (ECM); and valence change mechanism (VCM). TCM effects exist in all transition metal oxides; one in which, NiO-based ReRAM, has been well studied [33, 34] and filaments (triggered thermally) have been directly observed by conducting AFM [35].

When applying a sufficient voltage in an ECM-ReRAM device, the electrochemically active metal electrode is dissolved into metal ions that migrate towards the inert electrode under a high electric field where they undergo reduction back to a ‘metal 0’ state leading to cathodic deposition. This process results in formation of a metallic filament. Formation/rupture is driven by similar electrochemical reactions that results from voltage cycling. SET is completed when a metallic bridge forms inside the oxide and connects both electrodes. RESET is considered an opposite process to SET where local oxidation ruptures the conducting pathway along the filament. Metallic filaments have been experimentally observed by high resolution transmission electron microscopy (HRTEM) [18, 21, 36], as shown an example in Figure 1.3 [18] where a Ag filament was formed in a ZnO:Mn layer.
Figure 1.3 HRTEM image of Ag filament inside Mn doped ZnO layer. Adapted with permission from Ref. [18]. Copyright 2009 American Chemical Society.

In VCM-ReRAM, oxygen ion related defects, typically positively charged oxygen vacancies, play a critical role in resistance switching. An enrichment or a depletion of oxygen vacancies can affect the valence state of the transition metal cations in the metal oxide layer, which may result in substantial changes in local electronic conductivity. There are 2 fundamentally different scenarios of VCM-ReRAM resistive switching. Those are the filamentary switching scenario and the area-distributed switching scenario. In the former scenario, oxygen vacancies accumulate into vacancy chains under an electric field, building up a conducting filament inside the oxide. In the latter scenario, resistance switching occurs homogeneously over the entire area of the electrode of the memory cell. Devices with the latter switching scenario are also known as memristors. In either case, oxygen vacancies are created and drift towards the cathode and/or O$_2^-$ ions drift towards the anode, where O$_2$ gas may be generated according to the oxygen exchange reaction.
\[ \text{Oo} \leftrightarrow \frac{1}{2} \text{O}_2 (g) + \text{Vo}^{2+} + 2e \tag{1.1} \]

Where Oo represents the oxygen ions at regular lattice sites and Vo\(^{2+}\) denotes the doubly charged oxygen vacancies. The oxygen gas formation and the physical deformation in the device due to O\(_2\) outgassing have been experimentally observed during electroforming and SET processes for TiO\(_2\)-based devices [37, 38]. Figure 1.4(a) shows a hole formed inside TiO\(_2\) when a negative forming voltage was applied to the top electrode [37]. Oxygen vacancy filament formation was also experimentally demonstrated in TiO\(_2\) (Figure 1.4(b)) [39], and other oxide-based ReRAM devices (Figure 1.4(c)) [40].

The resistive switching mechanism is material dependent. ReRAM devices with distinct material sets – or similar material sets with different dopants – may exhibit distinct switching mechanisms or conductive filament formation pathways. For example, switching in HfO\(_2\)-based ReRAMs with TiN or Pt electrodes was reported to be based on formation and rupture of a vacancy filament, which was enhanced by thermal heating [41, 42]. In contrast, the resistive switching in HfO\(_2\)-based ReRAMs with Cu anode and Pt cathode was attributed to the formation and rupture of Cu filaments via electrochemical reactions [16, 43]. Table 1.1 lists HfO\(_2\)-based ReRAMs reported in the past several years, with various switching types and various proposed switching mechanisms.

Indeed, HfO\(_2\)-based ReRAMs are particularly interesting due to their great performance potential – set/reset voltages less than 1 V, good endurance (> 10\(^8\) cycles) and fast switching speeds as low as 5 ns. In this work, we are focusing on 2 types of
HfO$_2$-based ReRAM devices – VCM-type (TiN/HfO$_2$/TiN(W)) and ECM-type (Pt/HfO$_2$:Cu/Cu and Cu/HfO$_2$/Ni).

Figure 1.4 (a) Atomic force micrograph of physical deformation after forming of Pt/TiO$_2$/Pt ReRAM device with negative bias applied to the top electrode. Adapted with permission from Ref. [37], copyright 2009 IOP Publishing Ltd. (b) High-resolution TEM image of a Ti$_4$O$_7$ conical-shape nanofilament after SET. Adapted by permission from Macmillan Publishers Ltd: Nature Nanotechnology [39], copyright 2010. (c) Cr XRF map, showing vacancy filament formed in Cr-doped SrTiO$_3$ single crystal. In the color scale, red represents oxygen vacancies in the Cr octahedral position of the perovskite cell. Adapted with permission from Ref. [40], copyright 2007 Wiley-VCH.
Table 1.1 HfO$_2$-based ReRAMs with various electrodes. BE and TE represent the bottom and top electrodes sandwiching the HfO$_2$ layer, respectively. SM represents the switching mode, U and B letters in the table denotes the unipolar and bipolar switching modes respectively. NS and IL are an abbreviation of “Not Specified” and “Insertion Layer”.

<table>
<thead>
<tr>
<th>BE</th>
<th>TE</th>
<th>Thickness (nm)</th>
<th>Device Size</th>
<th>SM</th>
<th>$V_{set}$/$V_{reset}$ (V)</th>
<th>Speed</th>
<th>Endurance</th>
<th>Mechanism</th>
<th>Remarks</th>
<th>Ref</th>
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<tr>
<td>Pt</td>
<td>TiN</td>
<td>5</td>
<td></td>
<td>B</td>
<td>1.8/-1</td>
<td>~ 10ns</td>
<td>$\sim 10^6$</td>
<td>Vo CF</td>
<td>Al$_2$O$_3$ IL Gd-doped</td>
<td>44</td>
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<tr>
<td>Pt</td>
<td>TiN</td>
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<td>B</td>
<td>0.89/-0.7</td>
<td>~ 1µs</td>
<td>NS</td>
<td>Vo CF</td>
<td>Ti IL, 1T1R</td>
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<td>B</td>
<td>1.5/-1.4</td>
<td>~5ns</td>
<td>$&gt;10^6$</td>
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<td>TiN</td>
<td>TiN</td>
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<td>$1\times1$ µm$^2$</td>
<td>B</td>
<td>1/-1</td>
<td>DC</td>
<td>$10^3$</td>
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<td>TiN</td>
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<td>3 mm$^2$</td>
<td>U</td>
<td>2.4/-1.7</td>
<td>DC</td>
<td>NS</td>
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<td>TiN</td>
<td>TiN</td>
<td>5 – 7</td>
<td>$2\times10^{-3}$ cm$^2$</td>
<td>B</td>
<td>0.5/-1</td>
<td>DC</td>
<td>$&gt;10^6$</td>
<td>Vo CF</td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>TiN</td>
<td>Au</td>
<td>27</td>
<td></td>
<td>U</td>
<td>3/1.5</td>
<td>80ns(set)</td>
<td>120ns(reset)</td>
<td>&gt;100</td>
<td>CF</td>
<td></td>
</tr>
<tr>
<td>TiN</td>
<td>W</td>
<td>5</td>
<td>$1\times1$ µm$^2$</td>
<td>B</td>
<td>0.5/-1/0.4 to -0.5</td>
<td>200ns</td>
<td>$&gt;10^8$</td>
<td>Vo CF</td>
<td>Zr IL</td>
<td>50</td>
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<tr>
<td>Pt</td>
<td>Au</td>
<td>10</td>
<td>2mm (D)</td>
<td>B</td>
<td>4/-1.5 to -3.5</td>
<td>DC</td>
<td>NS</td>
<td>Vo CF</td>
<td></td>
<td>51</td>
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<tr>
<td>Pt</td>
<td>Pt</td>
<td>10, 20, 30</td>
<td>$4.7\times10^7$ cm$^2$</td>
<td>B</td>
<td>1.7 to 4/-0.7 to -1</td>
<td>DC</td>
<td>$&gt;140$</td>
<td>Vo or metal CF</td>
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<tr>
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<td>Cu</td>
<td>20</td>
<td>100×10 0 µm$^2$</td>
<td>B</td>
<td>1.35/-0.75</td>
<td>DC</td>
<td>$&gt;120$</td>
<td>Cu CF</td>
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<tr>
<td>Pt</td>
<td>Cu</td>
<td>30</td>
<td>100 µm (D)</td>
<td>B</td>
<td>2/-1.8</td>
<td>DC</td>
<td>NS</td>
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<tr>
<td>Pt</td>
<td>Cu</td>
<td>40</td>
<td>9-900 µm$^2$</td>
<td>U/B</td>
<td>4/2</td>
<td>10ns(set)</td>
<td>100µs(reset)</td>
<td>&gt;100</td>
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<td>P$^+$-Si</td>
<td>Cu, Ni</td>
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<td>100×10 0 µm$^2$</td>
<td>U/B</td>
<td>4/1</td>
<td>DC</td>
<td>NS</td>
<td>Cu CF, Ni CF</td>
<td></td>
<td>55</td>
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<tr>
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<td>B</td>
<td>5.1/-1.2</td>
<td>DC</td>
<td>NS</td>
<td>Ni CF</td>
<td></td>
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<td>30</td>
<td>$10^4$ cm$^2$</td>
<td>U/B</td>
<td>1-5/0.5-1</td>
<td>&lt;1 µs</td>
<td>$&gt;150$</td>
<td>Ni CF</td>
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<td>p$^+$-Si</td>
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<td>4.2</td>
<td>NS</td>
<td>U</td>
<td>1.2/0.4</td>
<td>~30ns(reset)</td>
<td>$&gt;10^6$</td>
<td>Local Joule-heat-induced redox of NiO$_x$</td>
<td></td>
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<tr>
<td>n$^+$-Si</td>
<td>Ni</td>
<td>3</td>
<td>5625-99225 µm$^2$</td>
<td>U</td>
<td>1.9-2.32/1.1-1.62</td>
<td>50ns</td>
<td>$&gt;10^5$</td>
<td>Local Joule-heat-induced redox of NiO$_x$</td>
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<tr>
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<td>TiN</td>
<td>5-20</td>
<td>100×10 0 µm$^2$</td>
<td>U/B</td>
<td>-1/-0.5</td>
<td>DC</td>
<td>$&gt;10^4$</td>
<td>Ni CF</td>
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1.2 Irradiation basics and effects

1.2.1 Irradiation basics

Irradiation is a process whereby energetic particles travel in a straight line through a medium, depositing energy to the material. This is of particular concern when the media are comprised of fabricated devices, such as solid-state nanoelectronics, that may undergo operational impact from the energy deposited. The types of radiated particles of concern are photons, electrons, protons and heavy ions, which can be found in various radiation environments. In general, radiation environments include space radiation environments, high-energy physics experiment environments, nuclear reactor environments, terrestrial and man-made environments, and processing-induced radiation environments [61, 62, 63]. Each of these environments is characterized by its own spectrum of particles and corresponding energy distributions. For example, the trapped radiation belts surrounding the Earth (Van Allen belts) consists mainly of protons from ~keV up to 100s MeV in energy and electrons up to a few MeV, as well as a small portion of heavy ions with relatively low energy. However in general, the concentration, type and energy of particles present in space radiation environments vary significantly with altitude, angle of inclination, and time with/without solar activities. Detailed discussion on radiation environments can be found in Ref. [61, 62, 63].

The amount of damage done to a solid-state nanoelectronic device by ionizing radiation is closely related to the amount of energy deposited into the constituent materials. This is referred to as the absorbed dose or total ionizing dose (TID). The SI unit of radiation absorbed dose is J/kg, which is given the special name Gray (Gy),
representing the amount of radiation required to deposit 1 joule of energy in 1 kilogram of any kind of matter. The rad (radioactivity absorbed dose), is the corresponding traditional unit which is 0.01 J deposited per kg and thus has the relation: 1 Gy = 100 rad = 1 J/kg. As the unit “rad” is still an active working unit for most published papers in radiation effects and also for current medical practice, it is also used in this work even though Gray is the SI unit. Since the absorbed dose depends on the material of interest, the specific material should always be referenced in parentheses directly following the name of the unit, e.g. rad(Si). In this work, Si is used as the reference material to characterize the radiation absorbed dose for the ReRAM devices, thus with the TID unit of rad(Si).

Absorbed dose rate (or dose rate) is the time rate of change of the absorbed dose, in the unit rad/s or Gy/s. On the other hand, flux (also known as fluence rate) is the number of particles passing through some defined zone per unit time, with the unit: cm$^{-2}$s$^{-1}$; while fluence is a term for radiation exposure dose, which is the time-integrated flux of photons or particles with the unit cm$^{-2}$.

### 1.2.2 Ion irradiation effects on dielectrics

A single energetic charged particle penetrating a target material loses its energy to the target material, causing two main effects – ionization and displacement damage. The ionization energy loss results in generation of electron-hole pairs along the ion track, as demonstrated schematically in Figure 1.5, in the material of interest, which in the case of ReRAM devices are primarily the insulating dielectrics. The amount of this ionizing energy deposited by an incident particle per unit of track length is expressed in terms of its “stopping power” in units of keV/μm, or its linear energy transfer (LET) in units of
MeV/mg-cm$^2$. The absorbed ionizing dose is proportional to the integral of the product of the particle fluence and the stopping power over the specimen thickness.

Figure 1.5 Schematic representation of a single ionizing particle penetrating a dielectric material, creating an ionization track with electron-hole pairs.

Along with the electron-hole generation process, chemical bonds in the oxide structure may be broken. Some of these bonds may reform when the electrons and holes recombine, while others may remain broken and give rise to electrically active defects that can then serve as trap sites for carriers or interface traps leading to an increase in the number of bulk or interface traps [64]. The fraction of electron-hole pairs that escape recombination is called the electron-hole yield, which can then be trapped inside the oxide bulk leading to a net charge build-up or some of the electrons or holes may move to the interface through hopping process creating interface traps. In addition, the defects induced by irradiation may themselves migrate in the strained region near the interface resulting in formation of interface traps [64]. All these effects are also material dependent. For instance, ionization can lead to a net positive charge build-up in irradiated SiO$_2$ by hole trapping [64], whereas net negative trapping is resulted in HfO$_2$ by trapping a significant amount of electrons [65, 66]. As the number of electron-hole pairs generated is directly proportional to the TID, the total ionizing damage is also roughly proportional
to the TID. These total dose effects can degrade or permanently damage electronic devices. For example, in MOS transistors, the radiation-induced charge build-up can shift the threshold voltage, and the radiation-induced interface traps cause a degradation in mobility of the carriers in the channel leading to a decrease in gain [64].

While a portion of the energy of the incident particle is given up to ionization, the rest of the energy loss contributes to the displacement damage – the other main radiation effect in electronic materials. This portion of energy is referred to as nonionizing energy loss (NIEL). Displacement is introduced when an energetic incident charged particle transfers sufficient energy (as long as the imparted energy is greater than the threshold energy for displacement, usually 5 – 30 eV for most electronic materials [63]) to knock out the atom in the target material from its lattice site to an interstitial site creating a vacancy at the same time [67]. The atom displaced is the so-called primary knock-on atom (PKA) or primary recoil atom. If the PKA gains sufficient energy, it can further displace other atoms creating secondary recoils, as well as further ionization, and in such a manner a collision cascade can be resulted with large defect clusters, as seen the schematic in Figure 1.6.
Various types of defects can occur due to the displacement damage, such as vacancy-interstitial pairs (also called Frenkel pairs), larger local groupings of vacancies or interstitials, defect-impurity complexes, point defects, dislocations, or defect clusters. In particular, radiation-induced defects generate deep and shallow level traps in the material that in turn affect device electrical properties [63]. Thus, radiation-sensitive electronic components used in space usually require shielding, which tends to be heavy and can significantly increase the launch cost of a satellite or a spacecraft.

In general, the manner in which ionizing radiation interacts with solid materials depends on the type, kinetic energy, mass and charge state of the incoming particle and the mass, atomic number and density of the target material. Each device system has to be considered carefully.

1.3 Dissertation overview

The purpose of this research is to investigate the impacts of ion irradiation on two types (vacancy-type (VCM) and electrochemical-type (ECM)) of HfO$_2$-based ReRAM devices. This approach will enable a comparative analysis of the effect of irradiation and
irradiation-induced defects on two distinct resistive switching mechanisms and provide quantitative empirical data on the efficacy of specific ReRAM devices for future applications in various radiation environments. Chapter 2 presents an overview of the fabrication and characterization of n⁺-Si/HfO₂/Pt ReRAM devices and reviews their doping-enhanced resistive switching performance. In addition, electrical test results and resistive switching models are presented for the two types of HfO₂-based ReRAM devices investigated: VCM-type TiN/HfO₂/TiN and TiN/HfO₂/W ReRAM devices; and ECM-type Pt/HfO₂:Cu/Cu and Cu/HfO₂/Ni ReRAM devices. Lastly, the experimental method for radiation bombardment of all HfO₂-based ReRAM devices is also described.

Chapter 3 and Chapter 4 present and review the impacts of light-ion irradiation (proton and helium) and heavy-ion irradiation (Nitrogen, Neon, Argon), respectively, of the 2 types of ReRAM devices followed with analyses and discussion of the impacts of the irradiation relative to the resistive switching models for each type. Also, a comparative analysis of irradiation responses between VCM and ECM ReRAM devices is summarized in each chapter.

Chapter 5 compares the results of light-ion and heavy-ion radiation on both types of VCM and ECM devices in terms of static R_{off} and static R_{on}, V_f and R_{fresh}, with respect to total ionizing doses.

The final chapter (Chapter 6) summarizes the important results of this research and suggestions for further research.
1.4 References


2. Preparation and Characterization of HfO$_2$-based ReRAM devices

As one of the potential advantages of ReRAM devices is high scalability, the memory stack has to become thinner and smaller in size, yet at the same time maintain or achieve superior resistive switching performance including large memory windows, low power consumption, high endurance, and good retention. This chapter introduces the two types of HfO$_2$-based ReRAM devices – VCM (vacancy-type) n$^+$-Si/HfO$_2$/Pt, TiN/HfO$_2$/TiN or W, in section 2.1 and ECM-type (electrochemical-type) Pt/HfO$_2$:Cu/Cu, Cu/HfO$_2$/Ni in section 2.2. Each description is followed by a discussion of the respective resistive switching models. In section 2.3, the experimental method for radiation bombardment of all HfO$_2$-based ReRAM devices is described. Note to the reader: The VCM n$^+$-Si/HfO$_2$/Pt devices investigated in this work did not exhibit sufficiently stable or repeatable ReRAM performance to warrant investigation with respect to ion irradiation. An overview of the VCM n$^+$-Si/HfO$_2$/Pt ReRAM device structure and resistive switching performance is included, however, for purposes of comparison with VCM and ECM ReRAM devices that were deemed suitable.

Note that the various VCM and ECM-type HfO$_2$-based ReRAM devices investigated for this dissertation were fabricated with varying electrode or stack configurations (e.g. HfO$_2$ layer thickness). These variations reflected the availability of fabricated devices. However, there is no expectation from a technical vantage point that these configurational differences (other than the overall switching mechanism) would manifest distinct responses to ion irradiation. For example, HfO$_2$ film thickness is not expected to substantially affect ReRAM response to ion irradiation since the switching volume at the terminus of the conducting filament is relatively insensitive to HfO$_2$ film thickness. This
assumption was validated by the experimental results – especially the global ion irradiation threshold behavior observed for VCM devices and documented in Chapter 5.

### 2.1 VCM-type HfO$_2$-based ReRAM devices

#### 2.1.1 Improvement of resistive switching performance of n$^+$-Si/HfO$_2$/Pt ReRAM devices

Resistive switching memory devices (about 800 µm in diameter) were fabricated on an n$^+$-Si wafer after a chemical cleaning in 5% HF and H$_2$SO$_4$:H$_2$O$_2$ (3:1) solutions. A 30 nm layer of HfO$_2$ was deposited by electron beam evaporation using a Hf target in O$_2$ atmosphere at room temperature, followed by rapid thermal annealing at 400 °C. Pt top electrodes of 100 nm thick were then deposited by electron beam evaporation.

Previous studies have shown that introducing external defects or traps could improve resistive switching performance in such systems [1]. In this study, doping of the HfO$_2$ was investigated to introduce oxygen vacancies to improve resistive switching properties. Our approach was to use Hf-doping to modify the HfO$_2$ stoichiometry. In addition to the Hf-doping approach, we also doped HfO$_2$ with Au nanoparticles to introduce additional defects at the interface between Pt and HfO$_2$ for resistive switching improvement [2].

Hf doping was realized by depositing 3 nm of Hf in the absence of O$_2$ flow at a point midway through the HfO$_2$ deposition process. For Au doping, HfO$_2$ surfaces were incubated in a solution of citrate-stabilized Au nanoparticles (80 nM, ~5 nm) for 30 min, followed by a rinse and N$_2$ drying. Figure 2.1 shows the schematic structure of the 3 types of n$^+$-Si/HfO$_2$/Pt ReRAM devices. Sample morphology and composition were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and x-ray photoelectron spectroscopy (XPS). Electrical measurements utilized a Keithley 4200 characterization system.
Figure 2.1 Schematic HfO$_2$-based devices: (a) undoped HfO$_2$, (b) Hf-doped, (c) Au-doped.

Figure 2.2(a) displays a SEM image of the cross-section of a HfO$_2$:Au device. Cross-sections of undoped HfO$_2$- and HfO$_2$:Hf-based ReRAM devices were similar (not shown). The top layer in Figure 2.2(a) is Pt which was deposited for protection from the focused ion beam during cross-section. The measured thickness of the Pt top electrode layer is ~140 nm, and the HfO$_2$ layer is ~27 nm thick. The surface of a non-doped HfO$_2$-based ReRAM device is shown in Figure 2.2(b), where Figure 2.2(b-1) is the surface image on HfO$_2$ and Figure 2.2(b-2) is taken at the Pt top electrode surface. During the experiment, it was found that HfO$_2$:Hf-based ReRAM devices exhibited similar surface morphologies as shown in Figure 2.2(b). Stress-induced cracking of the Pt layer was observed for the device shown in Figure 2.2(b-2). Figure 2.2(c) shows the surface images of Au-doped HfO$_2$ ReRAM devices, where Figure 2.2(c-1) shows the HfO$_2$ surface and Figure 2.2(c-2) shows the Pt top electrode surface. The micrograph in Figure 2.2(c-1) reveals Au nanoparticles at the HfO$_2$ surface with an average diameter about ~5 nm and density of 625 /µm$^2$. 
Figure 2.2 SEM images of (a) cross-section of HfO$_2$-based ReRAM devices, (b-1) HfO$_2$ surface, and (b-2) Pt top electrode, for non-doped HfO$_2$-based devices; (c-1) HfO$_2$ surface, and (c-2) Pt top electrode, for Au-doped devices.

The cross-sections of ReRAM devices were investigated with TEM. Figure 2.3(a) is taken from a HfO$_2$:Au-based ReRAM device. For that device the Pt top electrode layer thickness is ~147 nm and the HfO$_2$ layer thickness is ~22 nm. Au nanoparticles in this sample were difficult to distinguish at the interface of Pt and HfO$_2$ due to low contrast with Pt. A higher magnification image of the Si/HfO$_2$ interface is shown in Figure 2.3(b). An interface oxide layer (~3 nm) is observed between HfO$_2$ and Si. Figure 2.3(c) shows a typical cross-section image of HfO$_2$:Hf-based devices. The HfO$_2$ sample clearly has 2 distinct layers, which resulted from the Hf doping.
The three types of n⁺-Si/HfO₂/Pt ReRAM devices were further analyzed with XPS. Figure 2.4(a), (b) and (c) present the depth profiles for ReRAM devices with non-doped HfO₂, Hf-doped HfO₂, and Au-doped HfO₂, respectively. For non-doped HfO₂-based devices (Figure 2.4(a)), the relative intensity ratio of Hf and O is constant with the exception of slight increase in O concentration at the interface between HfO₂ and Si. This is attributed to the native oxide layer on the Si substrate. In Figure 2.4(b), a minimum oxygen concentration is apparent in the middle of the HfO₂ region, consonant with the design of the HfO₂ layer with Hf-doping. For HfO₂:Au-based devices, Au-4f peaks in the XPS spectra appear only at the top level before sputtering. This is not unexpected as Au nanoparticles were deposited on the HfO₂ surface.
Figure 2.4 XPS depth profiles for (a) undoped HfO$_2$-based ReRAM devices, (b) HfO$_2$:Hf-based ReRAM devices, (c) HfO$_2$:Au-based ReRAM devices. (d) representative Hf$_{7/2}$ 4f peak shift from 2 different depth levels, each corresponding to HfO$_2$ layer (black) and interface layer (red).

Figure 2.4(d) shows the typical Hf$_{7/2}$-4f peaks selected from different sputtering levels (and therefore different depths) that corresponded to the HfO$_2$ film (in black) and the HfO$_2$-Si interface (in red), respectively. The measured Hf$_{7/2}$-4f peak in black color is at the binding energy of 16.24 eV, whereas the red one is at the binding energy of 15.02 eV. Comparing these two Hf$_{7/2}$-4f peaks with the standard binding energy, we conclude that the black trace corresponds to Hf in HfO$_2$ and the red trace corresponds to metallic Hf. This confirms that a distinct Hf-O-Si interface exists in all 3 types of ReRAM devices, consistent with the TEM results (Figure 2.3(b)).
Figure 2.5 shows the typical I-V characteristics of the n\textsuperscript{+}-Si/HfO\textsubscript{2}/Pt ReRAM devices with non-doped HfO\textsubscript{2}. The black and red curves are from 2 individual devices (device #1 and #2) respectively. The arrows represent the bias sweeping direction. As seen from the black curve (device #1) in Figure 2.5(a), sweeping a positive bias voltage from 0 on the top electrode, switches the device from its off-state to its on-state when the current “jumps” to the preset current compliance (CC) at a certain set voltage (V\text{set}). The device in the on-state can be reset to an off-state when applying another positive bias voltage sweep at a certain reset voltage (V\text{reset}). This process is termed unipolar resistive switching since both V\text{set} and V\text{reset} are of the same polarity. However, bipolar resistive switching for these HfO\textsubscript{2}-based ReRAM devices is also seen (device #2 in Figure 2.5(a)) with V\text{set} and V\text{reset} at different polarities. Thus, these HfO\textsubscript{2}-based ReRAM devices have nonpolar resistive switching, as V\text{set} and V\text{reset} are independent of bias polarity. For devices with undoped HfO\textsubscript{2}, the absolute value of the set voltage, |V\text{set}|, is 11 – 15 V and |V\text{reset}| is 7 – 10 V, which are too large for practical device use. Also, these devices have low endurance and no longer exhibit resistive switching after a few set/reset cycles.
Figure 2.5 I-V curves for (a) undoped HfO$_2$ ReRAM showing unipolar switching (black - device #1) and bipolar switching (red - device #2), (b) HfO$_2$:Hf ReRAM showing unipolar switching under both polarities (black - device #1, red - device #2), (c) HfO$_2$:Au ReRAM.

I-V electrical measurement results of doped n$^+$-Si/HfO$_2$/Pt ReRAM devices are presented in Figure 2.5(b) and (c). In Figure 2.5(b) for HfO$_2$:Hf devices, the black curves (device #1) show both set and reset processes under negative bias and the red curves (device #2) show both set and reset at positive bias. Figure 2.5(c) shows unipolar switching at positive bias polarity for HfO$_2$:Au devices. Compared with Figure 2.5(a) for non-doped HfO$_2$ devices, the ReRAM devices with doping exhibit improved uniformity of set and reset and enhanced endurance (> 30 cycles). Doped ReRAM devices display lower $|V_{\text{set}}|$ and $|V_{\text{reset}}|$ values. For HfO$_2$:Hf devices, $|V_{\text{set}}|$ ~7 – 9 V and $|V_{\text{reset}}|$ ~3 – 5 V.
For HfO$_2$:Au devices, $|V_{\text{set}}| \sim 7 - 10$ V and $|V_{\text{reset}}| \sim 3 - 5$ V. HfO$_2$-based ReRAM devices doped with Hf and Au show improved performance. The average values of $|V_{\text{set}}|$ and $|V_{\text{reset}}|$ for the 3 types of ReRAM devices are summarized in Figure 2.6(a), indicating improvement with respect to lower $|V_{\text{set}}|$ and $|V_{\text{reset}}|$ and better uniformity. Resistances of the devices at off-state and on-state are read at $V_{\text{read}} = \pm/- 1$ V. $R_{\text{off}}$ of all ReRAM devices ranged from $10^6 - 10^{10}$ Ω. However, as seen in Figure 2.6(b), the average $R_{\text{on}}$ decreases for devices with Hf-doping ($\sim 3800$ Ω) and Au-doping ($\sim 560$ Ω) compared to an average $R_{\text{on}}$ of $\sim 22$ kΩ for non-doped devices. This implies an increased memory window after doping. This is likely because doping increased the oxygen vacancies inside HfO$_2$ and resulted in a stronger vacancy-based filament.

![Figure 2.6](image)

**Figure 2.6** Comparison of parameters for HfO$_2$-based ReRAM devices; (a) average $V_{\text{set}}$ and $|V_{\text{reset}}|$, (b) average $R_{\text{on}}$. $R_{\text{off}}$ (not shown) exhibited the same range ($10^6$-$10^8$ Ω) for all three types of devices.

In summary, n$^+$-Si/HfO$_2$/Pt ReRAM devices have been fabricated and demonstrated nonpolar switching behavior. With Hf or Au doping, n$^+$-Si/HfO$_2$/Pt ReRAM devices show improved resistive switching performance in terms of lower $V_{\text{set}}$ and $V_{\text{reset}}$, better uniformity, and cycle endurance. Moreover, with Hf or Au-doping, the HfO$_2$-based ReRAM devices show larger conductivity at on-state. The improvement in resistive
switching can be attributed to enhanced defects and oxygen vacancies inside HfO$_2$. However, these devices with large $V_{\text{set}}$ and $V_{\text{reset}}$ ($|V_{\text{set}}| \sim 4\text{V}$, $|V_{\text{reset}}| \sim 8\text{V}$) as well as relatively low endurance ($\sim 30$ cycles), which might be limited by the interfacial layer at Si/HfO$_2$, are not desirable for practical NVM applications and, hence, were not pursued for our purposes of the investigation of the effects of ion irradiation.

2.1.2 Improved resistive switching performance of TiN/HfO$_2$/TiN (W) ReRAM devices

For the TiN/HfO$_2$/TiN ReRAM devices, 20 nm HfO$_2$ was deposited in between the top and the bottom electrodes via atomic layer deposition (ALD) [3, 4]. The as-fabricated TiN/HfO$_2$/TiN ReRAM devices have a size of $7 \times 7 \ \mu \text{m}^2$ and the HfO$_2$ layer is polycrystalline with a monoclinic phase [3, 4]. As seen from the typical I-V curves for a TiN/HfO$_2$/TiN device in Figure 2.7(a), a forming process (in black) is required for a fresh device by applying a negative voltage ($V_f \sim -0.8 - -1\text{V}$). After this forming, the fresh device – which initially exhibits a typical resistance ($R_{\text{fresh}}$) of $\sim 100\text{s k}\Omega$ – can be switched into an on-state with $R_{\text{on}} \sim 600 – 1000 \ \Omega$ when the current jumps to the preset compliance current (CC). By applying a positive voltage ($\sim 0.5 – 0.6 \ \text{V}$), a reset process, where the on-state is switched to an off-state with $R_{\text{off}} \sim 4000 – 10,000 \ \Omega$, can then be achieved (this reset curve is not shown). After the first on/off cycle, the devices can be switched reversibly between on- and off-states by applying different voltages with opposite polarities, as seen in the typical I-V characteristics of VCM devices after the forming process (I-V curves in red). The arrows indicate the current flow direction. By sweeping the bias voltage from 0 to -1 V, the device at its off-state can be set to the on-state when the current reaches the preset CC at $V_{\text{set}}$ of approximately -0.42 V. The low resistive state remains while the bias voltage is swept from -1 to 0. Increasing the bias
voltage from 0 to 1 V, the current starts to decrease (or stop increasing) at a threshold voltage \(V_{\text{reset}} \approx 0.46\) V, after which the current signal noise increases substantially. An off-state occurs when the applied voltage is higher than \(V_{\text{reset}}\), and the device remains in its off-state while the voltage sweeps back from 1 to 0 V. The process \(\text{off} \rightarrow \text{on} \rightarrow \text{on} \rightarrow \text{off}\) at 4 different voltage sweeps \(0 \rightarrow -1 \rightarrow 0 \rightarrow 1 \rightarrow 0\) V is a so-called set/reset cycle. \(R_{\text{on}}\) and \(R_{\text{off}}\) are read at \(V_{\text{read}} = 0.05\) V when the device is in the on- and off-state, respectively. Figure 2.7(b) shows the retention performance of the on- and off-state for a typical device at 0.05 V read voltage at room temperature. The resistances in both states are very stable, exhibiting only slight changes over more than \(10^5\) s.

In addition, these TiN/HfO\(_2\)/TiN ReRAM devices have undergone cycle-testing and shown good resistive switching performance with an endurance of more than \(10^5\) cycles [3, 4]. Figure 2.7(c) and (d) show cumulative frequency plots (percentage) of \(V_{\text{set}}/V_{\text{reset}}\) and \(R_{\text{on}}/R_{\text{off}}\) for a typical device switched for 100 cycles. It is seen that \(V_{\text{set}}\) ranges from -0.5 V to -0.39 V and \(V_{\text{reset}}\) ranges from 0.38 to 0.5 V. \(R_{\text{on}}\) ranges from 70 to 3000 \(\Omega\) and \(R_{\text{off}}\) ranges from 4000 to 10550 \(\Omega\).
Figure 2.7 (a) A typical I-V characteristic of a TiN/HfO₂/TiN ReRAM device and (b) the corresponding resistance retention. The arrows in (a) indicate the current flow direction. Cumulative frequency of a typical device with 100 resistive switching cycles of (c) $V_{\text{set}}$ and $V_{\text{reset}}$, (d) $R_{\text{on}}$ and $R_{\text{off}}$.

Similar structures were fabricated that employed a W top electrode and a reduced HfO₂ thickness of 5 nm. Fabrication details are listed in Ref. [5]. These TiN/HfO₂/W ReRAM devices exhibited also similar resistive switching properties, as shown in Figure 2.7(a). Typically, the $R_{\text{fresh}}$ (for a fresh, unformed TiN/HfO₂/W device) is on the order of 100 MΩ. Similarly, a forming process (black curve) initiates regular set/reset resistive switching behavior (red curve) at a $V_f \sim 1.7 - 1.9$ V. The devices switch between off- and on-states at $V_{\text{set}} \sim 0.43$ V and $V_{\text{reset}} \sim -0.41$ V. These devices have also exhibited good data retention ($> 10^5$ s) with little $R_{\text{on}}$ and $R_{\text{off}}$ variations, as seen in Figure 2.8(b).
Endurance testing has demonstrated that TiN/HfO$_2$/W ReRAM devices have good and uniform resistive switching performance (> $10^6$ cycles [5]). The cumulative frequency counts (percentage) are shown in Figure 2.8(c) and (d), demonstrating a relatively narrow distribution of $V_{\text{set}}$ (0.45 – 0.56 V), $V_{\text{reset}}$ (-0.45 – -0.35 V), $R_{\text{on}}$ (500 – 750 Ω) and $R_{\text{off}}$ (7 – 11 kΩ) for TiN/HfO$_2$/W ReRAM devices.

It should be pointed out that W is an inert metal and is not expected to diffuse or interact electrochemically at the HfO$_2$ interface. Consequently, TiN/HfO$_2$/W ReRAM devices are expected to exhibit similar resistive switching characteristics as TiN/HfO$_2$/TiN ReRAM devices; in other words TiN/HfO$_2$/W ReRAM devices are presumed to be based on formation and rupture of a vacancy-based filament.

Both the TiN/HfO$_2$/TiN and TiN/HfO$_2$/W ReRAM device sets exhibited suitable performance, stability, and reliability metrics to warrant investigation of the effects of ion irradiation. The sub 1-V switching performance, being compatible with CMOS control circuitry, is a reasonable benchmark for an integratable NVM device. The $R_{\text{off}}$/R$_{\text{on}}$ ratio (> 10:1), is sufficient for CMOS-based control and logic circuitry (for prevailing values of $V_{\text{dd}}$ < 1 V). And, the cycle endurance (> $10^5$) is suitably competitive to flash memory, considering that ReRAM technology is relatively immature. With these benchmarks in place, an investigation of the effects of ion irradiation is appropriate since the resulting effects on ReRAM technology performance can be meaningfully compared against the ‘radiation hardness’ of baseline NVM systems (e.g. flash).
Figure 2.8 (a) A typical I-V characteristic of a TiN/HfO₂/W ReRAM device and (b) the corresponding resistance retention. The arrows in (a) indicate the current flow direction. Cumulative frequency of a typical device with 100 resistive switching cycles of (c) $V_{\text{set}}$ and $V_{\text{reset}}$, (d) $R_{\text{on}}$ and $R_{\text{off}}$.

Before moving on to consider specific conducting filament models for the TiN/HfO₂/TiN and TiN/HfO₂/W ReRAM device systems it is worthwhile to discuss temperature dependence of the resistive switching. The representative dependence of $R_{\text{on}}$ and $R_{\text{off}}$ on temperature for a typical device is presented in Figure 2.9. Both $R_{\text{on}}$ and $R_{\text{off}}$ decrease with temperature and clearly exhibit semiconductor-like behavior. This is indicative of the conducting filament in these ReRAM devices consisting of oxygen vacancies. Note that 8 devices in the ‘on-state’ and another 8 devices in the ‘off-state’ were also tested with increasing temperature, and all of them exhibited similar behavior.
This semiconductor-like conduction behavior involving electronic transport via V\textsubscript{O}-related defects can be described by the expression [6]:

\[
R = \frac{\rho_0 t_{\text{ox}}}{A} \exp\left(\frac{E_a}{kT}\right)
\]  \hspace{1cm} (2.1)

Where \(\rho_0\) is an Arrhenius pre-exponential factor for the resistivity, \(t_{\text{ox}}\) is the thickness of the oxide layer, \(A\) is the effective cross sectional area of the filament, \(k\) is the Boltzmann constant, and \(E_a\) is the activation energy of the conduction, representing half of the energy band gap of the material [6]. \(E_a\) was reported to be \(\sim 0.15\) eV for a conducting filament based on a percolation path in a TiN/HfO\textsubscript{2}/TiN ReRAM device [6]. For the devices studied in this work, the value of the activation energy \((E_a)\) extracted from \(R_{\text{on}}\) versus temperature plots was \(0.0028 \pm 0.0009\) eV. The low value of \(E_a\) suggests the filament in these devices in the \emph{on}-state is more metallic-like (with \(E_g \sim 0\) eV) due to a high \(V_o\) density. This is consistent with our experimentally observed linear relationship between current and voltage. The metallic conduction in HfO\textsubscript{x} with high concentrations of oxygen vacancies \((x < 2)\) has also been predicted via density functional theory (DFT) calculations [6].

However, note that \(R_{\text{on}}\) shows only a 3% decrease and \(R_{\text{off}}\) shows only a 9% decrease at 86 °C. Thus, the \emph{on}- and \emph{off}-states are still considered to be stable with increasing temperature from 10°C up to 90°C. Moreover, the temperature dependence of \(V_f\) was also investigated and the result is shown in Figure 2.10. Clearly, \(V_f\) decreases with increasing temperature. At 83 °C the forming voltage has decreased by approximately 19% from the value measured at 10 °C.
2.1.3 Vacancy-based filamentary model

Interpretation and analysis of the effects of irradiation on the HfO$_2$-based ReRAM devices considered in this dissertation require an understanding of the proposed conducting filament structures for those systems. The exact forming and switching mechanism for transition metal oxide ReRAMs remains a topic of study. For the TiN/m-HfO$_2$/TiN(W) system, it is believed that oxygen vacancy activation energies are more
stable at the grain boundaries than in the bulk of a grain by up to 0.8 eV [4]. In addition, due to a low diffusion energy barrier, substantial oxygen vacancy segregation can occur along grain boundaries [4, 7, 8]. This was confirmed by first principle calculations [7, 8] that estimated a diffusion energy barrier of 0.65 – 0.7 eV for doubly positively charged oxygen vacancies (V^{2+}) and is schematically illustrated in Figure 2.11(a) [4, 8]. In that figure the low energy diffusion pathways are shown towards and along the (101) grain boundary (within the dashed lines) of the m-HfO\(_2\) crystal structure. The diffusion and segregation of oxygen vacancies (typically 10^{18} -10^{19} \text{cm}^{-3} in the as-processed HfO\(_2\) film) along grain boundaries results in an increase in defect concentration (V^{2+} states) in those regions. The conversion of V^{2+} to V^{+} by electron capture, together with the increase in defect density, eventually enables electron tunneling through the process V^{+} + e \rightarrow V \rightarrow V^{+} + e [4] and leads to a trap-assisted tunneling (TAT) current. TAT in metal oxides has been extensively studied and numerical simulations of TAT current have been reported [4, 9, 10, 11, 12, 13]. A simplified schematic of TAT conduction (the phonon-assisted process is ignored) is given in Figure 2.12(a). Considering a trapezoidal-like potential barrier – without taking electrostatic image forces into account – the simplified tunneling probability P\(_T\) has been calculated using the WKB approach [9, 14],

\[
P_T = \exp \left[ -\frac{4}{3\hbar q F} \sqrt{2m^* (E_t^{3/2} - (E_t - qFd)^{3/2})} \right]
\]  \hspace{1cm} (2.2)

Where \(\hbar\), \(q\), \(m^*\) are the reduced Planck’s constant, electronic charge quantity, and the effective mass of electrons in HfO\(_2\). \(F\) is the electric field in HfO\(_2\), \(E_t\) is the trap energy below the conduction band, and \(d\) is the trap-to-trap distance. It is obvious that the tunneling probability is exponentially dependent on the trap energy and the adjacent trap distance.
Figure 2.11 (a) Atomic structure near the (101) twin boundary in monoclinic HfO$_2$, Hf ions (large spheres) and O ions (small spheres). The 4 Å wide region near the grain boundary where vacancy segregation is most favorable is indicated. Paths for vacancy diffusion toward and along the grain boundary are also shown. Adapted with permission from Ref. [8]. Copyright 2009, American Institute of Physics. (b) Schematic of the dependency of the chemical bond energy of the generalized coordinate of the atomic configuration forming the bond. Under the applied electric field, $F_{ox}$, the probability of the bond breakage process increases due to reduction of the activation barrier, $E_a$, caused by the bond polarization, $bF_{ox}$, and the temperature population of the excited vibration states. Adapted with permission from Ref. [4]. Copyright 2011, American Institute of Physics. (c) SEM top view of a hole formed in a TiN/HfO$_2$/TiN device after SET/RESET cycles.

During the forming process in the HfO$_2$-based ReRAM structures considered here, the initial current was believed to be dominated by TAT current, considering the relatively large oxygen vacancy density ($10^{18}$ - $10^{19}$ cm$^{-3}$) for the as-processed ReRAM devices. Besides the process-induced oxygen vacancies, the generation of new defects
(mostly oxygen vacancies) assisted by the local electrical field, should be also considered. The corresponding defect generation rate $G$ can be described by the equation [4]

$$G = G_0 e^{-(E_a - bF)/k_B T}$$

(2.3)

where $G_0$ is a rate constant, $b$ is the bond polarization factor, $F$ is the applied field, $k_B$ is Boltzmann’s constant, $T$ is the local temperature and $E_a$ is the effective activation energy for defect generation which is associated with the relocation of the oxygen ion from its regular position after Hf-O breakage. A schematic illustrating this is shown in Figure 2.11(b). The defect generation rate increases exponentially with the local electrical field and the local temperature. The increased defect density reduces the trap-to-trap distance and leads to a higher TAT current. The enhanced TAT current can then increase the local temperature. These processes form a positive feedback loop and enhance the defect generation rate. When this trap density associated with O-vacancies reaches a critical concentration ($10^{20} - 10^{21} \text{ cm}^{-3}$ [15]) at grain boundaries, TAT current can generate Joule-heating sufficient to dissociate oxygen and lead to formation of a Hf-rich conducting filament with an electrical resistance corresponding to an on-state.

As an aside, physical deformation of the device itself has been observed and is attributed to this ‘thermal runaway’ process. Figure 2.11(c) shows a micrograph of hole-formation in a TiN/HfO$_2$/TiN device after a SET/RESET process. It is speculated that a high rate of oxygen vacancy generation resulted in $O_2$ gas bubble formation leading to the rupture.

The exact composition and geometry of the CF in HfO$_2$ ReRAM devices is still unknown and requires further investigation. A cone-shaped CF has considered assuming
a non-uniform profile of oxygen vacancy density along grain boundaries throughout the HfO$_2$ layer [16]. Still, the temperature assisted mechanism for HfO$_2$ filament formation agrees with the experimental result of decreased $V_f$ with increased forming temperature (Figure 2.10) in section 2.1.2.

![Diagram](image.png)

Figure 2.12 Band diagram illustration of trap-assisted tunneling processes through a HfO$_2$ dielectric layer; (a) virgin resistant state, (b) off-state after a primary conducting filament is formed. Adapted with permission from Ref. [4]. Copyright 2011, American Institute of Physics.

During the reset process, as seen in Figure 2.13, the high ohmic current flowing in the metallic conducting filament generates sufficient Joule-heating at the narrowest tip of the Hf-rich filament – presumably adjacent to the electrode – to induce oxidation of the Hf and create a tunneling barrier. Thus, an on-state is switched to an off-state, with the measured current limited by the TAT process through the barrier, as displayed in Figure 2.12(b). During the set process, as most of the applied voltage drops over the tip barrier, the high local electric field is presumed to lead to Hf-O bond breakage and regeneration of oxygen vacancies, thus resulting in the ‘re-formation’ of the CF and completion of the set process.

Consequently, the investigation of ion-irradiation on the HfO$_2$-based ReRAMs considered in this work will specifically focus on defect (oxygen vacancy) generation...
and/or the induction of microstructural changes which may affect the local oxygen vacancy density or transport. The specific experimental approach in terms of ion species, energy, dose, and fluence is described in section 2.3.

![Figure 2.13 Schematic of resistive switching (SET/RESET) for VCM-type HfO$_2$-based ReRAMs based on formation and rupture of Hf-rich conducting filament (CF) by O-vacancies-involved reduction/oxidation.](image)

### 2.2 ECM-type HfO$_2$-based ReRAM devices

#### 2.2.1 Pt/HfO$_2$:Cu/Cu ReRAM devices

As for the VCM-based ReRAM devices described in the previous section, interpretation and analysis of the effects of irradiation on ECM-based ReRAM devices likewise require an understanding of the proposed conducting filament structures for those systems. The fabrication of the ECM-type ReRAM device Pt(80nm)/HfO$_2$:Cu(50nm)/Cu(70nm) (with Au protection layer on the top of Cu electrode) has been described in Ref. [17] by our collaborator. Specifically, the bottom electrode Pt was deposited onto the substrate Si/SiO$_2$(100 nm)/Ti(20 nm) via e-beam evaporation. Subsequently, the resistive switching layer, HfO$_2$/Cu/HfO$_2$ with the thickness of 25/3/25 nm, and the top electrode Cu (30 nm) were deposited consecutively via e-beam evaporation. The schematic view of the structure is shown in Figure 2.14(a). The size of these devices is 700×700 µm$^2$, defined by a lithography and lift-off process.
Figure 2.14(b) shows an atomic-composition depth profile across an as-fabricated device using Auger electron spectroscopy (AES). It is also noted that the ratio of O/Hf throughout the HfO₂ layer is ~ 1.12 – 1.32. Cu content rises up in the middle of the HfO₂ layer and corresponds to the Cu layer insertion during the HfO₂ deposition. This approach was employed to increase the Cu atom concentration within the HfO₂ and enhance electrochemical filament formation and the resistive switching performance. As a result, the initial resistance of the as-fabricated devices is low and repeatable resistive switching behavior is achieved after an initial RESET process.

Figure 2.14 (a) Schematic view of the Pt/HfO₂:Cu/Cu ReRAM device structure. (b) AES depth profile for a typical Pt/HfO₂:Cu/Cu ReRAM device.

The typical I-V curves for SET and RESET resistive switching for these devices, after an initial RESET process, are shown in Figure 2.15(a). For this type of device, the SET and RESET processes followed an off → on → off sequence using voltage sweeps 0 → 1 V & 0 → -1 V. This is considered as a SET/RESET cycle. It is seen that the current ‘jumps’ at a threshold voltage of ~ 0.54 V, and the device is set to the preset CC at V_{set} ~ 0.91 V. During the RESET process, the current reaches a maximum at V_{reset} ~ -0.65 V. R_{on} and R_{off} are read at V_{read} = +/-0.1 V respectively. Figure 2.15(b) gives the on- and off-
state retention characteristic of the device at room temperature. The resistances in both states have only modest changes for more than 10^5 s.

![I-V Characteristic and Resistance Retention](image)

**Figure 2.15** (a) A typical I-V characteristic of a Pt/HfO₂:Cu/Cu ReRAM device and (b) the corresponding resistance retention, data from Y. Wang [17].

Figure 2.16 shows the cumulative frequency in percentage for a Pt/HfO₂:Cu/Cu ECM-ReRAM device with 100 cycles. As seen in Figure 2.15(a), Vᵣᵣₑₜₑᵗ ranges from 0.5 – 1.1 V and Vᵣₑₛₑᵗ ranges from -0.28 - -1V. Figure 2.15(b) shows Rᵣₒᵣₜ ranges from 25 – 203 Ω and Rᵣₒᵣₜ ranges from 5 - 40 kΩ. A temperature study of the on- and off-states in Figure 2.17 [17] shows that Rₒᵣₜ decreases with temperature – a semiconductor behavior, and Rₒᵣₜ increases linearly with temperature, which is a metallic property that can be expressed as

\[ R(T) = R₀[1 + \alpha(T - T₀)] \]  \hspace{1cm} (2.4)

where \( \alpha \) is the temperature coefficient and \( T \) is the temperature. From the linear fit of Rₒᵣₜ as a function of temperature in Figure 2.17, the temperature coefficient is 2.02 × 10⁻³ K⁻¹ for the device [17], which is comparable to previous report in Cu-doped ZrO₂ ReRAMs [18] and a Cu nanowire with diameter larger than 15 nm (\( \alpha = 2.5 \times 10^{-3} \) K⁻¹) [19]. Therefore, it is believed that the CF is a Cu metallic filament. This is important for interpretation of irradiation data presented later in this dissertation.
Figure 2.16 Cumulative frequency of a typical Pt/HfO$_2$:Cu/Cu ReRAM device with ~100 resistive switching cycles of (a) $V_{\text{set}}$ and $V_{\text{reset}}$, (b) $R_{\text{on}}$ and $R_{\text{off}}$.

Figure 2.17 [17] Temperature dependence of off- and on-state resistances of Pt/HfO$_2$:Cu/Cu ReRAM devices with the size of 20 × 20 µm$^2$. The blue dashed line is the linear fit.

2.2.2 Cu/HfO$_2$/Ni ReRAM devices

Cu/HfO$_2$/Ni ReRAM devices were provided by Prof. Nathaniel Cady’s group at the College of Nanoscale Science and Engineering, University at Albany, State University of New York. The fabrication details can be found in Ref. [20]. Briefly, Cu is used as the bottom electrode and was deposited on a Si/SiN/SiO$_2$/TaN/Ta substrate via an electrochemical deposition method, which was then planarized via chemical mechanical
planarization (CMP). A 55 nm HfO$_2$ layer was deposited onto the Cu bottom electrode by physical vapor deposition (PVD) at room temperature, followed with an e-beam deposition of a 100 nm Ni film served as the top electrode. A shadow mask was employed to define the size (50 × 50 µm$^2$) of ReRAM devices. A schematic view of the device structure is given in Figure 2.18(a). Figure 2.18(b) gives the SIMS depth profile for a Cu/HfO$_2$/Ni ReRAM device. The depth is calibrated to 100 nm Ni. It is seen that the HfO$_2$/Cu interface exhibited a higher oxygen concentration than that of the HfO$_2$ bulk or HfO$_2$/Ni interfaces. This might be due to the native oxidation of Cu at the HfO$_2$/Cu interface.

![Fig 2.18 Diagram](image)

**Figure 2.18** (a) Schematic view of the Cu/HfO$_2$/Ni ReRAM device structure. (b) SIMS depth profile for a typical Cu/HfO$_2$/Ni ReRAM device.

Figure 2.19 shows a typical forming process (black curve) of a Cu/HfO$_2$/Ni ReRAM device followed by a SET/RESET reversible resistive switching (red curve). The arrows in the figure indicate the corresponding switching behavior at $V_f$, set voltage ($V_{\text{set}}$) and reset voltage ($V_{\text{reset}}$), respectively. As seen from the figure, a fresh device was formed at a large $V_f \sim 15$ V. After the forming process, the device can then repeatedly switch between the *on*- and *off*- states at $V_{\text{set}} \sim 3$ V and $V_{\text{reset}} \sim -0.5$ V.
Figure 2.19 A typical I-V characteristic of forming process of Cu/HfO\textsubscript{2}/Ni ReRAM devices (black curve), and a typical I-V curve (red curve) of a repeatable SET/RESET resistive switching cycle after devices are formed.

These Cu/HfO\textsubscript{2}/Ni ReRAM devices have been tested and the endurance is > 10\textsuperscript{4} cycles. The cumulative frequency of the parameters for a typical device with 500 cycles is shown in Figure 2.20. \( V_{\text{set}} \) and \( V_{\text{reset}} \) have a relatively large distribution – \( V_{\text{set}} \sim 0.8 – 3.81 \) V and \( V_{\text{reset}} \sim -0.27 – -1 \) V. \( R_{\text{on}} \) and \( R_{\text{off}} \) vary over large ranges of 20 – 400 \( \Omega \) and 5 \( \times 10^5 – 3.5 \times 10^{10} \) \( \Omega \), respectively.

Figure 2.20 Cumulative frequency of a typical Cu/HfO\textsubscript{2}/Ni ReRAM device with 100s resistive switching cycles of (a) \( V_{\text{set}} \) and \( V_{\text{reset}} \), (b) \( R_{\text{on}} \) and \( R_{\text{off}} \).

For these ReRAM devices it has been assumed that ECM-type formation of a Ni filament is responsible for resistive switching. Assuming the Ni filament formed has a
diameter of 5 – 10 nm, its resistivity, $\rho \sim 12 – 48 \, \mu \Omega \cdot \text{cm}$, can be obtained from the relation: $R = \rho \cdot \frac{L_{CF}}{A_{CF}}$ using the median value of $R_{on} \sim 84 \, \Omega$, where $L_{CF}$ is the length of the filament (55nm) and $A_{CF}$ is the effective cross-section area of the filament. The obtained resistivity value for the Ni filament is close to the reported value, $10.9 \sim 28.5 \, \mu \Omega \cdot \text{cm}$ [21] and $35 \, \mu \Omega \cdot \text{cm}$ [22] for Ni nanowires.

### 2.2.3 Electrochemical metallization effect-based filamentary model

Electrochemical metallization is one of the better-studied mechanisms for ReRAM devices, especially those with one electrode using an electrochemical active metal (Cu, Ag, etc.) and the other electrode using an electrochemical inert metal (Pt, W, etc.) [23, 24]. Physical evidence of metal filament formation [25, 26, 27] and associated simulations [28] have been reported. For a fresh device, the electro-forming process involves [23]: (i) anodic dissolution of the electrochemical active metal M with the reaction $M \rightarrow M^{z+} + ze$; (ii) migration of the $M^{z+}$ cations across the solid-electrolyte thin film under the electric field; and (iii) reduction and electrocrystallization of M on the surface of the inert electrode with the reaction: $M^{z+} + ze \rightarrow M$. Step (iii) leads to formation of a metal filament growing preferentially towards the active electrode, as seen in the schematic in Figure 2.21. Note that metallization referred to in step (iii) is electric-field enhanced and the electrocrystallization preferentially occurs at the tip of the filament where the electric field is the strongest. This is demonstrated in Figure 2.22, using a simple simulation of an electric field near a metallic filament inside HfO$_2$. Once the metal filament reaches the active electrode, the device is then switched to an on-state. By applying an opposite voltage polarity, the electrochemical dissolution of the metal filament at the tip region occurs under the reversed electric field and the on-state is
switched back to an off-state (Figure 2.21). Because of the rupture of the local filament tip, the following SET process requires a lower $V_{set}$ to set the device again.

Figure 2.21 Schematic of resistive switching (SET/RESET) for ECM-type HfO$_2$-based ReRAMs based on formation and rupture of metal filament (CF) by electrochemical reduction/oxidation of metal ions (M$^{z+}$).

Figure 2.22 Electric field simulation inside HfO$_2$ in ECM-type ReRAM devices, using COMSOL multiphysics 4.2. The curves are equipotential lines after applying a voltage of 1 V on the top electrode with the bottom electrode grounded. This is given as an ideal reference and does not include the intrinsic electron traps that would exist due to processing.

Previous studies have demonstrated Ni/Cu metallic filaments inside HfO$_2$-based ReRAMs with Ni or Cu electrodes [17, 29, 30, 31]. The electric current during the forming process governed by this electrochemical metallization mechanism is an ionic
current. The magnitude of the current is determined by the overall rate-limiting step in the electrochemical metallization process. The determination of this step depends on the materials used in each system. For a system with a solid electrolyte with high ionic conductivity, such as Ag-Ge-Se, charge transfer kinetics at the electrode/electrolyte interfaces is reported to be the rate-limiting step [32]. However, for ECM cells with low ionic conductivity, bulk diffusion limited kinetics may play an import role instead. In our work, bulk diffusion is considered as the rate-limiting step, as the HfO$_2$ layer in our devices is relatively thick (50 – 55 nm) and metal oxides are generally not considered as ion conductors, with low ionic conductivity at room temperature comparing to electronic conductivity [33]. Using the ion hopping model, the current density ($J_{ion}$) determined by the ion diffusion is given by [23]

$$J_{ion} = \textit{zecav} \exp\left(-\frac{W^0_a}{kT}\right) \exp\left(\frac{azeE}{2kT}\right), \text{ when } E \gg \frac{kT}{aze} \quad (2.5)$$

where $a$ is the ion hopping distance between adjacent sites, $W^0_a$ is the hopping energy barrier, $E$ is the electric field, $c$ is the concentration of mobile metal (Ni or Cu) ions, $v$ is a frequency factor, and $z$ is the charge state of the metal ions. $e$, $k$, $T$ and $E$ represent the electronic charge, the Boltzmann constant, the temperature, and the electric field, respectively.

However, as mentioned earlier, electronic conductivity is predominant over ionic conductivity in HfO$_2$. Hence, the current leakage in HfO$_2$ (before the ReRAM device is formed) could also be due to electronic conduction as well. Thus, the current leakage for our ReRAM devices during forming process can be dominated by either ionic current ($J_{ion}$) or electronic current ($J_{ele}$) or a mixture of both, described as the following

$$J_{total} = J_{ion} + J_{ele} \quad (2.6)$$
Electronic current leakage in HfO$_2$-based MIM structure has been extensively studied and the Poole-Frenkel (P-F) effect is well recognized as the major conduction mechanism in HfO$_2$ [15, 34, 35, 36, 37], which is related to field-enhanced thermal excitation of trapped electrons in the dielectric. The current density ($J_{PF}$) associated with Poole-Frenkel conduction mechanism can be described by the equation [36]

$$J_{PF} = \sigma_0 E \exp \left( -\frac{q\phi_t}{kT} \right) \exp \left( \frac{q}{r kT} \sqrt{\frac{qE}{\pi \varepsilon_0 \varepsilon_d}} \right)$$

(2.7)

where $\sigma_0$ is the low-field conductivity, $\phi_t$ is the trap energy level with respect to the conduction band, $\varepsilon_0$ denotes the permittivity of free space, and $\varepsilon_d$ is the high-frequency dynamic dielectric constant. The coefficient $r$ ($1 \leq r \leq 2$) is introduced in the expression by taking into account the influence of the trapping or acceptor centers [36, 38].

As a baseline for ion irradiation experiments it is necessary to fully characterize the forming mechanism in this system to determine the dominant conduction process. This is particular critical in light of the fact that ion irradiation can readily alter local defect (trap) densities and/or local microstructure which can impact the filament forming process in HfO$_2$. Consequently, the forming process was investigated for Cu/HfO$_2$/Ni ReRAM devices. Note that the forming process for Pt/HfO$_2$:Cu/Cu ECM-ReRAMs was not discussed in this work as the Cu-doping eliminated the conventional forming process and added to the complexity of the Cu filament formation. It is presumed that electrical conduction is dominated by the Poole-Frenkel mechanism and ionic conduction mechanism (associated with electrochemical metallization). The forming I-V data from Cu/HfO$_2$/Ni ReRAM devices was analyzed using non-linear least squares fitting to both Poole-Frenkel and ionic conductions (with a $y^2$ weighting function). It was found that the Poole-Frenkel model describes this I-V data very well, as shown in Figure 2.23. The
expression, \( I = A_{PF} V \exp(B_{PF} \sqrt{V}) \) (modified from Equation (2.7)) and \( I = A_1 \exp(B_1 V) \) (modified from Equation (2.5) are respectively used for Poole-Frenkel analysis and ionic conduction analysis of the forming I-V data from a Cu/HfO\(_2\)/Ni ReRAM device. Compared to the ionic fit (in blue, \( \chi^2 = 0.08 \pm 0.017 \)), the Poole-Frenkel model exhibits a substantially lower value for the ‘quality of fit’ parameter \( \chi^2 \) (0.015 \( \pm \) 0.003). Similar fitting results were found in 5 different devices, with \( A_{PF} \) and \( B_{PF} \) parameters from the Poole-Frenkel fit given in the inset in Figure 2.23. This fitting strongly suggests that the electrical conduction during forming process in Cu/HfO\(_2\)/Ni ReRAM devices is dominated by Poole-Frenkel effect until the device is switched to its on-state. (The effects of ion-irradiation on this forming conduction mechanism will be discussed in later chapters.)

![Figure 2.23](image)

**Figure 2.23** Typical I-V fitting to Poole-Frenkel for Cu/HfO\(_2\)/Ni devices without radiation. The upper-left inset gives the dielectric constant calculated from the C-V measurement result versus frequency. The lower-right inset shows the fitting parameters \( A_{PF} \) and \( B_{PF} \) from Poole-Frenkel fitting for 5 individual devices, with the dashed lines in the inset corresponding to average \( A \) and \( B \) values.

To confirm the Poole-Frenkel conduction mechanism during the ReRAM forming process for our Cu/HfO\(_2\)/Ni devices, the dynamic dielectric constant was extracted from
the fitting parameter $B_{PF} = \frac{q}{r k T} \sqrt{\frac{q}{\pi \delta_0 E_{d} t}}$, where $t$ is the thickness of HfO$_2$ and the electric field $E = V/t$ is assumed for simplicity). The dynamic dielectric constant is expected to fall in between the optical dielectric constant ($\varepsilon_{\text{opt}} \sim n^2$, typically lower than 5 for HfO$_2$ [15, 39]) and the static dielectric constant ($\varepsilon_s$, estimated to be $\sim 13.5$ from C-V measurements for our devices, as seen in the upper-left inset in Figure 2.23). From the fitted data shown in Figure 2.23 the extracted value of the dynamic dielectric constant, $\varepsilon_d = 9.37 \pm 0.53$, thus, we conclude that the conduction is consistent with the Poole-Frenkel effect. This self-consistency check for Poole-Frenkel conduction was also reported by S. M. Sze for Si$_3$N$_4$ systems [40], G. S. Oehrlein [41] and A. Persano et al. for Ta$_2$O$_5$ systems [42]. In addition, the forming process for Cu/HfO$_2$/Ni ReRAM devices was also conducted with an opposite polarity and an identical forming curve was obtained at $E > 1$ MV/cm. This also confirms the Poole-Frenkel effect dominating the conduction in the forming process [40, 41].

It should be pointed out that Fowler-Nordheim or direct electrode to electrode tunneling processes are not important [34], considering the thick HfO$_2$ film (55 nm) used in our devices. Schottky-Richardson (S-R) emission, as another possible effect reported by others [36, 43], was ruled out in this study, as the Schottky-Richardson fitting of experimental data (not shown) leads to a dielectric constant, $\varepsilon_r \sim 100s$, which is much higher than the known value ($\sim 20$) for HfO$_2$.

Lastly, previous work on these ECM-ReRAM structures has confirmed that on-state conduction is localized (i.e. a single conducting filament) with $R_{on}$ independent of device area [17, 23]. Consequently, for the irradiation studies in this work a reasonable
comparison of electrical response between VCM and ECM ReRAM devices can be achieved.

2.3 Experimental method for HfO$_2$-based ReRAM device irradiation

Based on the various resistive switching devices investigated and discussed in the previous sections, an experimental approach was devised to investigate the effect of ion irradiation on HfO$_2$-based ReRAM devices. Radiation bombardment was performed on an implantation beamline on a 4-Megavolte Dynamitron RPEA 4.0 in the ion beam lab (IBL), SUNY-Albany. This work involved various ion species in the +1 charge state, including 1-MeV protons (H$^+$), 1-MeV helium ions (He$^+$), 1-MeV nitrogen ions (N$_2^+$), 1.6-MeV neon ions (Ne$^+$), 2.75-MeV argon ions (Ar$^+$). The total ionizing dose (TID) can be calculated from fluence by the relation [44]:

$$D = \frac{1}{\rho_{Si}} \left( \frac{dE}{dx} \right)_{Si} \times \phi$$  \hspace{1cm} (2.8)

Where D is the TID in rad(Si), $\phi$ is the fluence in $#/cm^2$, $\rho_{Si}$ is the density of Si, $\left( \frac{dE}{dx} \right)_{Si}$ in eV/Å is the ionization energy loss of charged particles travelling through Si. The term $\frac{1}{\rho_{Si}} \left( \frac{dE}{dx} \right)_{Si}$ is also known as the stopping power or linear energy transfer (LET) of the incident ions in a Si target material, which is dependent on the incident ion mass, energy, and charge state and can be calculated from the Stopping Range of Ions in Matter (SRIM) simulation program [45]. The LET values of the radiation ion sources chosen in this work to investigate ReRAM devices are shown in Figure 2.24. Higher LET is noticed for heavier ions, therefore, larger dose is expected at a given fluence for heavy-ion radiation with larger ion mass.
To achieve a targeted dose, the target fluence is calculated from this equation (vice versa). The experimental fluence is calculated from the measured beam current with the relation

$$\phi = \frac{I_{beam} \times t}{q \times A_{beam}}$$

(2.9)

Where $I_{beam}$ is the beam current in amps, $t$ is the beam duration in second, $q$ is the charge of an electron in C, and $A_{beam}$ is the area of the beam in cm$^2$.

The samples were clipped or adhered to a horizontal mount on the inside door of the irradiation chamber so that the ion beam direction was perpendicular to the sample surface, as illustrated in Figure 2.25. In a typical memory application, ReRAM devices are normally electrically unbiased, except during a read or a write operation (10-100 ns). It is generally accepted that the probability of ion bombardment on a ReRAM device during a read/write operation is relatively small. Thus, during the radiation exposure, the ReRAM devices were unbiased. The chamber was under vacuum with pressure in $\sim 10^7$
Torr. More detailed irradiation parameters will be given in each section in the following chapters.

![Diagram of irradiation](image)

**Figure 2.25 Schematic of irradiation**

The SRIM program developed by J. F. Ziegler and J. P. Biersack [46] is widely utilized for ion interactions with matter. This program is based on the binary collision approximation (BCA), in which the movement of ions in the target material is treated as a succession of individual collisions between the recoil ion and atoms in the target, outputting profiles for occurrences such as vacancies, ionization, or phonon production in the target material with a relatively good accuracy. In this work, for each type of ion radiation on each type of ReRAM device, the SRIM program was used to simulate the process and estimate the radiation-induced vacancy density. The details are listed in Appendix I. However, it should be pointed out that the SRIM program does not take into account the crystal structure of the target material. Therefore, the accuracy of the simulation is still limited for materials wherein details of the crystal structure are severely anisotropic or inhomogeneous.

It is also noted that all units and graph labels of the form “rad” for TID in this dissertation can be assumed to be “rad(Si)” unless otherwise stated in the text.
2.4 References


3. Impacts of Light-Ion Irradiation on HfO$_2$-based ReRAM devices

In this chapter, the effects of light-ion radiation (proton and helium) on two types of ReRAM devices are described. Section 3.1 gives the results of light-ion radiation on VCM-ReRAM devices (TiN/HfO$_2$/TiN(W)). Section 3.2 presents the results and discussion of light-ion radiation on ECM-ReRAM devices (Pt/HfO$_2$:Cu/Cu and Cu/HfO$_2$/Ni). Section 3.3 compares the radiation responses between VCM and ECM ReRAM devices.

3.1 Proton and helium irradiation of VCM-type HfO$_2$-ReRAMs

VCM ReRAM devices (7×7 µm$^2$) investigated in this work have a polycrystalline m-HfO$_2$ layer as the insulator, with the thickness of 20 nm in TiN/HfO$_2$/TiN and 5 nm in TiN/HfO$_2$/W ReRAM devices. The structure of the two devices is schematically illustrated in Figure 3.1. Both devices have shown excellent resistive switching performance, as demonstrated in section 2.1.2. A summary of resistive switching parameters of both sets of ReRAM devices is given in Table 3.1.

![Figure 3.1 Schematic of the two VCM-type ReRAM structures.](image)
Table 3.1 Summary of resistive switching parameters for TiN/HfO$_2$/TiN and TiN/HfO$_2$/W ReRAM devices.

<table>
<thead>
<tr>
<th></th>
<th>TiN/HfO$_2$/TiN</th>
<th>TiN/HfO$_2$/W</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_f$ (V)</td>
<td>-0.8 ± 0.02</td>
<td>1.79 ± 0.02</td>
</tr>
<tr>
<td>$R_{\text{fresh}}$ (MΩ)</td>
<td>0.35 ± 0.052</td>
<td>138.30 ± 4.53</td>
</tr>
<tr>
<td>$V_{\text{set}}$ (V)</td>
<td>-0.44 ± 0.008</td>
<td>0.49 ± 0.004</td>
</tr>
<tr>
<td>$V_{\text{reset}}$ (V)</td>
<td>0.43 ± 0.008</td>
<td>-0.42 ± 0.002</td>
</tr>
<tr>
<td>$R_{\text{on}}$ (Ω)</td>
<td>946.04 ± 76.08</td>
<td>812.74 ± 4.6</td>
</tr>
<tr>
<td>$R_{\text{off}}$ (kΩ)</td>
<td>7.07 ± 0.43</td>
<td>12.88 ± 0.57</td>
</tr>
<tr>
<td>Endurance (cycle)</td>
<td>$&gt; 10^5$</td>
<td>$&gt; 10^6$</td>
</tr>
<tr>
<td>Retention (s)</td>
<td>$&gt; 10^5$</td>
<td>$&gt; 10^5$</td>
</tr>
</tbody>
</table>

In this work, TiN/HfO$_2$/TiN ReRAM devices were used for the study of proton irradiation with total dose ranging from $10^5$ to $10^9$ rad(Si), and TiN/HfO$_2$/W devices were utilized for the investigation of helium irradiation with total dose ranging from $10^7$ – $10^{10}$ rad(Si). Table 3.2 gives the summary of irradiation conditions for each exposure experiment. Before each radiation exposure, 16 ReRAM devices were cycled, 8 of which were kept at on-state and another 8 at off-state. The devices underwent radiation exposure and electrical measurements were carried out immediately afterwards on a Keithley 4200 semiconductor characterization system. In addition to the 16 cycled devices, another 8 – 10 fresh devices were also subjected to the same radiation exposure for study of irradiation effects on forming voltage and $R_{\text{fresh}}$. Each device was measured in a DC sweep mode for several set/reset cycles at a current compliance (CC) of 500 µA. For all devices, bottom electrodes were grounded and voltages were applied to the top electrode.
Table 3.2 Summary of VCM ReRAM devices exposure to a 1 MeV H$^+$ and He$^+$ ion energy.

<table>
<thead>
<tr>
<th>Radiation source</th>
<th>Total Doses (rad(Si))</th>
<th>Fluence (ions/cm$^2$)</th>
<th>Exposure time (min)</th>
<th>Number of devices</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 MeV H$^+$ (TiN/HfO$_2$/TiN)</td>
<td>10$^5$</td>
<td>3.56 $\times$ 10$^{10}$</td>
<td>0.5</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>10$^6$</td>
<td>3.56 $\times$ 10$^{11}$</td>
<td>2</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>10$^7$</td>
<td>3.56 $\times$ 10$^{12}$</td>
<td>10</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>10$^8$</td>
<td>3.56 $\times$ 10$^{13}$</td>
<td>30</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>1.5 $\times$ 10$^9$</td>
<td>5.32 $\times$ 10$^{14}$</td>
<td>130</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>3 $\times$ 10$^9$</td>
<td>1.06 $\times$ 10$^{15}$</td>
<td>240</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>5 $\times$ 10$^9$</td>
<td>1.77 $\times$ 10$^{15}$</td>
<td>420</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td>1 MeV He$^+$ (TiN/HfO$_2$/W)</td>
<td>2.1 $\times$ 10$^7$</td>
<td>1 $\times$ 10$^{14}$</td>
<td>2</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>2.1 $\times$ 10$^9$</td>
<td>1 $\times$ 10$^{14}$</td>
<td>68</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>2.1 $\times$ 10$^{10}$</td>
<td>1 $\times$ 10$^{15}$</td>
<td>80</td>
<td>8 (on) + 8 (off)</td>
</tr>
</tbody>
</table>

3.1.1 Effects on resistive switching

In order to eliminate the intrinsic variation of the ReRAM devices and elucidate the performance change due to irradiation effects, the average changes in $V_{set}$, $V_{reset}$, $R_{on}$ and $R_{off}$ for all 16 TiN/HfO$_2$/TiN devices under each irradiation case were obtained and normalized to the pre-rad case. Figure 3.2 plots the average percentage changes of these quantities with dose for the devices after proton radiation, compared with the pre-radiation control values. The latter were calculated from electrical measurements of the control samples within 4-hours of irradiation. Error bars show the corresponding standard errors. It can be seen from Figure 3.2(a) that $V_{set}$ and $V_{reset}$ exhibited little effects from the proton irradiation, with the changes after irradiation at all doses lower than 5% which is comparable to the pre-radiation (intrinsic) changes. The average percentage changes for $R_{on}$ and $R_{off}$ (Figure 3.2(b)) were also modest, although the variation after irradiation is larger than that of $V_{set}/V_{reset}$. It is therefore reasonable to conclude that TiN/HfO$_2$/TiN
ReRAM devices have high proton irradiation tolerance (with no degradation) up to a TID of 5 Grad.

![Graphs showing percentage change in V_{set}, V_{reset}, and R_{on} and R_{off} for proton and He irradiation.]

**Figure 3.2** Average changes of (a) V_{set}, V_{reset}, and (b) R_{on} and R_{off}, for all 16 TiN/HfO_{2}/TiN devices after proton irradiation, and average changes of (c) V_{set}, V_{reset}, and (d) R_{on} and R_{off}, for all 16 TiN/HfO_{2}/W devices after Helium irradiation. The changes are all normalized to pre-radiation values. The pre-radiation changes are calculated from the control devices with a 4 hour interval of measurement.

Similarly, small changes in V_{set} and V_{reset} (< 5%, as shown in Figure 3.2(c)) were found for TiN/HfO_{2}/W devices after He irradiation. R_{on} and R_{off} decreased after He irradiation (see Figure 3.2(d)), although the decreases were still comparable to the device-to-device variations. Thus again, in terms of resistive switching, TiN/HfO_{2}/W ReRAM devices have a high radiation tolerance to a TID of He-irradiation up to 21 Grad.
3.1.2 Effects on forming

Figure 3.3 shows the forming voltage and resistance of fresh devices as a function of radiation dose. $V_f$ increased slightly at the lower radiation doses (below $10^9$ rad) for the TiN/HfO$_2$/TiN ReRAM devices after proton irradiation (Figure 3.3(a)). But at higher doses (3 and 5 Grad) $V_f$ exhibited a slight decrease. Correspondingly, $R_{\text{fresh}}$ (Figure 3.3(b)) increased with dose (for TID below $10^9$ rad) but decreased with dose at higher TID (above $10^9$ rad). For TiN/HfO$_2$/W ReRAM devices exposed to He irradiation (Figure 3.3(c)), $V_f$ decreased with radiation dose up to 2.1 Grad, above which a reversed trend was observed. Similar phenomenon was observed in $R_{\text{fresh}}$ for the TiN/HfO$_2$/W ReRAM devices after He irradiation. However, it should be pointed out that the observed changes in $V_f$ for both types of irradiation are low ($\leq 5\%$) for all doses.
3.1.3 Improved resistive switching uniformity by irradiation

Interestingly, proton irradiation of TiN/HfO₂/TiN ReRAM devices did result in improved resistive switching uniformity. To compare the resistive switching uniformity of TiN/HfO₂/TiN ReRAM devices, Figure 3.4(a) and (b) plots the I-V curves for all devices before and after irradiation at a TID of 3 Grad. Visual inspection of the I-V curves in Figure 3.4(a) and (b) suggests greater switching uniformity (i.e. less device-to-device variation) for the post-radiated devices. Similar enhanced switching uniformity
(less cycle-to-cycle variation) was also observed for 100 cycles of one device after proton irradiation with different TIDs (see Appendix II).

Figure 3.4 I-V curves for all devices with all cycles for (a) the pre-irradiation case and (b) the post-irradiation case. Comparison of (c) resistance variation range ($\Delta R_{on}$ and $\Delta R_{off}$), and (d) on and off state separation ($\Delta R_{on-off} = \text{Min}(R_{off}) - \text{Max}(R_{on})$) of all the devices for the pre-radiation case and the post radiation case as a function of TID. Reprinted with permission from Ref. [1], copyright Materials Research Society 2012.

For a quantitative measure of this effect, Figure 3.4(c) plots the resistance ranges, $\Delta R_{on}$ and $\Delta R_{off}$ for pre- and post-irradiated ReRAM devices. As diagrammatically illustrated in Figure 3.4(a) and (b), $\Delta R_{on}$ and $\Delta R_{off}$ are defined as the total variation in the measured on- and off-state resistance at the 0.05 V read voltage (Note that the intrinsic resistance measurement error is less than the symbol size). It is clearly evident that the
pre-irradiated ReRAM devices have a larger range of resistance variation in the $on$- and $off$- states than the post-irradiated devices. However, the values for $\Delta R_{on}$ and $\Delta R_{off}$ evolve differently with increased TID. $\Delta R_{on}$ exhibits a monotonic decrease with increased dose (-240 ± 89 $\Omega$/decade for doses from 0.1 Mrad). In contrast, $\Delta R_{off}$ exhibits an abrupt (approximately 50%) drop with radiation dose at 0.1 Mrad with no statistically significant change at higher dose (the slope of the blue dashed line in Figure 3.4(c) for $\Delta R_{off}$ is 27 ± 230 $\Omega$/decade). Figure 3(d) shows the minimum $on$- and $off$- state separation, $\Delta R_{on-off}$, which is defined as the absolute resistance difference between the maximum $R_{on}$ and the minimum $R_{off}$. This is schematically defined in Figure 3.4(a) and (b). This state separation, $\Delta R_{on-off}$, exhibited a nominal increase with TID (the blue dashed line in Figure 3.4(d) is a guide to the eye), however the large sample-sample variation precluded a meaningful slope extraction.

3.1.4 Discussion

It is well established that dielectric materials are more sensitive to effects of irradiation as compared to metals [2, 3]. For the Hf-based VCM device studied here the 50 nm TiN electrodes possess a resistivity near 30 $\mu\Omega$-cm. The bulk TiN resistivity is approximately 22 $\mu\Omega$-cm [4]. Therefore, the resistance of each TiN electrode is only 4 - 6 $\Omega$, which can be ignored when in series with HfO$_2$ dielectrics in our devices considering $R_{\text{fresh}} \sim 100\text{s k}\Omega$, $R_{\text{off}} \sim 1000\text{s }\Omega$ and $R_{\text{on}} \sim 100\text{s }\Omega$. As a result, irradiation of the TiN electrodes is unlikely to affect the results presented above.

Previous work has demonstrated that the intrinsic electron trap density in HfO$_2$ is dominated by bulk processing [5, 6, 7, 8], and that electron trap density can be significantly enhanced by ionizing radiation [9, 10, 11], specifically, O$_2^-$ ion centers
coupled to hafnium ions, and oxygen vacancies [12, 13]. In our case, oxygen vacancies play a dominant role in the resistive switching of this type of HfO$_2$-ReRAM device. As described in section 2.1.3, the mechanism of forming and resistive switching in TiN/HfO$_2$/TiN(W) ReRAM devices is associated with trap-assisted tunneling (TAT) and the corresponding voltage-induced formation/rupture of a portion of the vacancy-based (or Hf-rich) conducting filament near the cathode/dielectric interface. From SRIM simulations [14], radiation-induced vacancy densities (presumably all oxygen vacancies, and thus electron traps) in both types of HfO$_2$-based ReRAM structures were estimated and presented in Table 3.3.

Table 3.3 Radiation-induced vacancy density in both stacks calculated from SRIM simulations for different radiation doses.

<table>
<thead>
<tr>
<th>Total Dose (rad(Si))</th>
<th>H$^+$-rad on TiN/HfO$_2$/TiN</th>
<th>He$^+$-rad on TiN/HfO$_2$/W</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rad-induced vacancy density</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(/cm$^3$)</td>
<td>Total Dose (rad(Si))</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rad-induced vacancy density</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(/cm$^3$)</td>
</tr>
<tr>
<td>$10^5$</td>
<td>$1.17 \times 10^{14}$</td>
<td>$2.1 \times 10^7$</td>
</tr>
<tr>
<td>$10^6$</td>
<td>$1.17 \times 10^{15}$</td>
<td>$2.1 \times 10^8$</td>
</tr>
<tr>
<td>$10^7$</td>
<td>$1.17 \times 10^{16}$</td>
<td>$2.1 \times 10^9$</td>
</tr>
<tr>
<td>$10^8$</td>
<td>$1.17 \times 10^{17}$</td>
<td>$2.1 \times 10^{10}$</td>
</tr>
<tr>
<td>$1.5 \times 10^9$</td>
<td>$1.76 \times 10^{18}$</td>
<td>$2.1 \times 10^{11}$</td>
</tr>
<tr>
<td>$3 \times 10^9$</td>
<td>$3.52 \times 10^{18}$</td>
<td>$5.62 \times 10^{20}$</td>
</tr>
<tr>
<td>$5 \times 10^9$</td>
<td>$5.87 \times 10^{18}$</td>
<td>$5.62 \times 10^{19}$</td>
</tr>
</tbody>
</table>

As seen from Table 3.3, for TiN/HfO$_2$/TiN ReRAM devices after proton irradiation, the maximum irradiation-induced vacancy density is on the order of $10^{18}$ /cm$^3$ for irradiation with TID in the Grad range. This is ≤ 1% of the critical trap density ($10^{20}$ – $10^{21}$/cm$^3$ [13, 15]) required for conducting filament formation. In other words, the additional (oxygen vacancy) defects introduced are wholly insufficient to dramatically alter conducting filament formation. This is consistent with our experimental
observations regarding the absence of modification or degradation of TiN/HfO₂/TiN ReRAM resistive switching parameters (i.e. \(V_{\text{set}}\), \(V_{\text{reset}}\), \(R_{\text{on}}\), \(R_{\text{off}}\)) after proton irradiation (all doses). Similar reasoning holds for the observed minimal variations in resistive switching parameters for TiN/HfO₂/W ReRAM devices after He irradiation.

For a fresh device with an intrinsic oxygen density about \(10^{18} \sim 10^{19} \text{ cm}^{-3}\) in HfO₂ [15], the electrical conduction before forming is attributed to TAT along grain boundaries. A significant amount of additional oxygen vacancies must be created by the applied bias to reach the critical value (\(10^{20} \sim 10^{21}/\text{cm}^3\) [13, 15]) necessary for conducting filament formation. It is reported that the activation energy for oxygen vacancy defect generation, \(E_A\), is \(\sim 4.4\) eV [15]. The low vacancy density induced by irradiation explains the slight decrease in \(V_f\) (< 5%), although the origin of the slight \(V_f\) increase for TiN/HfO₂/TiN ReRAM devices after proton radiation at lower TIDs is still not clear and needs further study.

It was also noticed that the irradiation-induced oxygen vacancy density is comparable to the intrinsic oxygen vacancy density when the irradiation dose is above a certain level (\(10^9\) rad for the proton irradiation case and \(10^8\) rad for the He irradiation case, as seen in Table 3.3). This relatively substantial amount of oxygen vacancies induced by irradiation can reduce the trap-to-trap distance and thus increase the TAT probability, which would result in enhanced current leakage. This is consistent with the observed reduction in \(R_{\text{fresh}}\) at higher dose. However, a quantitative description of the variation of \(R_{\text{fresh}}\) at lower irradiation dose for TiN/HfO₂/TiN also requires further investigation.
The origin of the improved resistive switching (device-to-device, cycle-to-cycle) uniformity with dose, reflected by the evolution of $\Delta R_{on}$, $\Delta R_{off}$ and $\Delta R_{on-off}$ in TiN/HfO$_2$/TiN ReRAM devices with increasing proton irradiation dose, remains a topic of investigation. However, it is speculated that the dose-induced reduction in $\Delta R_{on}$ results primarily from local segregation of radiation-induced defects (e.g. oxygen vacancies) at grain boundaries which could provide more repeatable oxygen diffusion pathways upon switching. Also, the formation of increased oxygen vacancies with increased radiation dose may also expand the effective radius of the conducting filament in the on state enhancing the overall downward trend of $\Delta R_{on}$. As to the abrupt decrease in $\Delta R_{off}$, it is quite possible that localized radiation-induced oxygen vacancies lead to more repeatable oxygen diffusion pathways upon switching (similar to the case for $\Delta R_{on}$). The device-to-device variation uncertainty might be responsible for the fact that such an effect would not be enhanced at higher dose. It may be possible to confirm the speculation through a series of radiation experiments wherein oxygen vacancy and grain structure could be carefully controlled. Although outside of the scope of this work, it is hoped that such experiments will be undertaken.

In summary, the resistive switching of vacancy-based (VCM) HfO$_2$-ReRAM devices have been investigated after exposure to 1MeV proton and helium irradiation with a series of different total doses ranging from $10^5$ to $10^{10}$ rad(Si). The electrical measurements for the pre- and the post-irradiated ReRAM devices show that: 1) All devices were still functioning after irradiation; 2) These devices have high radiation tolerance up to a TID of 21 Grad with no obvious degradation in resistive switching performance including $V_{set}$, $V_{reset}$, $R_{on}$ and $R_{off}$; 3) Irradiation induces slight variations in
$V_f (< 5\%)$ and increased leakage current for fresh devices at higher doses; and 4) TID irradiation can improve the overall uniformity of resistive switching by reducing resistance variations (from device to device and cycle to cycle) in $on$- and $off$-states for TiN/HfO$_2$/TiN ReRAM devices. The high radiation tolerance of TiN/HfO$_2$/TiN(W) ReRAM devices is attributed to the relatively low radiation-induced vacancy density that is needed for trap-assisted-tunneling associated with formation of Hf-rich conductive filaments. And this relatively low radiation-induced vacancy density, on the contrary, promoted charge trapping and improved the conductive filament stability. This work suggests that these types of VCM HfO$_2$-ReRAM devices are inherently radiation ‘hard’ and may be highly suitable for rad-hard electronics applications.

3.2 Proton and helium irradiation of ECM-type HfO$_2$-ReRAMs

As presented in section 2.2, ReRAMs including Pt/HfO$_2$:Cu/Cu and Cu/HfO$_2$/Ni ReRAM devices have good resistive switching performance. The schematic structures of these devices are shown in Figure 3.5. Table 3.4 gives a summary of resistive switching parameters for these two ReRAM device geometries. In this work, Pt/HfO$_2$:Cu/Cu ReRAM devices were subjected to 1 MeV proton irradiation and Cu/HfO$_2$/Ni ReRAM devices were subjected to 1MeV He$^+$ irradiation. A summary of irradiation conditions for each set of devices is given in Table 3.5. Fully formed and cycled devices in programmed $on$- and $off$-states were investigated over various H$^+$ and He$^+$ irradiation doses. In addition, another 8 – 10 fresh devices were also subjected to He$^+$ irradiation to study resultant effects on forming voltage for Cu/HfO$_2$/Ni ReRAM devices. Since the Pt/HfO$_2$:Cu/Cu ReRAM devices do not involve a forming process, Cu/HfO$_2$/Ni ReRAMs were also used to investigate the effect of proton irradiation on the forming process.
Figure 3.5 Schematic of the two ECM-type ReRAM structures.

Table 3.4 Summary of resistive switching parameters for ECM Pt/HfO$_2$:Cu/Cu and Cu/HfO$_2$/Ni ReRAM devices.

<table>
<thead>
<tr>
<th>Device</th>
<th>Pt/HfO$_2$:Cu/Cu</th>
<th>Cu/HfO$_2$/Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_f$ (V)</td>
<td>-</td>
<td>14.08 ± 0.46</td>
</tr>
<tr>
<td>$R_{\text{fresh}}$ ($\times 10^{10}$ Ω)</td>
<td>-</td>
<td>7.09 ± 1.31</td>
</tr>
<tr>
<td>$V_{\text{set}}$ (V)</td>
<td>0.81 ± 0.10</td>
<td>1.5 ± 0.42</td>
</tr>
<tr>
<td>$V_{\text{reset}}$ (V)</td>
<td>-0.64 ± 0.13</td>
<td>-0.45 ± 0.04</td>
</tr>
<tr>
<td>$R_{\text{on}}$ (Ω)</td>
<td>141.76 ± 24.41</td>
<td>155.14 ± 40.57</td>
</tr>
<tr>
<td>$R_{\text{off}}$ (MΩ)</td>
<td>1.36 ± 1.14</td>
<td>17022 ± 18481</td>
</tr>
<tr>
<td>Endurance (cycle)</td>
<td>&gt; 10$^5$</td>
<td>&gt; 10$^4$</td>
</tr>
<tr>
<td>Retention (s)</td>
<td>&gt; 10$^5$</td>
<td>&gt; 10$^5$</td>
</tr>
</tbody>
</table>

Table 3.5. Summary of ECM ReRAM devices exposure to a 1 MeV H$^+$ and He$^+$ ion energy.

<table>
<thead>
<tr>
<th>Rad source</th>
<th>Devices</th>
<th>Total Doses (rad(Si))</th>
<th>Fluence (ions/cm$^2$)</th>
<th>Exposure Time (min)</th>
<th>Number of devices</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 MeV H$^+$</td>
<td>Pt/HfO$_2$:Cu/Cu</td>
<td>$1.5 \times 10^9$</td>
<td>$5.32 \times 10^{14}$</td>
<td>102</td>
<td>10 (on) + 10 (off)</td>
</tr>
<tr>
<td></td>
<td>Pt/HfO$_2$:Cu/Cu</td>
<td>$3 \times 10^9$</td>
<td>$1.06 \times 10^{15}$</td>
<td>210</td>
<td>15 (on) + 15 (off)</td>
</tr>
<tr>
<td></td>
<td>Pt/HfO$_2$:Cu/Cu</td>
<td>$5 \times 10^9$</td>
<td>$1.77 \times 10^{15}$</td>
<td>366</td>
<td>15 (on) + 15 (off)</td>
</tr>
<tr>
<td></td>
<td>Cu/HfO$_2$/Ni</td>
<td>$1 \times 10^{10}$</td>
<td>$3.54 \times 10^{15}$</td>
<td>110</td>
<td>8 (fresh)</td>
</tr>
<tr>
<td></td>
<td>Cu/HfO$_2$/Ni</td>
<td>$5 \times 10^{10}$</td>
<td>$1.77 \times 10^{16}$</td>
<td>95</td>
<td>8 (fresh)</td>
</tr>
<tr>
<td>1 MeV He$^+$</td>
<td>Cu/HfO$_2$/Ni</td>
<td>$2.1 \times 10^9$</td>
<td>$1 \times 10^{14}$</td>
<td>68</td>
<td>6 (on) + 6 (off)</td>
</tr>
<tr>
<td></td>
<td>Cu/HfO$_2$/Ni</td>
<td>$2.1 \times 10^{10}$</td>
<td>$1 \times 10^{15}$</td>
<td>80</td>
<td>6 (on) + 6 (off)</td>
</tr>
</tbody>
</table>
The electrical measurements were carried out on a Keithley 4200 semiconductor characterization system for Pt/HfO$_2$:Cu/Cu and on an Agilent 1500A parametric analyzer for Cu/HfO$_2$/Ni ReRAM devices. I-V characteristics are obtained before irradiation (pre-rad), immediately after irradiation (post-rad) and 5 days after irradiation (post-rad(5-days)). Each device was measured in a DC sweep mode for several set/reset cycles at a CC of 500 mA for Pt/HfO$_2$:Cu/Cu devices and 500 µA for Cu/HfO$_2$/Ni. For all devices, bottom electrodes were grounded and voltages were applied to the top electrode.

3.2.1 Effects on resistive switching

For ECM ReRAM devices, 75% of Pt/HfO$_2$:Cu/Cu ReRAM devices (out of 80 devices in total) survived (remained resistive switching) proton irradiation, and 83% of Cu/HfO$_2$/Ni devices (out of 24 devices in total) survived helium irradiation. Figure 3.6 gives the I-V characteristics of a typical Cu/HfO$_2$:Cu/Pt device that survived a 1.5 Grad dose of proton irradiation, with set and reset switching behavior for the pre-rad (in black), post-rad (in red), and post-rad (5-days, in blue) cases. Clearly, compared to the pre-rad case, $V_{set}$ and $|V_{reset}|$ exhibited positive shifts immediately after irradiation, but negative shifts 5-days after irradiation.
Figure 3.6 Comparison of I–V characteristics of a typical ECM device in the case of pre-radiation (in black), post-radiation (in red) and post-radiation 5 days later (in blue). The devices were subjected to proton radiation to a total dose of $1.5 \text{ Gra(Si)}$.

$V_{\text{set}}$, $V_{\text{reset}}$, $R_{\text{on}}$, and $R_{\text{off}}$ were measured for all ECM ReRAM devices exposed to proton radiation with TID of 1.5, 3 and 5 Grad. The average values with respective error bars for each case were summarized and presented in Figure 3.7. In order to eliminate the intrinsic variation of the 80 devices and elucidate the performance change due to irradiation effects, these average values were normalized to the pre-rad case. Significant shifts of $V_{\text{set}}$, $|V_{\text{reset}}|$, $R_{\text{on}}$ and $R_{\text{off}}$ for all devices under the 3 doses cases were observed.
Figure 3.7 The H-radation induced performance change in percentage of Pt/HfO$_2$:Cu/Cu devices (a) average of $V_{\text{set}}$, (b) average $V_{\text{reset}}$, (c) average $R_{\text{on}}$, and (d) average $R_{\text{off}}$. The dashed lines in (a, b, c) are linear fits for the corresponding shifts.

Figure 3.7(a) shows the $V_{\text{set}}$ response to H$^+$ irradiation. In this figure, the post-rad (in red) value is positively shifted by $\sim 40\%$ from the pre-rad case. Comparing the 1.5 Grad data with that of the 3 and 5 Grad, it can be seen that $V_{\text{set}}$ was positively shifted with very small fluctuation as the dose increases from 1.5 Grad (40\%) to 3 Grad (42\%) and finally to 5 Grad (50\%). However, the $V_{\text{set}}$ response measured 5 days after irradiation (in blue) shows a significant reduction in the $V_{\text{set}}$ percentage-shift. The reduction in the 1.5 Grad case is -30\% (less than the initial $V_{\text{set}}$ for the pre-rad devices) and -25\% for the 3 Grad case. When the dose was 5 Grad, $V_{\text{set}}$ in the post-rad (5 days) case is close to the $V_{\text{set}}$ for
the pre-rad case. This reverse shifting of $V_{\text{set}}$ over time can be compared to the “rebound” or “super recovery” that has been observed in n-type CMOS devices [16, 17, 18]. This rebound effect occurs for all 1.5, 3 and 5 Grad cases, but the rebound in the 5 Grad case is not as significant as that for the 1.5 and 3 Grad doses. Such reduced rebound effect for higher total-doses has also been found in CMOS devices [16, 18].

The dashed lines in Figure 3.7 are linear fits, indicating the $V_{\text{set}}$ changes ($\Delta V_{\text{set}}$) in both post-rad and post-rad (5 days) cases. These increase approximately linearly with dose. The percentage-shift values of $V_{\text{reset}}$ ($\Delta V_{\text{reset}}$) in Figure 3.7(b) also exhibit a similar trend to those seen in the percentage-shift values of $V_{\text{set}}$ (Figure 3.7(a)); however, Figure 3.7(b) shows a larger deviation from the fitting line. It was confirmed using theoretical SRIM simulations [14] that the total number of vacancies produced per ion has a linear relationship with dose. Regardless of the slightly different shifts in reset and set voltages, the nearly linear increase of both $\Delta V_{\text{set}}$ and $\Delta V_{\text{reset}}$ with dose is likely due to the linear increase of electron/hole traps inside the HfO$_2$ region which is expected to scale with the increase of dose.

$R_{\text{on}}$ (Figure 3.7(c)) exhibited a similar trend to $V_{\text{set}}$ and $V_{\text{reset}}$. However, as shown in Figure 3.7(d), $R_{\text{off}}$ shows a completely different trend: the $R_{\text{off}}$ (post-rad) value decreases from the pre-rad case, and the post-rad (5 days) value is further reduced from the post-rad case. This monotonic $R_{\text{off}}$ reduction suggests that a certain amount of leakage current is enhanced by increasing the dose for devices in the $\text{off}$-state. In Figure 3.7(d), the variance of $R_{\text{off}}$ indicated by the error bars in the 5 Grad case is significantly reduced in the post-rad and post-rad(5-days) cases. Proton irradiation seems to reduce the $R_{\text{off}}$ variation seen in this type of ReRAM device.
The percentage change for $V_{\text{set}}$, $V_{\text{reset}}$, $R_{\text{on}}$ and $R_{\text{off}}$ for Cu/HfO$_2$/Ni ReRAM devices after He irradiation at 2 different doses is plotted in Figure 3.8. It should be noted that due to the relatively large intrinsic variation of the Cu/HfO$_2$/Ni ReRAMs, no obvious trends can be observed with irradiation dose in terms of the dynamic $V_{\text{set}}$, $V_{\text{reset}}$, $R_{\text{on}}$ and $R_{\text{off}}$.

Figure 3.8 The He-radiation induced performance change in percentage of Cu/HfO$_2$/Ni devices (a) average of $V_{\text{set}}$, (b) average $V_{\text{reset}}$, (c) average $R_{\text{on}}$, and (d) average $R_{\text{off}}$.

3.2.2 Effects on forming

Irradiation responses of the conducting filament forming process were investigated on Cu/HfO$_2$/Ni ReRAM devices for both proton and helium irradiation. The variations in $V_f$ and $R_{\text{fresh}}$ are shown in Figure 3.9. After proton irradiation (Figure 3.9(a)), the average
$V_f$ of 8 – 10 devices increased from 14.08 V (pre-rad) to 14.6 V (post-rad@10 Grad) and 15.09 V (post-rad@50 Grad), whereas the average $R_{\text{fresh}}$ (Figure 3.9(b)) decreased from 7.09 \times 10^{10} \Omega \text{ (pre-rad)}$ to $4.14 \times 10^{10} \Omega \text{ (post-rad@10 Grad)}$ and $5.14 \times 10^{10} \Omega \text{ (post-rad@50 Grad)}$. It is noted that the reduction in average $R_{\text{fresh}}$ is smaller at 50 Grad then that at 10 Grad. A similar trend was noticed for the devices after He irradiation, as seen in Figure 3.9(c) for $V_f$ and (d) for $R_{\text{fresh}}$. A monotonic increase in $V_f$ (14.12 V post-rad@2.1 Grad and 15.31 V post-rad@21 Grad), a decrease in $R_{\text{fresh}}$ under 2.1 Grad ($2.89 \times 10^{10} \Omega$), and a smaller decrease under 21 Grad ($6.54 \times 10^{10} \Omega$) were also observed.
Figure 3.9 (a) Average $V_f$ and (b) average $R_{\text{fresh}}$ as a function of TID after H-radiation and (c) average $V_f$ and (d) average $R_{\text{fresh}}$ as a function of TID after He-radiation on Cu/HfO$_2$/Ni ReRAM devices. The blue dash lines are used as a convenient visual reference to average pre-radiation values.

Similar Poole-Frenkel fitting on the forming process, as described in section 2.2.2 for non-irradiated devices, was performed for these ECM ReRAM devices after proton and helium irradiation. These fits are shown as the red curve in Figure 3.10. In addition, for comparison, an ionic fitting was also carried out for the same irradiated devices using the modified equation $I = A_l \exp(B_l V)$ from Equation (2.5), with the fitting curves shown in blue in Figure 3.10. As seen in that figure, for proton-irradiated devices with a dose of 50 Grad, a Poole-Frenkel conduction model agrees well with the experimental curves with smaller $\chi^2$ values compared to fits to an ionic conductivity model ($\chi^2 \sim 0.01$ for Poole-
Frenkel fitting versus $\chi^2 \sim 0.1$ for ionic fitting). Similar fitting results were found for all 5 proton-irradiated devices. The dynamic dielectric constant, $\varepsilon_d \sim 10.93 \pm 0.62$, was also extracted from the Poole-Frenkel fitting for all 5 devices. As expected, the value of the extracted dynamic dielectric constant falls between the values of the optical dielectric constant ($\varepsilon_{opt} \sim 4$ [13, 19]) and static dielectric constant ($\varepsilon_s \sim 17.94$ as derived from C-V measurement at a frequency of 500 Hz for devices after proton radiation). This result is an important confirmation of the validity of the Poole-Frenkel fitting analysis. All these results indicate that the Poole-Frenkel mechanism still dominates the conduction during forming process for the Cu/HfO$_2$/Ni ReRAM devices after proton irradiation.

Figure 3.10 Representative I-V fitting to both Poole-Frenkel effect and ionic conduction for Cu/HfO$_2$/Ni devices after (a) proton radiation at 50 Grad(Si), and (b) helium radiation at 21 Grad(Si). The inset gives the $A_{P-F}$ and $B_{P-F}$ parameters from Poole-Frenkel fitting for 5 devices. The dashed lines in the inset are the corresponding average A and B values.

Similar fitting results were noted for the devices after helium irradiation, as shown the representative fitting curves in Figure 3.10(b). The inset of that figure shows the Poole-Frenkel fitting parameters, $A_{P-F}$ and $B_{P-F}$, for 5 individual devices. Clearly, the Poole-Frenkel mechanism dominates the conduction during forming ($\chi^2 \sim 0.02$ for Poole-Frenkel fitting versus $\chi^2 \sim 0.09$ for ionic fitting). The extracted dynamic dielectric
constant (from Poole-Frenkel fitting), $\varepsilon_d \sim 17.53 \pm 1.19$, also falls between the optical dielectric constant ($\varepsilon_{\text{opt}} \sim 4$) and static dielectric constant ($\varepsilon_s \sim 21.26$, from C-V measurement at a frequency of 500 Hz for He-irradiated devices). It is interesting to note that the extracted dynamic dielectric constant increases after H and He irradiation. This will be discussed in the next section.

### 3.2.3 Discussion

As mentioned in section 3.1.4, electron traps in HfO$_2$ dominate the irradiation response [9, 10, 11, 12]. In our ECM-ReRAM irradiation study, to simplify the analysis, the irradiation-induced oxygen vacancies are considered to be the main source of electron trapping centers. For both ECM devices (Pt/HfO$_2$:Cu/Cu and Cu/HfO$_2$/Ni), the atomic composition depth profiles before and after proton and helium irradiation were analyzed by Auger Electron Spectroscopy (AES, Perkin Elmer PHI-660). The atomic ratio of O to Hf in the HfO$_2$ layer was examined. Figure 3.11(a) shows the depth profile of O/Hf ratio for devices (pre-radiation, post-radiation, and post-radiation(5-days)) for a dose of 1.5 Grad. It can be seen that the O/Hf ratio is almost constant across the HfO$_2$ layer profile. The average O/Hf ratio (indicated by the green lines) decreased from 1.218 (pre-rad) to 1.118 (post-rad) after proton radiation. However, 5 days after the proton irradiation, O/Hf ratio increased back to 1.197. The change in O/Hf ratio after proton irradiation with 3 different doses is calculated and normalized to the pre-rad value, as shown in Figure 3.11(b). After irradiation at a dose of 1.5Grad, the O/Hf ratio decreased by 8%, but this reduction shrank to 3.4% 5 days after the proton irradiation. Similar behavior regarding the O/Hf ratio was observed under 3 different doses, i.e. a reduction of the O/Hf ratio immediately after proton irradiation followed by a recovery of the O/Hf ratio 5 days after
proton irradiation. However, the AES measurements did not show an enhanced change in O/Hf ratio with increasing dose, which is counterintuitive and requires further investigation.

Figure 3.11 (a) AES depth profile of O/Hf ratio for the device pre- and post-radiation at 1.5 Grad(Si). Note that the O/Hf profile under post-rad case is offset by -0.4 vertically and the blue post-rad(5-days) curve is offset by 0.4 vertically. The dashed green lines are the corresponding average O/Hf ratio of HfO$_2$ layer. (b) Percentage of change in O/Hf ratio of the devices after H-radiation, and 5 days after H-radiation with TID of 1.5, 3, and 5Grad(Si).

The observed decrease in O/Hf ratio upon irradiation suggests an increase of oxygen vacancies induced by irradiation and therefore an increase of electron traps inside the HfO$_2$. These radiation-induced electron traps can then distort the internal electric field and lower the effective electric field inside HfO$_2$, as seen in Figure 3.12. To provide an illustration of the reduction of the electric field within HfO$_2$ resulting from radiation-induced traps, general simulations were carried out using COMSOL finite element modeling (FEM) software. Figure 3.12 (a) shows the results of a simulation of the electric field within a pre-rad device. The solid curves are equipotential lines resulting from a 1-V voltage between the filament tip and electrode. This simulation is provided as an ideal reference and does not include the intrinsic electron traps that would exist due to processing. With the same bias condition, a simulation result of the electric field for a
post-irradiated device is shown in Figure 3.12(b), assuming random electron traps (represented by the black dots) were generated by irradiation. Although these simulations do not represent a quantitative, predictive model they do provide importance guidance into the impact of irradiation on ReRAM performance. It can be seen in Figure 3.12(b) that the electric field is distorted; the electric field is weakened in the bulk HfO$_2$ and enhanced close to the filament surface and electrode/HfO$_2$ interfaces. As described in Equation (2.5)) in section 2.2.3, the ion diffusion through HfO$_2$ layer is the rate-limiting step in filament growth, so the weakening of the electric field can lead to a smaller current and therefore filament growth rate, which is consistent with the observed positive shift of $V_{\text{set}}$, $V_{\text{reset}}$ and $R_{\text{on}}$ after irradiation. However, the substantial amount of electron traps induced by irradiation can help enhance the current leakage when the device is in the off-state, thus decreasing the $R_{\text{off}}$ value after irradiation. 5 days after irradiation, the devices exhibited a rebound of the O/Hf ratio and thus a recovery of the O content. This would result in a latent discharge of electron traps and would contribute to the rebound effect of the set/reset voltages and $R_{\text{on}}$ values as was experimentally observed.
Figure 3.12 Field simulation results of internal electric field in HfO$_2$ for devices (off-state) pre- and post-irradiation, using COMSOL multiphysics 4.2. The curves are equipotential lines after applying a voltage of 1 V on the top electrode with the bottom electrode grounded; the black dots represent the radiation-induced electron traps.

For He-irradiated Cu/HfO$_2$/Ni devices, the O/Hf ratio depth profile is plotted in Figure 3.13(a). Unlike the Pt/HfO$_2$:Cu/Cu devices, the O/Hf ratio is non-uniformly distributed inside the HfO$_2$ layer for the Cu/HfO$_2$/Ni devices. To compare the O/Hf ratio before and after He irradiation, the O/Hf ratio was integrated along the depth between the red dashed lines, and the integrated O/Hf area is listed in the inset table. The percentage change in this integrated area was then calculated following 2.1 and 21 Grad irradiation (plotted in Figure 3.13(b)). It can be seen that the O/Hf ratio was also reduced by $\sim$5% after irradiation at a dose of 2.1Grad and by $\sim$12% after irradiation with a dose of 21Grad. Thus, it can be expected that He irradiation also introduced oxygen vacancies and therefore electron traps inside HfO$_2$. 
Figure 3.13 (a) AES depth profile of O/Hf ratio for the devices before He-radiation (in black) and after he-radiation (in red and blue). The table inserted displays the integrated area of O/Hf curve of HfO$_2$ layer (depth between the red dashed lines) (b) Percentage of change in integrated area of O/Hf ratio from the table in (a).

These irradiation-enhanced electron traps were also implied by C-V measurements, as seen in Figure 3.14 which plots the normalized capacitance versus frequency for ECM ReRAD devices: pre-rad (in black), post H-rad (in red) and post He-rad (in blue). The higher $C_f/C_{1M}$ at lower frequency is consistent with the intrinsic interface or bulk traps existing in the as-fabricated HfO$_2$ [13]. The decrease in $C_f/C_{1M}$ observed with increased frequency was enhanced after proton irradiation and even more so after helium irradiation. This indicates that irradiation results in an increased trap density inside the HfO$_2$ layer after proton and helium irradiation. These irradiation-induced electron traps, similar to the case of Pt/HfO$_2$:Cu/Cu devices, reduce the internal electric field (as illustrated in Figure 3.12(b)), contributing to the increase in $V_f$ after proton and helium irradiation. Furthermore, due to the increase in trap density, the Poole-Frenkel current can be enhanced thus reducing the $R_{\text{fresh}}$ of fresh ReRAM devices. Also, note that the dielectric constant was assumed to be uniform and constant while fitting the forming I-V curves to Poole-Frenkel current expression. Thus, after irradiation, the weakened
effective electric field resulting from irradiation is represented by an increased $\varepsilon_d$, consistent with what was observed in the experiment.

![Normalized capacitance, $C_f/C_1M$, as a function of frequency for the devices before and after proton and helium irradiation.](image)

**Figure 3.14** Normalized capacitance, $C_f/C_1M$, as a function of frequency for the devices before and after proton and helium irradiation.

To supplement the above analysis, the crystal structure of the ECM ReRAM devices for each case (pre-rad, post-H-rad and post-He-rad) was also investigated by X-ray diffraction (XRD, Scintag XDS 2000 for Pt/HfO$_2$:Cu/Cu devices and Bruker D8 for Cu/HfO$_2$/Ni devices) with Cu Kα irradiation ($\lambda = 0.15406$ nm). According to previous studies, proton-based irradiation will increase intrinsic bonding defects inside crystalline HfO$_2$ due to displacement damage [20]. As shown in Figure 3.15(a) for the Pt/HfO$_2$:Cu/Cu devices before and after radiation at 1.5, 3 and 5 Grad, the (\(\bar{1}02\)) and (\(\bar{1}21\)) XRD peaks for pre-rad devices (circled) implies a polycrystalline HfO$_2$. These peaks disappear for the post-rad cases under different total doses, except for the 5 Grad dose case for which the (\(\bar{1}02\)) peak remains. For a better comparison, the (\(\bar{1}21\)) peak was smoothed and displayed as the dashed lines in Figure 3.15(b). The disappearance of the (\(\bar{1}21\)) peak was clearly observed after irradiation, suggesting a radiation-induced
amorphization of the crystalline structure that may lead to the reduction in $R_{\text{off}}$ of the devices. Thus, no recovery of $R_{\text{off}}$ was observed 5 days after proton irradiation.

![Figure 3.15](image)

Figure 3.15 Comparison of XRD results of ECM-type ReRAMs before and after radiation for (a) Pt/HfO$_2$:Cu/Cu device subjected to proton radiation, with (b) the comparison of the individual peak of HfO$_2$ (121) at different TIDs; (c) Cu/HfO$_2$/Ni devices subjected to He-radiation, with (d) the comparison of HfO$_2$ (111) peak at different dose. The dashed lines in (b) and (d) are the corresponding smoothed peak curves. The inset in (d) is the smoothed curves for the purpose of a better comparison, and the dashed vertical line corresponds to the (111) peak position at 28.35° in a perfect crystalline structure.

For Cu/HfO$_2$/Ni devices, only one HfO$_2$ peak, the monoclinic (111) peak, was observed for devices before and after He irradiation with different doses (Figure 3.15(c)). Figure 3.15(d) shows a comparison of the (111) peak after the subtraction of the background for all cases. The dashed lines are the corresponding smoothed curve for each
peak. For a better comparison, the inset in Figure 3.15(d) shows the smoothed (\(\bar{1}11\)) curves only in all cases, where it can be seen that the peak position shifted to a higher angle with increasing dose. In addition, the full width half maximum (FWHM) of the peak (values summarized in Table 3.6) decreased with increasing dose, suggesting an increase in domain size of crystallites perpendicular to (\(\bar{1}11\)) plane. This peak-position shifting (or lattice expansion) with decreasing size has also been reported for monoclinic HfO\(_2\) and it was attributed to surface dipole repulsion \([21, 22]\). Thus for Cu/HfO\(_2\)/Ni devices, unlike the case of H-irradiated Pt/HfO\(_2\):Cu/Cu devices, the HfO\(_2\) peak remains and the size of crystallites increases with dose after He irradiation. This microstructural change is likely responsible for the reverse \(R_{\text{fresh}}\) change at higher dose at 21 Grad (Figure 3.9(b) and (d)).

### Table 3.6 FWHM values from Gaussian fitting of the (\(\bar{1}11\)) peak for the Cu/HfO\(_2\)/Ni devices before and after helium irradiation with different doses.

<table>
<thead>
<tr>
<th>Case</th>
<th>FWHM (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-rad</td>
<td>1.402 ± 0.073</td>
</tr>
<tr>
<td>Post-He (2.1 Grad)</td>
<td>1.268 ± 0.061</td>
</tr>
<tr>
<td>Post-He (21 Grad)</td>
<td>1.165 ± 0.039</td>
</tr>
<tr>
<td>Post-He (210 Grad)</td>
<td>1.151 ± 0.056</td>
</tr>
</tbody>
</table>

In summary, the resistive switching properties of ECM-type ReRAM devices, Pt/HfO\(_2\):Cu/Cu and Cu/HfO\(_2\)/Ni, were investigated under proton and helium irradiation with different total doses. The measurement results demonstrate that proton irradiation introduces positive shifts in \(V_{\text{set}}\), \(V_{\text{reset}}\), and \(R_{\text{on}}\) for Pt/HfO\(_2\):Cu devices with rebound effects observed 5 days after irradiation. Furthermore, proton and helium irradiation on Cu/HfO\(_2\)/Ni ReRAM devices increase \(V_f\) with dose. These irradiation responses are attributed to the irradiation-induced electron trap changes in HfO\(_2\) and their impact on
electrochemical metallization. Irradiation also reduces $R_{\text{off}}$ for Pt/HfO$_2$:Cu/Cu devices and $R_{\text{fresh}}$ for Cu/HfO$_2$/Ni devices by creating more electron trap defects and potentially increasing device leakage current. Also, the forming conduction is well-described by a Poole-Frenkel conduction mechanism with an increased dynamic dielectric constant observed for Cu/HfO$_2$/Ni devices after proton and helium irradiation. The effects of H$^+$ and He$^+$ irradiation were consistent with AES, C-V measurement and XRD analyses.

### 3.3 Comparison of irradiation response between VCM and ECM HfO$_2$-ReRAMs

As mentioned in section 2.2.3, the difference of device area does not impact the VCM-ECM comparison. With respect to film thickness, measurements imply that the length-scale of ECM metallic filament rupture/formation is on the order of 5 nm [23, 24] localized at the electrode. Similarly, there is a consensus that filament rupture/formation occurs on a ~1 nm length scale for HfO$_2$ VCM devices, likewise, near the electrode (TiN) interface [15]. SRIM modeling shows that the density of radiation-induced vacancies is relatively insensitive to device film thickness for the Pt/HfO$_2$:Cu/Cu and TiN/HfO$_2$/TiN stack geometries considered. These factors facilitate a direct, experimental comparison between the ECM and VCM ReRAM device geometries with respect to radiation hardness.

To directly compare the pre- and post-rad resistive switching behavior between HfO$_2$-based VCM and ECM ReRAMs, Figure 3.16 plots the percentage change in switching parameter averages (normalized to pre-radiation values) for 1.5 Grad total dose of proton radiation (Figure 3.16(a)) and 2.1Grad dose of helium radiation (Figure 3.16(b)). As seen in Figure 3.16(a) after proton radiation, $\Delta V_{\text{set}}^{\text{avg}}$ denotes the fractional
(percentage) change in the average value of $V_{\text{set}}$. The same convention is used for $V_{\text{reset}}$, $R_{\text{on}}$ and $R_{\text{off}}$. The values of $\Delta V_{\text{set}}^{\text{avg}}$ and $\Delta V_{\text{reset}}^{\text{avg}}$ for ECM devices exceed those from VCM ReRAMs by more than an order of magnitude. And, as noted above, $\Delta R_{\text{on}}^{\text{avg}}$ exhibited opposite trends for ECM compared to VCM ReRAMs. The latter exhibited a slight decrease in $\Delta R_{\text{on}}^{\text{avg}}$ while the former exhibited an upward shift nearly 10 times larger. Both ECM and VCM devices exhibited a reduction in $\Delta R_{\text{off}}^{\text{avg}}$ after irradiation, although the fractional change for the ECM devices is approximately 10 times larger as well. Empirically, the clear conclusion is that HfO$_2$-based VCM ReRAMs are substantially more resistant to TID proton radiation than ECM ReRAM devices.

**Figure 3.16** Average percentage changes in parameters: $V_{\text{set}}^{\text{avg}}$, $V_{\text{reset}}^{\text{avg}}$, $R_{\text{on}}^{\text{avg}}$, $R_{\text{off}}^{\text{avg}}$ after (a) proton radiation at TID of 1.5 Grad(Si), (b) He radiation at the TID of 2.1Grad(Si). The values in percentage are all normalized to the pre-radiation values.

The comparison of percentage changes between VCM and ECM devices post He irradiation (with the dose of 2.1 Grad) is given in Figure 3.16(b). As seen from the figure, VCM devices exhibited little change in $V_{\text{set}}$, $V_{\text{reset}}$, $R_{\text{on}}$ (<-1.5%) and relatively larger variation in $R_{\text{off}}$ (~13.2%), whereas ECM devices have significantly larger variation in $V_{\text{set}}$ (~-16.8%), $R_{\text{on}}$ (123%) and $R_{\text{off}}$ (~61%). Also, both $R_{\text{on}}$ and $R_{\text{off}}$ have positive changes for ECM devices, which is completely the opposite behavior observed for VCM
devices. However, considering the large intrinsic variation of the $V_{set}$, $V_{reset}$, $R_{on}$, $R_{off}$ parameters for Cu/HfO$_2$/Ni devices, it is difficult to make hard and fast conclusions from comparisons between VCM and ECM devices under He irradiation. However, these comparisons do serve to support the conclusion that VCM devices seem to be more radiation resistant compared to ECM devices.

Since both ECM and VCM devices exhibit a forming process, it is also possible to compare $V_f$ and $R_{fresh}$ between VCM and ECM devices post H and He irradiation. Figure 3.17 presents the comparison of irradiation-induced changes in $V_f$ and $R_{fresh}$ (in percentage) between VCM and ECM devices. Figure 3.17(a) shows that, for post H irradiation at 1.5 Grad dose, $V_f$ for a VCM device exhibited a negative change (-1.8%) while $V_f$ for a ECM device exhibited a positive change (~4%). In addition, $R_{fresh}$ in both devices decreased after H irradiation, and the $|\Delta R_{avg}^{fresh}|$ was slightly larger for VCM devices (45%) than for ECM devices (41%). After He irradiation at 2.1 Grad, as shown in Figure 3.17(b), similar results were observed. $V_f$ changed in opposite directions between VCM (-4%) and ECM devices (0.3%, 8.5% for a 21Grad dose), and $R_{fresh}$ decreased for both types of devices while the $R_{fresh}$ change for VCM devices (-72%) was slightly larger than that for ECM (-59%).
Figure 3.17 Percentage changes in average parameters: $V_{f}^{avg}$, $R_{fresh}^{avg}$, after (a) proton radiation at TID of 1.5 Grad(Si), (b) He radiation at the TID of 2.1 Grad(Si). The values in percentage are all normalized to the pre-radiation values.

We surmise that the fundamental difference in forming and resistive switching mechanisms between ECM and VCM devices is responsible for these comparison results. Irradiation-induced electron traps play a different role in VCM and ECM devices. In VCM, the forming is based on a TAT current that is very sensitive to trap-to-trap distance. Irradiation-induced traps help reduce the trap-to-trap distance and enhance the TAT current ($R_{fresh}$) which further reduces $V_f$. For ECM devices, the forming conduction is related to Poole-Frenkel conduction and the switching is based on the electrochemical metallization. The irradiation-induced traps help enhance the forming current but at the same time inhibit the filament growth rate, which results in larger $V_f$ but also lower $R_{fresh}$ for ECM devices.

An intriguing aspect of the post-irradiation data is related to the impact of proton irradiation on variations within the ReRAM parameter set. Specifically, as described in section 3.1.3, a significant reduction in the standard deviations for the $R_{off}$ and $R_{on}$ values of TiN/HfO$_2$/TiN ReRAMs and thus an increased uniformity in the resistive switching performance were observed after irradiation. Figure 3.18 plots the percentage changes in
the standard deviations for $V_{\text{set}}$, $V_{\text{reset}}$, $R_{\text{on}}$ and $R_{\text{off}}$ following 1.5 Grad proton radiation for both VCM (TiN/HfO$_2$/TiN) and ECM (Pt/HfO$_2$:Cu/Cu) ReRAM devices. These are denoted $\Delta V_{\text{set}}^{\text{sd}}$, $\Delta V_{\text{reset}}^{\text{sd}}$ and $\Delta V_{\text{avg}}^{\text{set}}$, $\Delta R_{\text{on}}^{\text{sd}}$ and $\Delta R_{\text{off}}^{\text{sd}}$. Negative values for VCM ReRAMs (in black) represent decreased standard deviations after radiation, which was believed to result from the creation of preferential conducting paths between filaments which could serve to reduce cycle-to-cycle variations and/or variations from one device to another. In contrast, for ECM ReRAMs, $\Delta V_{\text{set}}^{\text{sd}}$, $\Delta V_{\text{reset}}^{\text{sd}}$, and $\Delta R_{\text{on}}^{\text{sd}}$ exhibit increased standard deviations following irradiation, which likely originated from the variability in trapping/detrapping probabilities of irradiation-introduced traps and the resultant variations in field screening. In general, it is reasonable to conclude that TID proton radiation can serve to improve the uniformity of resistive switching for VCM ReRAM devices, but inhibits the uniformity of resistive switching in ECM devices.

Figure 3.18 Changes in standard deviations: $\Delta V_{\text{set}}^{\text{sd}}$, $\Delta V_{\text{reset}}^{\text{sd}}$, $\Delta R_{\text{on}}^{\text{sd}}$, $\Delta R_{\text{off}}^{\text{sd}}$ for VCM TiN/HfO$_2$/TiN (in black) and ECM Pt/HfO$_2$:Cu/Cu (in red) ReRAMs after proton radiation with TID of 1.5 Grad. The values in percentage are all normalized to the pre-radiation values.
In conclusion, analysis of TID radiation responses of VCM-type and ECM-type ReRAMs under proton and helium irradiation shows that VCM ReRAMs have superior TID radiation-hardness: (1) Parameters including average $V_{\text{set}}$, $V_{\text{reset}}$, $R_{\text{on}}$, $R_{\text{off}}$ in VCM ReRAMs exhibit relatively modest effects due to irradiation, while substantially larger changes were observed for ECM ReRAMs; (2) Irradiation reduces $V_f$ for VCM but increases $V_f$ for ECM; (3) TID radiation improves the overall uniformity of resistive switching in VCM ReRAMs while degrading switching uniformity in ECM ReRAMs. The different radiation responses in VCM and ECM ReRAM devices result from the distinct conduction filament (CF) formation mechanisms. For the VCM ReRAM system the proton-induced vacancy density does not inhibit the trap-assisted-tunneling associated with Hf-rich CF formation. On the contrary, vacancy-promoted charge trapping promotes VCM CF stability. In strong contrast, proton-induced vacancies for the ECM ReRAMs inhibit the formation of the metallic filament through internal field reduction due to charge trapping.

At last, it should be pointed out that for practical application ReRAM devices with lower $V_f$ or even $V_f$-free are more desirable. For VCM devices, radiation leads to reduced $V_f$, as well as enhanced switching uniformity, suggesting that VCM devices are not only rad-hard but also 'rad-philic', and that radiation could be used to optimize the VCM ReRAMs performance.
3.4 References


4. Impacts of Heavy-Ion Irradiation on HfO₂-based ReRAMs

As heavy ions comprise a substantial fraction of the radiation exposure suffered by space-borne devices, attention should be paid to effects of heavy-ion irradiation on ReRAMs. This chapter presents a study of the effects of heavy-ion irradiation on both VCM-type and ECM-type ReRAM devices carried out with a variety of ion sources, including N, Ne, and Ar. Section 4.1 presents the results of heavy-ion irradiation on VCM ReRAM devices (TiN/HfO₂/W)) at ion fluences ranging from $10^{12}$ to $10^{15}$ cm$^{-2}$, followed by a discussion on the irradiation effects. Section 4.2 presents the results of heavy-ion irradiation (N and Ar at a fluence of $10^{15}$ cm$^{-2}$) on ECM ReRAM devices (Cu/HfO₂/Ni), with an accompanying discussion. Finally, a comparison of the irradiation responses between VCM and ECM ReRAM devices is given in section 4.3.

4.1 Heavy-ion irradiation of VCM-type HfO₂-ReRAMs

15-16 TiN/HfO₂/W ReRAM devices were employed in each irradiation experiment. Half of the devices were programmed into the off-state and the other half were programmed into the on-state before radiation exposure. These devices were then irradiated at fluences of $10^{12}$, $10^{14}$, $10^{15}$ cm$^{-2}$ (vertically incident on the top electrode) using N, Ne, Ar ion sources. Table 4.1 summarizes the irradiation experimental conditions and the number of devices exposed.
Table 4.1 Summary of Radiation Experiment Parameters.

<table>
<thead>
<tr>
<th>Irradiation source</th>
<th>Total Doses (rad(Si))</th>
<th>Fluence (ions/cm²)</th>
<th>Exposure time (min)</th>
<th>Number of devices</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 MeV N⁺²</td>
<td>7.55 × 10⁷</td>
<td>1 × 10¹²</td>
<td>0.7</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>7.55 × 10⁹</td>
<td>1 × 10¹⁴</td>
<td>39</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>7.55 × 10¹⁰</td>
<td>1 × 10¹⁵</td>
<td>36</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td>1.6 MeV Ne⁺</td>
<td>9.61 × 10⁷</td>
<td>1 × 10¹²</td>
<td>1.3</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>9.61 × 10⁹</td>
<td>1 × 10¹⁴</td>
<td>51</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>9.61 × 10¹⁰</td>
<td>1 × 10¹⁵</td>
<td>78</td>
<td>8 (on) + 7 (off)</td>
</tr>
<tr>
<td>2.75 MeV Ar⁺</td>
<td>1.28 × 10⁹</td>
<td>1 × 10¹²</td>
<td>1.3</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>1.28 × 10¹⁰</td>
<td>1 × 10¹⁴</td>
<td>88</td>
<td>8 (on) + 8 (off)</td>
</tr>
<tr>
<td></td>
<td>1.28 × 10¹¹</td>
<td>1 × 10¹⁵</td>
<td>84</td>
<td>8 (on) + 8 (off)</td>
</tr>
</tbody>
</table>

Electrical measurements were carried out on a Keithley 4200 semiconductor characterization system prior to and immediately after irradiation. Each device was measured in a DC-voltage sweep mode at a CC of 500 µA. All ReRAM irradiation and switching measurements were carried out at ambient temperature. 8-10 non-formed fresh ReRAM devices were also used for investigation of irradiation effects on the forming.

4.1.1 Effects on static resistance state

After the irradiation, substantial on and off resistance changes were observed for the TiN/HfO₂/W ReRAM devices. Thus, following each radiation exposure, the static on and off resistances of all devices without any resistive switching cycles were recorded at V_{read} = -0.05V and compared with the resistances before irradiation. Figure 4.1 shows the comparison of static resistance before and after irradiation at an ion fluence of 10¹⁵ cm⁻² for 16 devices (8 off–resistances on the left and 8 on–resistances on the right for each panel). Note that the static resistance result after He-irradiation is also given for comparison. It is important to note that, despite water cooling of the sample chuck in the ion implanter, the incident ion fluxes used for this study do result in heating of the ReRAM devices. Especially, for heavy-ion radiation at a fluence of 10¹⁵ cm⁻², the
substrate temperature increase due to beam heating can range from 90 to ~ 150 °C depending on ion energy. To rule out the influence of temperature on the static resistance change shown in Figure 4.1, a set of non-irradiated TiN/HfO$_2$/W ReRAM devices (8-off + 8-on + 10-fresh) were annealed for 2 hours at 320 °C. For reference, the static on-/off-resistance comparisons for control devices and post-annealed devices at 320 °C, as well as He-irradiated devices at an ion fluence of $10^{15}$ cm$^{-2}$, are given in Figure 4.1. Note that the dashed green lines at $R = 1500$ Ω in the plots of Figure 4.1 represent the maximum $R_{\text{on}}$, below which resistances are considered in the on-state.
Figure 4.1 Comparison of off- and on-state resistance for devices (a) without radiation at room temperature, R1 (red bars) was measured ~4 hours after R0 (black bars) measurement; (b) before and after annealing at 320 °C for 2 hours; (c – f) before and after radiation at the fluence of $10^{15}$ cm$^{-2}$ with ion (c) He, (d) N, (e) Ne, (f) Ar.

Figure 4.1(a) and (b) are the control resistance comparisons for devices without and with an anneal at 320 °C for 2 hours, respectively. It should be noted that R1 (red bars) in Figure 4.1(a) were measured ~ 4 hours after R0 at room temperature. In the absence of irradiation, 7 out of 8 devices maintained the off-state, and all 8 devices maintained the on state over 4 hours at room temperature. The resistance variation was very small except for 1 exception in each state that was considered an outlier.
However, after radiation (fluence – 10^{15}\text{cm}^{-2}), as seen in Figure 4.1 (c) – (f) for He, N, Ne, and Ar radiation, respectively, decreases for both R_{off} and R_{on} were observed in almost all TiN/HfO_{2}/W ReRAM devices. A resistance state transition from off-state to on-state (i.e. R_{off} decreases to a resistance below 1500 \Omega) was also observed under irradiation for all ion species. The numbers of devices that exhibited this off-to-on transition event for all ion-irradiation sequences at 3 fluences are given in Table 4.2. At the low fluence of 10^{12} \text{cm}^{-2}, there was no resistance state transition; but at the medium fluence of 10^{14} \text{cm}^{-2}, one off-to-on transition occurred for Ne radiation. A significant number of off-to-on transitions (5 out of 8 devices) took place under Ar radiation at this same fluence. At the high fluence of 10^{15} \text{cm}^{-2}, off-to-on transitions occurred in most devices. Under Ne and Ar radiation, all off-state devices changed to the on-state (8 out of 8 VCM-ReRAM devices). It is noteworthy that nearly all irradiated ReRAM devices remained functional after the static resistance measurements despite the radiation-induced off-to-on transitions, suggesting an intrinsic radiation hardness of these TiN/HfO_{2}/W ReRAMs with respect to heavy ion irradiation.

### Table 4.2 Number of Devices with off-to-on Resistance State Transition

<table>
<thead>
<tr>
<th>Irradiation source</th>
<th>Number of off-to-on transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 × 10^{12}/\text{cm}^{2}</td>
</tr>
<tr>
<td>He</td>
<td>0/8</td>
</tr>
<tr>
<td>N</td>
<td>0/8</td>
</tr>
<tr>
<td>Ne</td>
<td>0/8</td>
</tr>
<tr>
<td>Ar</td>
<td>0/8</td>
</tr>
</tbody>
</table>

To further investigate the effect of radiation on static resistance, Figure 4.2 plots the percent change of the average static resistance of all irradiated off and on TiN/HfO_{2}/W ReRAM devices versus fluence for all ion species. It can be seen from Figure 4.2 (a) that:

1) The static R_{off} changes (\Delta R_{off}) are all negative under ion heavy-ion irradiation,
meaning static $R_{\text{off}}$ decreased for all ion species; 2) $\Delta R_{\text{off}}$ decreases with fluence; 3) Radiation at a fluence of $10^{12}$ cm$^{-2}$ (and, presumably, below) has no impact on static resistance, independent of ion type. At a fluence of $10^{12}$ cm$^{-2}$, $\Delta R_{\text{off}}$ is comparable to the intrinsic variation among devices ($< -5\%$). However at $10^{14}$ cm$^{-2}$ and $10^{15}$ cm$^{-2}$, $\Delta R_{\text{off}}$ increased negatively for all ion species. Moreover, $\Delta R_{\text{off}}$ increased with ion mass: from -5.6\% (He) to -74.4\% (Ar) at $10^{14}$ cm$^{-2}$ and from -65.9\% (He) to -96\% (Ar) at $10^{15}$ cm$^{-2}$.

Static $R_{\text{on}}$ (see Figure 4.2(b)) exhibited similar behavior. However, the overall fractional change of the static $R_{\text{on}}$ ($\Delta R_{\text{on}}$) values were much smaller than the corresponding values of $\Delta R_{\text{off}}$ for all ion species and fluences: from 0.7 \% (N) to -10.3\% (Ar) at $10^{14}$ cm$^{-2}$ and from -9.2\% (N) to -39.3\% (Ar). This indicates that the off-state static resistance is substantially more sensitive to radiation than the on-state static resistance. Surprisingly, it is also noticed that $\Delta R_{\text{on}}$ for He irradiation was relatively large compared to the corresponding change after heavy-ion radiation: -17.2\% (He) at $10^{14}$ cm$^{-2}$ and -38.2\% (He) at $10^{15}$ cm$^{-2}$.
Figure 4.2 Static resistance change in percentage normalized to pre-radiation values. (a) \(R_{\text{off}}\) change; (b) \(R_{\text{on}}\) change.

It should be pointed out that \(\Delta R_{\text{off}}\) for devices annealed at 320 °C (−18.1%) was less than the change observed under He irradiation at \(10^{15}\) cm\(^{-2}\); whereas \(\Delta R_{\text{on}}\) for the devices annealed at 320 °C is positive (30.2%), in complete contrast to the irradiation-induced changes in the static \(R_{\text{on}}\). Thus, we expect that beam heating effects are not responsible for the static resistance changes observed after irradiation.

4.1.2 Effects on forming

Figure 4.3(a) shows the average forming voltage \((V_f)\) of 8 – 10 non-formed TiN/HfO\(_2\)/W ReRAM devices under each radiation exposure. Also shown on the plot is an average \(V_f\) measured for non-irradiated devices without annealing (room temperature) and with an annealing at 320 °C. Annealing resulted in only minor changes to \(V_f\) (1.793 V for non-annealed devices vs. 1.796 for annealed devices). This suggests that ion-beam heating of the sample during irradiation did not affect \(V_f\). After irradiation, \(V_f\) decreased with irradiation (all ion species) up to a fluence of \(10^{14}\) cm\(^{-2}\). This trend is reversed at a fluence of \(10^{15}\) cm\(^{-2}\). At each fluence, the reduction of \(V_f\) is larger with larger ion mass, although the observed value of \(V_f\) at Ar \(10^{12}\) cm\(^{-2}\) deviates from this trend.
Figure 4.3 (a) Dependence of forming voltage with fluence. (b) Dependence of initial resistance of fresh devices with fluence.

The average initial resistances of fresh devices were also measured (Figure 4.3(b)) for TiN/HfO$_2$/W ReRAMs. $R_{\text{fresh}}$ is relatively unchanged for fluences from $10^{12}$ to $10^{14}$ cm$^{-2}$ but exhibits a marked increase (> 10$\times$) for a fluence of $10^{15}$ cm$^{-2}$. For devices not exposed to radiation $R_{\text{fresh}}$ exhibits virtually no change following an anneal at 320 °C. This implies beam heating has negligible effect on $R_{\text{fresh}}$, compared with ion irradiation.

4.1.3 Effects on resistive switching

Figure 4.4 shows the percentage changes in resistive switching parameters normalized to corresponding pre-rad values for TiN/HfO$_2$/W devices after N, Ne and Ar irradiation at 3 different fluences. For reference, the same number of control devices (without irradiation and annealing) was measured within a 4-hour interval and the percentage changes of all parameters are shown in each figure. Also, devices were measured before and after annealing at 320 °C for 2 hours and the percentage changes in resistive switching parameters normalized to the pre-annealed values are also shown. As seen in Figure 4.4(a), compared to the percentage variation of the control value of $V_{\text{set}}$ ($\Delta V_{\text{set}} \sim -0.4\%$), $V_{\text{set}}$ for the post-annealed devices slightly decreased ($\Delta V_{\text{set}} \sim -2.1\%$). At
a fluence of $10^{12}$ cm$^{-2}$, the resulting change in $\Delta V_{\text{set}}$ was within the intrinsic variation ($|\Delta V_{\text{set}}| < 1.5\%$) for all 3 types of ion irradiation. Similarly at a fluence of $10^{14}$ cm$^{-2}$, $V_{\text{set}}$ exhibited only slight variations ($\Delta V_{\text{set}} \sim -1.59\%$ (N), -3\% (Ne), -0.3\% (Ar)). However, at the fluence of $10^{15}$ cm$^{-2}$, $V_{\text{set}}$ increased after each irradiation for the 3 different ions ($\Delta V_{\text{set}} \sim 3.3\%$ (N), 1.1\% (Ne), 3.3\% (Ar)). Although small, these positive shifts contrasted with the negative shifts observed for the lower fluences. The changes in $V_{\text{reset}}$ are presented in Figure 4.4(b), where no obvious trends can be observed ($|\Delta V_{\text{reset}}|<5\%$).

![Graphs showing percentage change in $V_{\text{set}}$, $V_{\text{reset}}$, $R_{\text{on}}$, and $R_{\text{off}}$ versus fluence for different ions and temperatures.]

Figure 4.4 The heavy ion radiation induced performance change in percentage of TiN/HfO$_2$/W devices (a) average $V_{\text{set}}$, (b) average $V_{\text{reset}}$, (c) average $R_{\text{on}}$, and (d) average $R_{\text{off}}$. 

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As seen from Figure 4.4(c), compared to the pre-rad values (-1.2% (control) and -2% (post-anneal)), only very slight $R_{\text{on}}$ changes ($\Delta R_{\text{on}}$) occurred at the ion fluences of $10^{12}$ and $10^{14}$ cm$^{-2}$ for all 3 ion species. At a fluence of $10^{15}$ cm$^{-2}$, $\Delta R_{\text{on}}$ exhibited relatively large positive changes ($\Delta R_{\text{on}} \sim 4.6\%$ (N), 2.9% (Ne), 8.6% (Ar)), which is completely opposite to variations in the pre-rad $R_{\text{on}}$. In terms of $R_{\text{off}}$, a negative $\Delta R_{\text{off}}$ was observed for all fluences and all 3 ion species. However, compared to the pre-rad $R_{\text{off}}$ variation (-12.6% (-12.6% (control) and -20.1% (post-anneal)), post-rad $\Delta R_{\text{off}}$ values are smaller than or close to the intrinsic $\Delta R_{\text{off}}$, indicating insignificant impact of heavy-ion radiation on $R_{\text{off}}$ for TiN/HfO$_2$/W ReRAM devices.

Thus, it can be concluded that the heavy-ion radiation exposure has little influence on $V_{\text{set}}$ and $R_{\text{on}}$ when the fluence is below $10^{14}$ cm$^{-2}$, whereas slight increases in $V_{\text{set}}$ and $R_{\text{on}}$ resulted from a fluence of $10^{15}$ cm$^{-2}$. Also, heavy-ion irradiation does not have substantial impact on $V_{\text{reset}}$ and $R_{\text{off}}$ under any fluence for any ion specie investigated.

### 4.1.4 Discussion

As described in section 2.1.3, for our specific TiN/HfO$_2$/W ReRAMs, the conduction mechanism during the forming process is based on trap-assisted tunneling (TAT). As the TAT current increases a Hf-rich ohmic conducting filament (CF) is formed. The voltage-induced formation/rupture of this CF comprises the on/off switching of the ReRAM device. Briefly, intrinsic oxygen vacancies and newly bias-induced oxygen vacancies segregate preferentially at grain boundaries, providing concomitant trap states. These traps form percolation paths for electron tunneling and result in a TAT current. When the trap density associated with oxygen vacancies reaches a critical concentration (on the order of $10^{21}$/cm$^3$) at grain boundaries, TAT current can generate Joule-heating sufficient
to dissociate oxygen and lead to formation of a Hf-rich CF. During the reset process the high ohmic current flowing in the metallic CF generates sufficient Joule-heating at the narrowest tip of the CF to induce oxidation of the Hf and create a tunneling barrier. Upon establishment of this barrier the system is in the off-state characterized by TAT.

Indeed, oxygen vacancies play an important role in the resistive switching of this type of HfO₂-ReRAM device. It is expected that heavy-ion irradiation would increase oxygen vacancy concentration in the HfO₂ layer, thus modulating the ReRAM device electrical properties. From SRIM model calculations for our device stack, the vacancy densities produced by irradiation with various ion species are plotted in Figure 4.5. On that plot the green solid line at $y = 10^{19}$/cm³ and the orange solid line at $y = 10^{21}$/cm³ are used as a reference, corresponding to the intrinsic vacancy density and the critical vacancy density for HfO₂ CF formation, respectively. At a fluence of $10^{12}$ cm⁻², the radiation-induced vacancy density is less than the intrinsic oxygen vacancy density (by more than 2 orders of magnitude for He radiation). The small radiation-induced changes in the oxygen vacancy density (compared to the intrinsic oxygen vacancy density) at a fluence of $10^{12}$ cm⁻² explain the negligible irradiation-induced variations in the static ReRAM on and off resistances.
Figure 4.5 Radiation-induced vacancy density calculated from SRIM simulations for different radiation fluence.

However, at a fluence of $10^{14}$ cm$^{-2}$, the oxygen vacancy densities generated by ion irradiation are close to the critical density for CF formation (except for the case of He radiation). If we assume the radiation-induced vacancy density is distributed uniformly inside the HfO$_2$ layer it is likely that the radiation-induced vacancies reduce the trap-to-trap distance (see the schematic view in Figure 4.6) and lower the static $R_{\text{off}}$. Moreover, the high density of radiation-induced oxygen vacancies may cause the formation of percolation path(s) between the CF tip and the electrode, leading to the observed $\text{off}-\text{to}-\text{on}$ transitions. This may be especially true for Ar radiation at $10^{14}$ cm$^{-2}$, where the radiation-induced vacancy density appears very close to the critical value necessary for CF formation. This is consistent with our experimental results (5 of 8 devices exhibited the $\text{off}-\text{to}-\text{on}$ transition under Ar at $10^{14}$ cm$^{-2}$, see Table 4.2). The increased static $\Delta R_{\text{off}}$ reduction with ion mass can be attributed to the increased radiation-induced vacancy formation under heavier ion irradiation. As for the He case, the radiation-induced
vacancy density is still close to the intrinsic level, which explains the small change in static $R_{\text{off}}$ ($\sim$ -5%).

Figure 4.6 Schematic view of radiation impact on conducting filament in VCM-type ReRAMs. Note that in this figure only the influence by radiation-induced traps are considered and represented by the black dots inside HfO$_2$.

Alternately, oxygen vacancies generated by ion irradiation in the neighborhood of the CF may self-diffuse to (or along) the filament, substantially expanding the CF region and contributing to the conduction thus lowering $R_{\text{on}}$ (see the schematic in Figure 4.6). As a small active region ($\sim$ 1 nm thick) determines $R_{\text{off}}$, the relative ease by which incident ions can create oxygen vacancies and reduce trap-to-trap distances (i.e. form current percolation paths) makes off-state devices substantially more sensitive to irradiation than on-state devices, in line with experimental observations of static $R_{\text{off}}$ and $R_{\text{on}}$. Similar reasoning holds for the larger $R_{\text{off}}$ and $R_{\text{on}}$ changes at the highest fluence of $10^{15}$ cm$^{-2}$. At this fluence, the vacancy density attributed to irradiation is on the order of the critical value for all ion species. This implies that oxygen vacancies in the active region are sufficiently dense to induce the conducting path(s) that connects the CF tip with the electrode. Thus, a resistance-state transition is not a surprise at this fluence.

The radiation-induced vacancies are also consistent with an EDS study along a line profile across the cross-section of TiN/HfO$_2$/W devices pre-/post-Ar irradiation at the
fluence of $10^{15}$ cm$^{-2}$, as shown in Figure 4.7. It is seen that the O intensity peak shifted away from the Hf-peak towards the W-electrode side after Ar irradiation. The shift of the oxygen peak suggests the increase of oxygen vacancy density inside the HfO$_2$ layer, especially close to the TiN electrode where the filament tip forms.

Figure 4.7 EDS line profile along the cross-section of TiN/HfO$_2$/W devices (a) pre-radiation, (b) post-Ar radiation at the fluence of $1 \times 10^{15}$ cm$^{-2}$.

For a fresh device with the intrinsic oxygen vacancy density in as-processed HfO$_2$ on the order of $10^{19}$/cm$^3$ [1], the conduction before forming is due to TAT along grain boundaries and a substantial amount of newly generated oxygen vacancies (due to bias stress) are expected to reach the critical vacancy density for CF formation, with an activation energy for defect generation $\sim 4.4$ eV [1]. However, irradiation results in oxygen vacancy generation, accelerating the CF formation process. Thus, less energy is needed for CF formation in a fresh device after radiation, resulting in smaller $V_f$, consistent with the observed $V_f$ decrease in our experiment up to $10^{14}$ cm$^{-2}$. The increase of oxygen vacancies by irradiation also decreases the trap-to-trap distance and increases the tunneling current. Thus, a lower $R_{\text{fresh}}$ is observed.

At the highest fluence of $10^{15}$ cm$^{-2}$, we speculate that the reverse change of $V_f$ can be attributed to irradiation-induced change in the microstructure of crystalline HfO$_2$. A
higher fluence may result in a non-negligible irradiation-induced amorphization or recrystallization. In either case the microstructure change may suppress grain boundaries and eliminate preferential conducting path(s). This also increases the resistance of the device, which is consistent with the observed increase of $R_{\text{fresh}}$ by an order of magnitude at a fluence of $10^{15}$ cm$^{-2}$. Radiation-induced microstructure changes probably also contributed to the relatively larger value of $R_{\text{fresh}}$ under N, Ne and Ar irradiation compared to He irradiation at $10^{14}$ cm$^{-2}$.

As mentioned in section 2.1.2, the CF is comprised of oxygen vacancies and is Hf-rich, thus, the CF is expected to behave more like a metal, which is consistent with the measured linear I-V curve at lower bias ($|V| < 0.3$ V) when the device is in on-state, as seen for the Ohmic fitting (I $\sim$ V) in red in Figure 4.8(a). When $|V| > 0.3$ V, the current deviates from the linear relation with voltage, which can be explained by a large current density through the Hf-rich filament generating substantial heating and increasing local temperature, and therefore decreasing the filament resistance according to Equation (2.4).
Figure 4.8 (a) A typical RESET I-V process (in black) for a device without irradiation, with the Ohmic linear fitting ($I \sim V$) at room temperature (in red) and a metallic conduction fitting ($I \sim f(R_{th}, R_0, V)$) considering temperature increase from room temperature (in blue). (b) A plot of thermal conductivity, $K_{th}$, of metal-like CF calculated from thermal resistance, $R_{th}$, obtained from (a). For a simplified case, the CF is assumed to have a uniform cylinder shape with a diameter of 4 nm (size of grain boundary region [2]), as shown in the upper-left inset in (b). The bottom-right table gives the $K_{th}$ values under different heavy ions at the fluence of $10^{15}$ cm$^{-2}$, with error given as standard deviation. Note: $K_{th} \sim 23$ W/K-m for bulk Hf.

If we substitute $T$ by $T_{CF} = T_0 + R_{th} \cdot (I \cdot V)$, the current can be derived taking thermal effects into account with the formula [2]:

$$I = f(R_{th}, R_0, V) = \sqrt{(2\alpha R_{th} V)^{-2} + (\alpha R_{th} R_0)^{-1}} - (2\alpha R_{th} V)^{-1}$$  \hspace{1cm} (4.1)

where $R_{th}$ is the thermal resistance of the Hf-rich CF, $R_0$ is the CF resistance at room temperature, $V$ is the voltage bias, and $\alpha$, $\sim 0.002$, is the thermal coefficient. From the current fitting at higher temperature (in blue) using this equation (as seen in Figure 4.8(a)), $R_{th}$ for the CF can be extracted at a specific $R_0$ determined by the experimental curve at lower bias. Furthermore, the thermal conductance $K_{th}$ of the CF can be also obtained from $R_{th} = L_{CF}/ (K_{th} \cdot A_{CF})$, assuming the CF has a uniform cylinder shape (see the upper-left inset in Figure 4.8(b)) with a diameter of 4 nm (size of grain boundary region [2]) and length of 5 nm. Figure 4.8(b) plots $K_{th}$ under different irradiation cases at a fluence of $10^{15}$ cm$^{-2}$. Without irradiation $K_{th} \sim 13.67 \pm 0.17$ W/K-m (see the table on the
bottom-right) is much smaller than $K_{\text{th}}$ (~ 23 W/K-m) of bulk Hf. This is reasonable as the CF is relatively Hf-rich. After irradiation, $K_{\text{th}}$ increases substantially and the value moves closer to the bulk value, which is wholly consistent with our conclusion that irradiation largely increases the oxygen vacancy density and improves the overall metallic properties of the CF. This effect is enhanced with higher ion mass. On the other hand, this increase in $K_{\text{th}}$ slightly lowers the efficiency of local Joule heating at the CF tip, leading to a slightly larger $V_{\text{set}}$ and thus $R_{\text{on}}$ after irradiation at this fluence.

In summary, VCM TiN/HfO$_2$/W ReRAM devices were irradiated with heavy ions – N, Ne, Ar ions at fluences of $10^{12}$, $10^{14}$, $10^{15}$ cm$^{-2}$, and the effects of these heavy-ion irradiations was investigated. It was found that almost all devices remained functional after irradiation under all fluences for all ion species. At a fluence of $10^{12}$ cm$^{-2}$, there is little change observed in electrical properties of the irradiated ReRAM devices. However beyond a fluence of $10^{14}$ cm$^{-2}$, the static off- and on-state resistance decreased with fluence and with ion mass; and the static off-state resistance was more sensitive to irradiation than the static on-state resistance. Severe off-to-on resistance-state transitions were observed at a fluence of $10^{15}$ cm$^{-2}$. Irradiation also resulted in the decrease of forming voltage and the increase of TAT current up to a fluence of $10^{14}$ cm$^{-2}$. At a fluence of $10^{15}$ cm$^{-2}$, reversed trends were noticed in $V_f$ and $R_{\text{fresh}}$ – a decrease was observed in $\Delta V_f$ and an order-of-magnitude increase was observed for $R_{\text{fresh}}$. Moreover, irradiations also resulted in slight increases in $V_{\text{set}}$ and $R_{\text{on}}$ but no obvious changes in $V_{\text{reset}}$ and $R_{\text{off}}$. These irradiation effects can be explained by the irradiation-induced defects and microstructure changes in the HfO$_2$ layer.
4.2 Heavy-ion irradiation of ECM-type HfO$_2$-ReRAMs

12 devices were employed in N and Ar irradiation experiments at a fluence of 10$^{15}$ cm$^{-2}$ (vertically incident on the top electrode) for Cu/HfO$_2$/Ni ReRAM devices. Half of the devices were programmed into the off-state and the other half were programmed into the on-state before radiation exposure. Table 4.3 summarizes the irradiation experimental conditions and the number of devices exposed. Extra irradiation experiments under Ar to a fluence of 10$^{13}$, 10$^{14}$, 10$^{16}$ cm$^{-2}$ were carried out on several other Cu/HfO$_2$/Ni ReRAM devices for additional characterization.

<table>
<thead>
<tr>
<th>Irradiation source</th>
<th>Total Doses (rad(Si))</th>
<th>Fluence (ions/cm$^2$)</th>
<th>Exposure time (min)</th>
<th>Number of devices</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 MeV N$_2^+$</td>
<td>7.55 × 10$^9$</td>
<td>1 × 10$^{15}$</td>
<td>36</td>
<td>6 (on) + 6 (off)</td>
</tr>
<tr>
<td>2.75 MeV Ar$^+$</td>
<td>1.28 × 10$^7$</td>
<td>1 × 10$^{13}$</td>
<td>8</td>
<td>&gt; 36 (fresh)</td>
</tr>
<tr>
<td></td>
<td>1.28 × 10$^9$</td>
<td>1 × 10$^{14}$</td>
<td>88</td>
<td>&gt; 36 (fresh)</td>
</tr>
<tr>
<td></td>
<td>1.28 × 10$^{11}$</td>
<td>1 × 10$^{15}$</td>
<td>84</td>
<td>6 (on) + 6 (off)</td>
</tr>
<tr>
<td></td>
<td>1.28 × 10$^{12}$</td>
<td>1 × 10$^{16}$</td>
<td>177</td>
<td>&gt; 36 (fresh)</td>
</tr>
</tbody>
</table>

All electrical measurements were carried out on an Agilent B1500A semiconductor parameter analyzer in DC-voltage sweep mode with a current compliance (CC) of 500 µA. During the electrical measurements, the top Ni electrode was biased while keeping the bottom Cu electrode grounded. Capacitance-voltage (C-V) measurement was carried out using a Hewlett Packard 4194A Impedance/gain-phase analyzer. The crystallinity of Cu/HfO$_2$/Ni ReRAM devices with and without irradiation were characterized using X-ray diffraction (XRD, Bruker D8) with Cu K$\alpha$ irradiation ($\lambda = 0.154$ nm).
4.2.1 Effects on forming

As seen in Figure 4.9(a), compared to the average $V_f$ value for the pre-rad case of 14.5 ± 0.35 V, $V_f$ exhibited no obvious change following N irradiation, but increased dramatically to 19.06 ± 2.36 V after Ar irradiation.

As mentioned in section 4.1.1, the beam heating at this fluence may approach temperatures nearing 150 °C. To rule out the beam heating effect, the forming voltage was also measured for non-irradiated devices after annealing at 160 °C and 320 °C, as shown in red in Figure 4.9(a). It was observed that $V_f$ decreased substantially with annealing temperature, which strongly contrasted the behavior observed for post-Ar-rad devices (which empirically exhibited the highest beam heating ≤ 150 °C in Si materials). Thus, the beam heating should be ruled out as an explanation of the observed irradiation impact on $V_f$.

Figure 4.9(b) shows the corresponding $R_{\text{fresh}}$ for devices pre- and post-irradiation. Similarly, $R_{\text{fresh}}$ showed only slight variation after N irradiation ($R_{\text{fresh}}$ ~ 73 GΩ (N-rad) vs 71 GΩ (pre-rad)), but a relatively large increase after Ar irradiation ($R_{\text{fresh}}$ ~ 241 GΩ (Ar-rad)). Similarly, $R_{\text{fresh}}$ for the annealed devices varied only slightly, and we conclude that beam heating effects did not contribute to the observed increases in $R_{\text{fresh}}$ following Ar irradiation.
Figure 4.9 (a) Average forming voltages and (b) initial resistance of fresh devices for 10 devices without radiation (control, in black), 10 devices post He radiation and 10 post Ar radiation (in blue), and 10 devices post annealing at 160 °C and another 10 at 320 °C for 2 hours (in red). The fluence of radiation is $1 \times 10^{15}$ cm$^{-2}$.

As mentioned in section 2.2.3 and section 3.2.2, for the ReRAM devices pre- and post-light-ion irradiation, the electrical current was well described by Poole-Frenkel conduction. The conduction during forming process for an Ar-irradiated Cu/HfO$_2$/Ni ReRAM device was also fit to a Poole-Frenkel model, as shown by the red curve in Figure 4.10. The large deviation of the fitted Poole-Frenkel curve from the experimental curve ($\chi^2 = 0.13 \pm 0.05$) suggests the Poole-Frenkel mechanism is not the dominant conduction mechanism. Consequently, an analysis of the I-V data for an Ar-irradiated Cu/HfO$_2$/Ni ReRAM device was carried out using the ionic conduction model ($I = A_I \exp(B_I V)$ from Equation (2.5)). The best fit of this model to the I-V data is represented by the blue curve in Figure 4.10. The ionic model agrees well with the experimental curve with the fit exhibiting a small $\chi^2$ of 0.017 $\pm$ 0.014. This indicates that the dominant conduction mechanism during forming has changed from a Poole-Frenkel type to an ionic conduction mode associated with an electrochemical (reduction-oxidation) mechanism. The ionic conduction model parameters $A_I$ and $B_I$ are given in the inset of Figure 4.10 for
5 different Ar-irradiated devices, showing good uniformity over multiple samples. From the ionic conduction model fitting, the ion hopping distance can be extracted for each device. The average hopping distance is $\sim 0.79 \pm 0.05$ nm, which is of the same order of the lattice constant ($\sim 0.5$ nm) for HfO$_2$ and therefore reasonable for a bulk diffusion limited process [3, 4].

![Graph](image)

**Figure 4.10** Typical I-V fitting to both Poole-Frenkel effect and ionic conduction for Cu/HfO$_2$/Ni devices after Ar irradiation at the fluence of $1 \times 10^{15}$ cm$^{-2}$. The inset displaces the $A_I$ and $B_I$ parameters from ionic fitting for 5 devices. The dashed lines in the inset are the corresponding average $A_I$ and $B_I$ values.

### 4.2.2 Effects on resistive switching

The percentage change in $V_{\text{set}}$, $V_{\text{reset}}$, $R_{\text{on}}$ and $R_{\text{off}}$ for irradiated Cu/HfO$_2$/Ni ReRAM devices as a function of ion mass is also shown in Figure 4.11. However, due to the large variations from device to device and the large variations between cycles in single devices, it is difficult to draw substantive conclusions. Further study with more uniform devices should be carried out for a more conclusive result of irradiation effects on resistive switching in ECM devices.
**Figure 4.11** Heavy-ion radiation induced performance change in percentage of Cu/HfO$_2$/Ni devices (a) average $V_{\text{set}}$, (b) average $V_{\text{reset}}$, (c) average $R_{\text{on}}$, and (d) average $R_{\text{off}}$.

### 4.2.3 Discussion

To interpret the results and the conduction mechanism transition observed for Cu/HfO$_2$/Ni ReRAM devices after heavy ion irradiation, C-V measurements were carried out for the pre- and post-Ar-irradiated devices. Figure 4.12(a) shows the normalized capacitance ($C_t/C_{1M}$) at an electric field of 0.2 MV/cm as a function of frequency before and after Ar irradiation at 3 different fluences. The observed monotonic frequency dispersion is related to the existence of bulk-dielectric traps near the metal-oxide interface. Similar behaviors were observed for HfO$_2$ MIM structure [5], and the higher
variation of the capacitance from low to high frequency was attributed to a greater concentration of defects present near the metal-oxide interface [5]. The frequency dispersion of capacitance for the non-irradiated Cu/HfO$_2$/Ni ReRAM devices in our case confirmed the existence of intrinsic traps in HfO$_2$, which mediate the preferential Poole-Frenkel conduction in non-irradiated HfO$_2$-based ReRAM devices. Compared to that of non-irradiated devices, the increased frequency dispersion of capacitance for the Cu/HfO$_2$/Ni ReRAM device following Ar irradiation at a fluence of $10^{13}$ /cm$^2$ indicates an increase in defect density and thus trap concentration. However, at a fluence of $10^{14}$ /cm$^2$, the low-frequency $C_f/C_{1M}$ decreased compared to the corresponding values measured at a fluence of $10^{13}$ /cm$^2$, but were still larger than the corresponding pre-rad values. Furthermore, at a fluence of $10^{15}$/cm$^2$, the $C_f/C_{1M}$ at lower frequencies was reduced even below that of the corresponding pre-rad values. This suggests that a trap-density reduction occurred for the Cu/HfO$_2$/Ni ReRAM devices after Ar radiation at a fluence of $10^{15}$/cm$^2$. This trap-density reduction behavior is also shown in the decrease in $C_f/C_{1M}$ with fluence in Figure 4.12(b) under 3 different frequencies. In particular, $C_f/C_{1M}$ measured for Cu/HfO$_2$/Ni ReRAM devices irradiated with Ar at a fluence of $10^{15}$/cm$^2$ is even smaller than the pre-rad values, represented by the dashed line at each frequency. Similar irradiation-induced reductions in trap density have also been observed in Si materials, which was attributed to irradiation-induced recrystallization [6, 7, 8]. Thus, a suppression of the Poole-Frenkel conduction mechanism can be expected due to irradiation-induced reduction of trap density associated with the irradiation-induced recrystallization.
For comparison, C-V measurements were carried out on non-irradiated devices annealed at 320 °C for 2 hours. The corresponding normalized capacitance (in red, in Figure 4.12(a)) for the annealed devices exhibits larger discrepancies at lower frequencies which could be due to Cu diffusion at the HfO$_2$/Cu interface creating more oxygen vacancies at elevated temperatures (This has been confirmed from SIMS analysis and is discussed in more detail later in this section). These data suggest that thermal annealing of Cu/HfO$_2$/Ni ReRAM devices yields substantially different results to the irradiation effects observed here at a fluence of $10^{15}$ cm$^{-2}$. Therefore, we conclude that the observed reduced frequency dispersion for the post-irradiated devices at an Ar fluence of $10^{15}$/cm$^2$ results from the interaction of Ar ions with the ReRAM devices and is not due to beam-induced heating.

![Figure 4.12](image.png)

Figure 4.12 (a) Capacitance normalized to capacitance at 1MHz as a function of frequency at an electrical field of 0.2 MV/cm for the devices of pre-irradiation (in black), post Ar-irradiation at different fluences of $1 \times 10^{13}$ cm$^{-2}$ (in blue), $1 \times 10^{14}$ cm$^{-2}$ (in green), $1 \times 10^{15}$ cm$^{-2}$ (in purple), and post-annealing at 320 °C (in red). (b) Normalized capacitance as a function of fluence at 3 frequencies: 1 kHz, 10 kHz and 100 kHz.

Figure 4.13(a) presents XRD data from large angle scans of Cu/HfO$_2$/Ni ReRAM devices before and after Ar-irradiation. These data indicated that the HfO$_2$ films in these
devices exhibit a monoclinic (111) texture (peaks shown in the red dashed box of Figure 4.13(a)). For a clearer comparison, XRD scans for devices before and after Ar irradiation at a fluence of $10^{15}$/cm$^2$ are shown in Figure 4.13(b). The inset shows high-resolution XRD scans (0.03°/min) for the HfO$_2$ (111) peak. It is evident that peak narrowing (suggesting an increase in crystallite size) and peak shift (corresponding to a variation of lattice spacing) occur after Ar irradiation at the highest fluence.

![Figure 4.13 XRD pattern for the devices of pre-radiation (in black) and post-radiation at the fluence of $1 \times 10^{13}$ cm$^{-2}$, $1 \times 10^{15}$ cm$^{-2}$, $1 \times 10^{16}$ cm$^{-2}$. (b) Direct comparison of XRD patterns for the devices before and after Ar radiation at the fluence $1 \times 10^{15}$ cm$^{-2}$. The inset displays the high resolution (111) peak for the pre-and post-radiation cases, with the vertical line representing the (111) peak position in a perfect lattice.](image)

The HfO$_2$ crystallite size in the (111) direction is obtained using the well known Scherrer’s equation after the background subtraction of the (111) peak and the correction for instrumental correction. Bragg’s law was used to calculate the (111) interplanar spacing, $d_{(111)}$, from $2\theta_{(111)}$. Table 4.4 gives the measured full width of half maximum intensity (FWHM) and the corresponding calculated crystallite size, as well as the peak position with the calculated $d_{(111)}$ for the devices pre-and post-Ar radiation at 3 different fluences: $10^{13}$, $10^{15}$, $10^{16}$/cm$^2$. It is seen that the HfO$_2$ crystallites increased in size after...
irradiation and, furthermore, increased as a function of fluence. This suggests that irradiation introduced the re-growth of the crystallite structure. Compared to the reference line of the (111) peak at 28.35° (d\textsubscript{(111)} ~ 0.3147 nm) in a perfect lattice, the observed (111) peak at 28.13° (d\textsubscript{(111)} ~ 0.3168 nm) for the pre-irradiated devices indicates a lattice expansion in these small crystallites. However, after radiation, the (111) peak shifted to a higher angle, as seen in Table 4.4. It should be pointed out that lattice expansion with decreasing crystalline size has also been reported for monoclinic HfO\textsubscript{2} and it was attributed to the surface dipole repulsion [9, 10]. In our case, however, the true cause of the peak shift still requires further investigation. In general, the XRD results indicate a significant increase of crystallite size and thus a recovery of defects in HfO\textsubscript{2} for the ECM devices after Ar irradiation. This radiation-induced crystallization has been also observed in other materials [7, 8]. Thus, a reduction of trap or defect density resulting from this induced crystallization can be expected, which is consistent with our C-V result.

Table 4.4 Characteristics of the m-(111) peak of the Cu/HfO\textsubscript{2}/Ni ReRAM devices before and after Ar irradiation. The lattice spacing of (111) planes is 0.3147 nm for a perfect HfO\textsubscript{2} crystal.

<table>
<thead>
<tr>
<th>Condition</th>
<th>FWHM (111)</th>
<th>Grain size (111) (nm)</th>
<th>2θ (deg.)</th>
<th>d\textsubscript{(111)} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-rad</td>
<td>1.756</td>
<td>4.7</td>
<td>28.13</td>
<td>0.3168</td>
</tr>
<tr>
<td>Post-Ar(@10\textsuperscript{13}/cm\textsuperscript{2})</td>
<td>1.50</td>
<td>5.3</td>
<td>28.23</td>
<td>0.3157</td>
</tr>
<tr>
<td>Post-Ar(@10\textsuperscript{15}/cm\textsuperscript{2})</td>
<td>1.049</td>
<td>7.8</td>
<td>28.42</td>
<td>0.3137</td>
</tr>
<tr>
<td>Post-Ar(@10\textsuperscript{16}/cm\textsuperscript{2})</td>
<td>0.574</td>
<td>13.84</td>
<td>28.52</td>
<td>0.3126</td>
</tr>
</tbody>
</table>

Radiation-induced annealing effects were also implied from SEM images of HfO\textsubscript{2} surface, as seen in Figure 4.14 for the devices before and after Ar irradiation at fluences.
of $10^{14}$ and $10^{16}$/cm$^2$. Figure 4.14(a), (c) and (e) display the plan view of HfO$_2$ surface pre-rad, post-Ar ($10^{14}$/cm$^2$) and post-Ar ($10^{16}$/cm$^2$), respectively. The dark spots on the HfO$_2$ surface correspond to areas surrounding a physical crack, as seen in the circled regions in the magnified images in Figure 4.14(b), (d) and (f). It was observed that a high density of dark spots occurred on the HfO$_2$ surface before radiation (Figure 4.14(a)), which decreased after Ar radiation (Figure 4.14(b) and (c)). Furthermore, the size of the crack decreased with Ar fluence. This implies a type of irradiation-induced ‘annealing’ although details such as depth dependence must be investigated. Further study is needed to confirm and quantify the origins of this effect.
Figure 4.14 Top view of SEM images on HfO$_2$ surface in the cases of (a) pre-radiation, (c) post-Ar radiation to a fluence of 1e14 cm$^{-2}$, (e) post-Ar-radiation to a fluence of 1e16 cm$^{-2}$. (b), (d), (f) are the corresponding magnified SEM image of a typical dark spot in (a), (c), (e), respectively.

Based on the entirety of the data presented above, the increase in $V_f$ of Cu/HfO$_2$/Ni ReRAM devices after irradiation can be explained by an increase in the local crystallinity of HfO$_2$, which is consistent with the result previously reported on similar ReRAM devices [11].

It should be pointed out that ion beam heating alone was determined to have little effect on the CF forming process in Cu/HfO$_2$/Ni ReRAM devices. As mentioned above,
the C-V measurement of post-annealed devices suggests that annealing has introduced more defects inside HfO$_2$, contrary to the suppression of trap concentration after Ar radiation. Also, a monotonic decrease in $V_f$ with annealing temperature strongly contrasts the behavior observed for the irradiated devices. To further support this conclusion, SIMS analysis was carried out for a control, annealed, and irradiated Cu/HfO$_2$/Ni ReRAM devices. It was initially noticed that oxygen was distributed non-uniformly inside the HfO$_2$ layer and that oxygen was asymmetrically richer at the interface of both electrodes as compared to the middle of the layer. This is shown in the insets in Figure 4.15(a). The uneven and asymmetrical distribution of oxygen, and Cu diffusion from Cu electrode into the HfO$_2$ layer was also monitored for irradiated devices and annealed devices. Figure 4.15(a) gives a comparison of the intensity ratio of the oxygen peak at the Cu/HfO$_2$ interface to that at the Ni/HfO$_2$ interface (denoted as $O_{Cu}/O_{Ni}$). The irradiated devices exhibited a slight decrease (from 1.75 for the control sample to 1.7 for the He-irradiated device and 1.5 for the Ar-irradiated device), whereas for the annealed devices, a dramatic reduction occurred from 1.75 for the control to approximately 1 after thermal annealing.
Figure 4.15 Results of SIMS depth profile ReRAM devices. The relative thicknesses of HfO$_2$ are calibrated to 100 nm Ni. (a) Ratio of O-peak intensity at the Cu/HfO$_2$ interface to O-peak intensity at the Ni/HfO$_2$ interface for irradiated devices (in red) and annealed devices (in black). The insets I) and II) are the O distribution in the HfO$_2$ layer of irradiated devices and annealed devices, respectively. (b) Percentage change of Cu intensity integrated over the HfO$_2$ layer of irradiated devices (in red) and annealed devices (in black). The insets I) and II) correspond to the Cu distribution in the HfO$_2$ layer of irradiated devices and annealed devices, respectively. In all inset figures, the x-axis is depth (nm) and y-axis is intensity (a.u). The green dashed lines in (a) and (b) correspond to the control values. The error associated with each of the data points in both figures is about 1%.

Additionally, SIMS analysis also revealed that all Cu/HfO$_2$/Ni ReRAM devices exhibited a similarly sharp Ni/HfO$_2$ interface but a different degree of Cu diffusion at the HfO$_2$/Cu interface (see the insets in Figure 4.15(b)). The insets in Figure 4.15(b) show Cu distribution inside the HfO$_2$ layer for irradiated and annealed devices. An enhanced Cu signal was observed within the HfO$_2$ layer. To give a better comparison, the Cu intensity was integrated over the HfO$_2$ layer (depth from 120 nm to 155 nm), and the integrated Cu intensity of post-treated devices (i.e. irradiation and annealing) was then normalized to the control, as plotted in Figure 4.15(b). The integrated area shows a significant increase in Cu content for the annealed devices as compared to the irradiated ones; 82.5% for the device annealed at 160 °C and 356.4% for the device annealed at 320 °C versus -44.5 % for the He-irradiated device and 13.1% for the Ar-irradiated device. From this
comparison, it is clear that the changes of composition induced by annealing are much more significant than those induced by irradiation. This analysis also supports our conclusions regarding the $V_f$ reduction and the trap increase in annealed devices (opposite to that of the irradiation results). Therefore, the beam heating effects should be completely ruled out as a contributing cause for the observed changes of Cu/HfO$_2$/Ni ReRAM devices after Ar-ion irradiation.

In summary, it is found that $V_f$ increased after Ar irradiation and that Ar irradiation induced a forming conduction mechanism transition from Poole-Frenkel emission (with the extracted dynamic dielectric constant about 9.37) to ionic conduction associated with electrochemical effects (with an extracted hopping distance of Ni ions about 0.8 nm). This transition of the conduction mechanism is attributed to the irradiation-induced reduction of traps and defects that resulted from the crystallinity improvement, confirmed from C-V result and XRD data. The improved crystallinity of HfO$_2$ is also responsible for the increased forming voltages observed in the devices after Ar irradiation.

### 4.3 Comparison of irradiation response between VCM and ECM HfO$_2$-ReRAMs

Figure 4.16 gives a direct comparison of $V_f$ (Figure 4.16(a)) and $R_{\text{fresh}}$ (Figure 4.16(b)) for the VCM (TiM/HfO$_2$/W) and ECM (Cu/HfO$_2$/Ni) ReRAM devices post-N and Ar irradiation with a fluence of $10^{15}$/cm$^2$. $V_f$ decreased by ~10% for VCM devices after N and Ar irradiation. In strong contrast, ECM devices exhibited a significant $V_f$ increase (~35%) after Ar irradiation, although an average decrease in $V_f$ was also observed after N irradiation. In terms of $R_{\text{fresh}}$, as seen in Figure 4.16(b), VCM devices exhibited large increases (>1000%) after N and Ar irradiation, but $R_{\text{fresh}}$ variation for
ECM devices was insignificant (~ 5%) under N irradiation. Although the value of $R_{\text{fresh}}$ for ECM devices exhibited a substantial increase (~ 240%) after Ar irradiation, it was still substantially smaller than $\Delta R_{\text{fresh}}$ for measured for VCM devices. These differences can be attributed to the fundamental difference in forming mechanisms between VCM and ECM devices. Comparison in $V_{\text{set}}$, $V_{\text{reset}}$, $R_{\text{on}}$ and $R_{\text{off}}$ between VCM and ECM devices remains as future work.

Figure 4.16 Percentage changes in average parameters: (a) $V_f^{\text{avg}}$, (b) $R_{\text{fresh}}^{\text{avg}}$, after N and Ar irradiation at the fluence of $1 \times 10^{15}$ cm$^{-2}$. The values in percentage are all normalized to the pre-radiation values.
4.4 References


5. Comparison of Light-Ion and Heavy-Ion Irradiation Effects on HfO$_2$-based ReRAMs

In this chapter, the results of light-ion and heavy-ion irradiation on both VCM and ECM ReRAM devices are compared in terms of static $R_{\text{off}}$, static $R_{\text{on}}$, $V_f$ and $R_{\text{fresh}}$. Section 5.1 presents the effects of light-ion and heavy-ion irradiation on VCM ReRAMs, and section 5.2 describes the effects of light-ion and heavy-ion irradiation on ECM ReRAMs, followed with a summary in section 5.3.

5.1 Comparison of light-ion and heavy-ion irradiation effects on VCM HfO$_2$-ReRAMs

As described by Equation (2.8), the radiation dose is linearly dependent on the fluence at a given LET (linear energy transfer). A plot of fluence versus dose in a log-log scale for all of the radiation exposure experiments carried out for this dissertation is shown in Figure 5.1. Due to the LET increase with ion mass, the fluence – dose line shifts to the right with larger ion mass. At a given fluence, i.e. $10^{14}$/cm$^2$, the radiation absorbed dose increases with ion mass, from $2.9 \times 10^8$ rad under H and $2.1 \times 10^9$ rad under He to ~ $1 \times 10^{10}$ rad under heavy ions. Correspondingly, a lower fluence of heavier ions is needed to reach a same radiation dose. For instance, at a given radiation dose at $5 \times 10^9$ rad, the fluence is $1.8 \times 10^{15}$/cm$^2$ for H-ions and $2.4 \times 10^{14}$/cm$^2$ for He-ions, whereas the fluence for heavy ions is 1 – 2 orders of magnitude smaller ($4 – 6 \times 10^{13}$/cm$^2$). To compare the effects of light-ion radiation with the effects of heavy-ion radiation on VCM and ECM ReRAM devices, the electrical parameters (static $R_{\text{off}}$, static $R_{\text{on}}$, $V_f$, $R_{\text{fresh}}$) are plotted as a function of the radiation dose.
Figure 5.1 Fluence of different ion species with various ion mass versus radiation dose.

Figure 5.2 displays the change in static \( R_{\text{off}} \) (Figure 5.2(a)) and static \( R_{\text{on}} \) (Figure 5.2(b)) of VCM ReRAM devices after light-ion and heavy-ion irradiation as a function of dose. It can be seen from Figure 5.2(a) that static \( R_{\text{off}} \) exhibited a threshold behavior. Above the dose threshold \( D_{\text{th}} \) (~ \( 5 \times 10^9 \) rad(Si)), static \( R_{\text{off}} \) decreased linearly with logarithm dose, as indicated by the dashed line. More importantly, at this dose regime, \textit{off-to-on} state transitions could occur giving errors of memory states, which should be taken into account for future device design for rad-hard applications. When the radiation dose is below this threshold, static \( R_{\text{off}} \) varies slightly, although relatively large negative changes in the static \( R_{\text{off}} \) at lower doses of proton irradiation was also observed which could be due to intrinsic variations of the devices.
Figure 5.2 Percentage change in (a) static $R_{\text{off}}$ and (b) static $R_{\text{on}}$ as a function of dose for VCM devices under light-ion (H, He) and heavy-ion (N, Ne, Ar) irradiations.

Similar results are also found for the behavior of the static $R_{\text{on}}$. Within that case, a higher dose threshold $D_{\text{th}} \sim 1 \times 10^{10}$ rad(Si), was observed, as can be clearly seen in Figure 5.2(b). This higher dose threshold for static $R_{\text{on}}$ is consistent with the aforementioned result that on-state resistance is less sensitive to irradiation. Therefore, in other words, ReRAM devices have higher fluence thresholds under light-ion radiation ($1.8 \times 10^{15}$/cm$^2$ for H-ions and $2.4 \times 10^{14}$/cm$^2$ for He-ions versus $4 - 6 \times 10^{13}$/cm$^2$ for heavy ions) for static $R_{\text{off}}$ and hence off-to-on state transition events.

Figure 5.3(a) shows the $V_f$ change of VCM ReRAMs versus irradiation dose under light-ion and heavy-ion irradiation. It can be seen that $V_f$ varies slightly ($< 5\%$) under light-ion irradiation, independent of dose, but decreases relatively quickly ($8\% - 18\%$) with heavy-ion irradiation in the higher dose regime ($> 10^{10}$ rad, labeled with the black dashed box).
Figure 5.3 Percentage change in (a) $V_f$ and (b) $R_{\text{fresh}}$ as a function of dose for VCM devices under light-ion (H, He) and heavy-ion (N, Ne, Ar) irradiations.

Correspondingly, Figure 5.3(b) plots the change in $R_{\text{fresh}}$ for VCM ReRAMs versus dose under light-ion and heavy-ion irradiation. Clearly, there are 3 dose-regimes: $< 10^8$ rad, $10^8 - 5 \times 10^{10}$ rad (in the black dashed circle), $> 5 \times 10^{10}$ rad (in the black dashed box). $R_{\text{fresh}}$ decreases by up to $\sim 75\%$ when the dose is in the second regime ($10^8 - 5 \times 10^{10}$ rad), but increases significantly (more than 1000%) in the third dose regime ($> 5 \times 10^{10}$ rad). However, when the dose is lower than $10^8$ rad, it is not clear why $R_{\text{fresh}}$ increases.

5.2 Comparison of light-ion and heavy-ion irradiation effects on ECM HfO$_2$-ReRAMs

Figure 5.4 presents the variations in static $R_{\text{off}}$ and static $R_{\text{on}}$ for ECM devices after light-ion and heavy-ion radiations. It was observed that at the lower dose range ($< 10^{10}$ rad) with light-ion irradiation, the static $R_{\text{off}}$ decreases up to 75%, as seen the inset in Figure 5.4(a). This decrease in static $R_{\text{off}}$ is likely related to the radiation-induced current leakage. However, as the dose exceeds $10^{10}$ rad, significant positive changes in static $R_{\text{off}}$ are found (up to 28000%), as indicated by the dashed line, which strongly contrasts the
behavior of VCM ReRAM devices (negative change in static $R_{\text{off}}$) described in the last section. The exact reason for this large static $R_{\text{off}}$ increase requires more investigation, but the current speculation includes: 1) Transition from electronic conduction to ionic conduction during off-state due to irradiation-induced trap reduction; 2) Increased rupture length between the filament tip and the electrode and/or the CF body damage from collisions between the bombarding ions or recoils and the metal atoms comprising the filament.

$R_{\text{on}}$ varies differently compared to static $R_{\text{off}}$, as seen from Figure 5.4(b). It is seen that static $R_{\text{on}}$ for Cu/HfO$_2$/Ni devices exhibits a minimal change, if any, below a dose $\sim 1 \times 10^{11}$ rad, but starts to decrease when the dose is above $1 \times 10^{11}$ rad. For Pt/HfO$_2$:Cu/Cu devices, even though static $R_{\text{on}}$ increases (50 – 100%) at lower dose range (1.5, 3, 5 Grad), the on-state still remains as on.

![Figure 5.4](image.png)

**Figure 5.4** Percentage change in (a) static $R_{\text{off}}$ and (b) static $R_{\text{on}}$ as a function of dose for ECM devices under light-ion and heavy-ion irradiations.

These results imply that ECM devices may be inherently more 'rad-hard' in terms of the stability of the off- and on-state after irradiation. This is reasonable in that we expect less influence from irradiation on the metal filament in ECM devices than on vacancy-
based filaments in VCM devices since conduction along VCM filaments are modulated by vacancy density, in contrast to the ECM filaments where conduction is modulated by metal ion transport. However, more irradiation experiments are needed for more detailed and accurate comparisons of the effects from light-ion irradiation and from heavy-ion irradiation.

Figure 5.5 shows the changes in $V_f$ and the corresponding $R_{\text{fresh}}$ for ECM devices under light-ion and heavy-ion irradiation. It is clearly seen that $V_f$ increases with increasing irradiation dose, independent of ion mass (or ion species), as indicated by the dashed line in Figure 5.5(a). This is completely opposite to the trends observed for $V_f$ for VCM devices. This further underscores the fundamental difference in switching mechanism of the two types of ReRAM devices.

![Figure 5.5](image)

**Figure 5.5** Percentage change in (a) $V_f$ and (b) $R_{\text{fresh}}$ as a function of dose for ECM devices under light-ion and heavy-ion irradiations.

Correspondingly, from Figure 5.5(b), a reduction in $R_{\text{fresh}}$ is observed when the dose is below $1 \times 10^{11}$ rad, and the reduction decreased with increasing dose. When the dose exceeds $1 \times 10^{11}$ rad, the ECM ReRAM devices exhibit a net increase in $R_{\text{fresh}}$ as a result of the conduction mechanism transition (section 4.2.1). Again, the root cause for the
observed changes in $R_{\text{fresh}}$ changes is related to the radiation-induced microstructure change at the highest dose.

5.3 Summary

The difference of the effects of light-ion and heavy-ion irradiations is reflected by the dependence of irradiation dose on ion fluence associated with specific LET for a given ion species. A heavier ion with larger LET leads to a higher radiation dose at a given ion fluence, resulting in more impacts on the device dielectric and resistive switching properties. In this chapter, effects of light-ion and heavy-ion radiation on both VCM and ECM ReRAM devices are compared, in terms of static $R_{\text{off}}$, static $R_{\text{on}}$, $V_f$, and $R_{\text{fresh}}$.

For VCM ReRAM devices, a dose threshold behavior was observed for static $R_{\text{off}}$ and static $R_{\text{on}}$. That is, static $R_{\text{off}}$ and static $R_{\text{on}}$ decrease dramatically and linearly with logarithm dose when the radiation dose is above the threshold dose, ($D_{\text{th}} \approx 5 \text{ Grad(Si)}$ for static $R_{\text{off}}$ and $\approx 10 \text{ Grad(Si)}$ for static $R_{\text{on}}$). When the radiation dose is below the threshold, the static $R_{\text{off}}$ and static $R_{\text{on}}$ vary only slightly. Note that beyond the static $R_{\text{off}}$ dose threshold, potential off-to-on transition events can happen. Secondly, $V_f$ varies slightly ($< 5\%$) under light-ion irradiation, but decreased ($8\% - 18\%$) under heavy-ion irradiation when the dose was higher than $10^{10}$ rad(Si). For $R_{\text{fresh}}$, there are three dose regimes that determine the relative change due to irradiation: $10^8$ rad, $10^8 - 5 \times 10^{10}$ rad, and $> 5 \times 10^{10}$ rad. Specifically, $R_{\text{fresh}}$ decreases when the dose is in the second regime, while $R_{\text{fresh}}$ increases significantly when the dose is in the third regime.

For ECM ReRAM devices, off- and on-states are more radiation resistant than VCM devices. In particular, no substantial decrease in static $R_{\text{off}}$ and $R_{\text{on}}$ (and thus no threats of
off-to-on transitions) were found after irradiation, although there was no clear variational trend for these type of devices. In strong contrast to the VCM devices, ECM devices showed increasing $V_f$ with increased dose. Moreover, $R_{\text{fresh}}$ for this type of ReRAM decreased after radiation when the dose was below $1 \times 10^{11}$ rad with the reduction decreasing with increased dose. When the dose was above $1 \times 10^{11}$ rad, $R_{\text{fresh}}$ increased. These distinct results originated from the fundamentally different switching mechanisms of the two types of devices.
6. Conclusions and Future Directions

6.1 Conclusions

The impacts of ion irradiation on two types of HfO$_2$-based ReRAM devices are investigated, using various irradiation ion sources: H$^+$ (1 MeV), He$^+$ (1 MeV), N$^+$ (1 MeV), Ne$^+$ (1.6 MeV) and Ar$^+$ (2.75 MeV). The corresponding results of ion irradiation responses of both types of ReRAMs can be explained from the distinct switching mechanisms – vacancy filament for VCM-ReRAMs and metal filament for ECM-ReRAMs. The impacts of ion irradiation on these device types are summarized as below:

After light-ion (H$^+$) irradiation of ECM Pt/HfO$_2$:Cu/Cu devices, $V_{\text{set}}$, $V_{\text{reset}}$, and $R_{\text{on}}$ exhibited positive shifts for Pt/HfO$_2$:Cu devices with rebound effects observed 5 days after irradiation. Also, $V_f$ increased with total dose for ECM Cu/HfO$_2$/Ni increase after light-ion (H$^+$, He$^+$) irradiation. Similar to the pre-radiation case, the forming conduction can be also fitted to a Poole-Frenkel mechanism but with an increased dynamic dielectric constant for Cu/HfO$_2$/Ni devices after proton and helium irradiation. These irradiation responses are attributed to irradiation-induced electron trap formation in HfO$_2$ and its concomitant impact on electrochemical metallization. Light-ion irradiation also reduced $R_{\text{off}}$ for Pt/HfO$_2$:Cu/Cu devices and $R_{\text{fresh}}$ for Cu/HfO$_2$/Ni devices by creating more defects and potentially increasing device leakage current. Compared to ECM ReRAMs, VCM ReRAMs (TiN/HfO$_2$/TiN(W)) exhibited superior TID radiation-hardness: (1) Parameters including average $V_{\text{set}}$, $V_{\text{reset}}$, $R_{\text{on}}$, $R_{\text{off}}$ in VCM ReRAMs exhibited relatively modest effects due to irradiation; (2) $V_f$ decreased after irradiation; (3) TID radiation improved the overall uniformity of resistive switching in TiN/HfO$_2$/TiN ReRAMs while degrading switching uniformity in ECM ReRAMs. The different irradiation responses in
VCM and ECM ReRAM devices resulted from their distinct CF formation mechanisms. For the VCM-type ReRAM system the proton-induced vacancy density did not inhibit the trap-assisted-tunneling associated with Hf-rich CF formation. In strong contrast, proton-induced vacancies for the ECM ReRAMs inhibit the formation of the metallic filament through internal field reduction due to charge trapping.

After heavy-ion (N⁺, Ne⁺, Ar⁺) irradiation of VCM-type devices, the static off- and on-state resistance decreased with fluence and with ion mass; and the static off-state resistance was more sensitive to irradiation than the on-state. Severe off-to-on resistance-state transitions were observed at higher fluence (10^{15} \text{ cm}^{-2}). Irradiation also caused the decrease of forming voltage and the increase of TAT current up to 10^{14} \text{ cm}^{-2}, although a large increase in R_{\text{fresh}} by an order of magnitude was observed at a fluence of 10^{15} \text{ cm}^{-2}. Moreover, irradiation also resulted in slight increases in V_{\text{set}} and R_{\text{on}} but no obvious changes in V_{\text{reset}} and R_{\text{off}}. These irradiation effects can be explained by radiation-induced defects and changes in microstructure in the HfO₂ layer. For ECM-type devices, heavy-ion irradiation resulted in V_f increase and the forming conduction mechanism transition from Poole-Frenkel emission to ionic conduction associated with electrochemical effects after Ar irradiaiton. These results are attributed to irradiation-induced reduction of traps and defects which resulted from the crystallinity improvement.

The difference in the effects of light-ion and heavy-ion irradiation on both types of ReRAM devices was also compared with respect to radiation dose, as a heavier ion with larger LET leads to a higher radiation dose at a given ion fluence. For VCM-type devices, a dose threshold behavior was discovered for static R_{\text{off}} and static R_{\text{on}}. That is, static R_{\text{off}} and static R_{\text{on}} decreased dramatically and linearly with logarithm dose when the radiation
dose was above the threshold dose, $(D_{th}, \sim 5 \text{ Grad(Si)})$ for static $R_{\text{off}}$ and $\sim 10 \text{ Grad(Si)}$ for static $R_{\text{on}}$), whereas when the radiation dose was below the threshold static $R_{\text{off}}$ and static $R_{\text{on}}$ varied only slightly. Secondly, $V_f$ varied slightly ($< 5\%$) under light-ion irradiation, but decreased relatively largely (8\% - 18\%) under heavy-ion irradiation when the dose was higher than $10^{10} \text{ rad(Si)}$. For $R_{\text{fresh}}$, there were three regimes for dose-induced variation: $10^8 \text{ rad}$, $10^8 - 5 \times 10^{10} \text{ rad}$, and $> 5 \times 10^{10} \text{ rad}$. Specifically, $R_{\text{fresh}}$ decreased when the dose was in the second regime, while $R_{\text{fresh}}$ increased significantly when the dose was in the third regime.

For ECM ReRAM devices, off- and on-states were more radiation resistant than VCM devices. In particular, no substantial decrease in static $R_{\text{off}}$ and $R_{\text{on}}$ and thus no threats of off-to-on transitions were found after irradiation. Secondly, ECM-type devices showed increasing $V_f$ with increased dose and $R_{\text{fresh}}$ decreased after irradiation when the dose was below $1 \times 10^{11} \text{ rad}$ but increased when the dose was above $1 \times 10^{11} \text{ rad}$.

In practical applications, ReRAM devices with lower $V_f$ or even $V_f$-free are more desirable. Irradiation of VCM-type devices lead to $V_f$ reduction, as well as enhanced switching uniformity, suggesting that VCM devices are not only rad-hard but also rad-philic, and that irradiation could be used to optimize the VCM ReRAM performance. However, off-to-on transition events may occur when the dose exceeds the threshold at $\sim 5\text{ Grad}$. This may be a drawback for VCM-type devices. On the contrary, irradiation – especially with heavy ions – should be avoided for ECM ReRAM devices to avoid $V_f$ increases and the potential deterioration of switching uniformity. On the other hand ECM ReRAM devices do not have the threat of off-to-on transition events, which is an advantage over VCM-type devices. In general, HfO$_2$-based ReRAM devices are
potentially inherently rad-hard, and constitute a potential advantage of ReRAMs for future NVM applications.

6.2 Future directions

Certainly, more work is needed to gain a solid understanding of the impacts of ion irradiation on various types of ReRAM devices and their relationship with various underlying resistive switching mechanisms. The author suggests the following work:

- The SRIM program does not take into account the crystalline structure of target materials, and therefore the accuracy of the calculated irradiation-induced vacancies in this work is compromised. Other programs taking account of the crystalline structure, such as MARLOWE and crystal-TRIM, should be employed for a more accurate simulation of the interaction between radiation ions and the target materials.

- More metrology characterization is desired for better understanding of the ion irradiation impact, such as HRTEM to obtain high resolution images of filaments inside HfO$_2$ pre- and post-irradiation.

- More I-V simulation work should be carried out for VCM-type devices based on TAT current.

- ECM-type HfO$_2$-ReRAMs with stable and uniform resistive switching behavior that is comparable with VCM-type HfO$_2$-ReRAM devices are more desirable in order to have a completely parallel comparison with VCM-type ReRAM devices. Furthermore, for the parallel ECM and VCM comparison, it is better to have ion irradiation studies based on the same device size with the same HfO$_2$ thickness.
Also, this work only completed a small portion of irradiation work with limited ion species and ion beam energy. More irradiation work should be performed for more in-depth understanding of the effects on ReRAM devices:

- Radiation ion sources with a variety of ion masses.
- Radiation ions with larger energy from 10s to 100s of MeV.
- Radiation impacts from electrons and photons such as X-ray, γ-ray.
- The dependence of resistive switching performance on irradiation dose rate or flux should be carried out.
Appendix I SRIM Simulation

Monte Carlo simulations of ion beams traversing all 4 types of ReRAM devices (TiN/HfO$_2$/TiN, TiN/HfO$_2$/W, Pt/HfO$_2$:Cu/Cu, Cu/HfO$_2$/Ni) were carried out using the SRIM program, and the radiation-induced oxygen vacancies were calculated based on the simulation result. The default values of threshold displacement energy for oxygen (28 eV) and hafnium (25 eV) in HfO$_2$ provided by SRIM were used. This section gives an example of H$^+$ (energy of 1MeV) radiation and Ar$^+$ (energy of 2.75 MeV) radiation on Cu/HfO$_2$/Ni.

Figure AI.1(a) shows the trajectories of 1000 protons traversing the Cu(1μm)/HfO$_2$(55nm)/Ni(100nm) ReRAM device layers (a smaller region is shown in the figure for clarity). The incident proton beam is perpendicular to the surface of the left Ni electrode (top electrode). It can be seen that the proton ion beam traverses a straight line and approximately 100% of the protons are transmitted according to the simulation result. Figure AI.1(b) presents the distribution of O and Hf recoils displaced by the incident protons. Figure AI.1(c) shows the distribution of vacancies produced by each ion (proton or recoil). From Figure AI.1(c), the total number of oxygen vacancies induced by one ion can be obtained by integrating the $V_O$ distribution profile over the whole HfO$_2$ layer. Then the irradiation-induced oxygen vacancy density can be further obtained at a given fluence.

For comparison, the same results are also presented for an Ar ion beam, as shown in Figure AI.1(d, e, f) for ion and recoil track, O and Hf recoil distribution, and total vacancy distribution, respectively. It is worth noting that about 100% Ar$^+$ ions are transmitted through the HfO$_2$ layer from the simulation. Clearly, compared with the result
of the proton beam impingement, many more displacements and vacancies are created by
the Ar ion beam. In addition, total vacancies with a 3D distribution generated by 1000
protons and 1000 Ar ions are also given in Figure A1.2.
Figure AI.1 TRIM simulation results for a 1-MeV proton beam (1000 protons) incident perpendicularly on the Ni top electrode of the Cu/HfO$_2$/Ni ReRAM devices: (a) Particle and ion tracks, (b) Distribution of displaced O and Hf atoms, (c) Distribution of total vacancies created by the ion beam; and simulation results for a 2.75-MeV Ar$^+$ beam: (d) Particle and ion tracks (from 50 Ar ions), (e) Distribution of O and Hf recoils (from 1000 Ar ions), (f) Distribution of total vacancies (from 1000 Ar ions).
Figure A1.2 3D distribution of total vacancies generated by (a) 1000 protons, (b) 1000 Ar⁺.

It should be also pointed out that for simplicity, the total vacancies induced by irradiation are assumed to be all O vacancies in this work. This likely overestimates the irradiation-induced oxygen vacancy density. However, the discussion in this work mainly considers an order of magnitude (not exact) value of the irradiation-induced vacancy
density. Since the inclusion of Hf-vacancies does not change the order of magnitude (see Figure AI.1(b, e)), it is assumed they would not affect the result.
Appendix II Improved Cycle-to-Cycle Resistive Switching Uniformity of TiN/HfO$_2$/TiN ReRAM Devices After Proton Irradiation

Improved cycle-to-cycle resistive switching uniformity was observed for TiN/HfO$_2$/TiN ReRAM devices after proton irradiation. Figure AII.1(a) and (b) plots the I-V curves for two devices respectively with 100 cycles before and after irradiation at a TID of 5 Grad. Clearly, the post-irradiated device exhibited greater switching uniformity, indicating less cycle-to-cycle variation in the devices after proton irradiation.

Figure AII.1 I-V curves of 100 resistive switching cycles for a TiN/HfO$_2$/TiN ReRAM device: (a) pre-irradiation and (b) post-irradiation at a dose of 5 Grad(Si). (c) Dose dependence of resistance variation range ($\Delta R_{on}$ and $\Delta R_{off}$) for on- and off-state. (d) On- and off- state separation ($\Delta R_{on-off} = \text{Min}(R_{off})-\text{Max}(R_{on})$) for the pre-radiation case and the post radiation case as a function of dose.
Figure AII.1(c) plots the resistance ranges, $\Delta R_{on}$ and $\Delta R_{off}$ for pre- and post-irradiated ReRAM devices. $\Delta R_{on}$ and $\Delta R_{off}$ are defined as the total variation in the measured on- and off-state resistance at the 0.05 V read voltage, as diagrammatically illustrated in Figure AII.1(a) and (b). It is clearly evident that the pre-irradiated ReRAM device have a larger range of resistance variation in the on- and off- states than the post-irradiated devices. Both $\Delta R_{on}$ and $\Delta R_{off}$ show a monotonic decrease with increased dose: $\Delta R_{on} \sim -50 \pm 30 \ \Omega/\text{decade}$ and $\Delta R_{off} \sim -65 \pm 43 \ \Omega/\text{decade}$. Figure AII.1(d) shows the minimum on- and off- state separation, $\Delta R_{on-off}$, which is defined as the absolute resistance difference between the maximum $R_{on}$ and the minimum $R_{off}$, as schematically demonstrated in Figure AII.1(a) and (b). This state separation, $\Delta R_{on-off}$, exhibited dramatic increases after proton irradiation, reaching its maximum at the 10 Grad(Si) dose.