Radiation effects in tantalum oxide-based resistive memory devices

Joshua Stuart Holt

University at Albany, State University of New York, josh.holt728@gmail.com

The University at Albany community has made this article openly available. Please share how this access benefits you.

Follow this and additional works at: https://scholarsarchive.library.albany.edu/legacy-etd

Part of the Aerospace Engineering Commons, Electrical and Electronics Commons, and the Nuclear Commons

Recommended Citation

This Dissertation is brought to you for free and open access by the The Graduate School at Scholars Archive. It has been accepted for inclusion in Legacy Theses & Dissertations (2009 - 2024) by an authorized administrator of Scholars Archive. Please see Terms of Use. For more information, please contact scholarsarchive@albany.edu.
Radiation Effects in Tantalum Oxide-based Resistive Memory Devices

By

Joshua S. Holt

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
2018
Abstract

There is an increasing need for radiation-hardened electronics as space programs grow in number and scope. Scientific interest in long-term exploration, particularly in high-radiation environments such as Europa, as well as commercial interest in establishing permanent outposts, requires high tolerance of radiation effects. A flash memory device might survive for several years in low Earth orbit, but only a few days in orbit around Europa due to the extremely high levels of radiation encountered there. Meanwhile, commercial interests, including asteroid mining and building a base on the moon or Mars would require electronic systems that could survive for long periods of time, or indefinitely, in each location. Flash memories are suitable for multi-year operation in low Earth orbit due to shielding of cosmic rays by Earth’s magnetic field. However, long-term missions beyond low Earth orbit have higher radiation requirements, which may not be suitable for even rad-hardened flash memories.

Resistive memory (RRAM) devices are promising candidates for inherently radiation-hard non-volatile memory. These devices rely on the movement of either metal cations or oxygen vacancies to switch resistance states. Since switching is based on movement of atoms, rather than electron movement or storage, RRAM devices are generally much more resilient to radiation effects than flash memory. Indeed, RRAM devices have been shown to be resistant to single event effects, total ionizing dose (TID), and cumulative displacement damage dose (DDD). However, radiation-induced device failures can still occur, and the limits of these devices need to be understood if they are to be used in high-radiation environments. Furthermore, the mechanisms of radiation-induced degradation in RRAM devices are not fully understood. In this work, we produced TaO$_x$-based RRAM devices and evaluated them for failure due to TID and DDD. A combination of electrical testing, metrology, and device modeling was used to investigate the physical mechanisms of radiation damage within the devices.
The devices were found to be resilient to TID effects from $^{60}$Co gamma radiation. No devices failed up to a tested TID level of 20 Mrad(Si). Furthermore, during ion beam experiments, our devices were exposed to TID levels greater than 1 Grad(Si) with no observed effect on switching parameters of resistance states. These devices are very resistant to TID effects compared to other RRAM devices in the literature, some of which fail around 1-5 Mrad(Si). However, nearly all reported RRAM devices surpass the 1 Mrad(Si) requirement of the NASA X2000 program for a visit to Europa, which serves as an example of a high-radiation target. Our devices might be more resilient to TID due to the thin oxide, or the high concentration of oxygen vacancies within the devices.

Our devices were also highly resistant to displacement damage effects. Displacement damage is normally a concern for RRAM devices since atomic displacements could directly affect the size and shape of the conductive filament. DDD was measured as radiation-induced oxygen vacancies per cm$^3$ to facilitate comparison between different studies. The lowest DDD level which caused a change in device resistance state was $10^{21}$ vacancies per cm$^3$. By comparison, most other studies reported device failures in the range of $10^{19}$-$10^{20}$ vacancies per cm$^3$, and a few even reported failures at $10^{17}$ vacancies per cm$^3$. An example flash memory device failed at a DDD level of $10^{15}$ vacancies per cm$^3$, lower than the failure threshold for any reported RRAM devices. It appears that our devices are very resistant to DDD effects compared to other RRAM devices. This high resilience is likely due to the very high intrinsic concentration of oxygen vacancies in our devices, $\sim 10^{22}$ vacancies per cm$^3$. Most of our devices failed at a DDD level of $10^{22}$ vacancies per cm$^3$, which is the level where radiation-induced vacancies would equal intrinsic vacancies within the device. At lower DDD levels, the radiation-induced vacancies would be a small fraction of the total vacancies, and would therefore not be expected to cause major changes in the devices.

Overall, our devices appear to be resilient to radiation effects even by RRAM standards. This very high resilience is likely due at least in part to the high intrinsic concentration of oxygen vacancies in our
devices. A Fermi calculation was used to estimate device time to failure in low Earth orbit (LEO), a relatively low-radiation environment, and at Europa, a high-radiation environment. In LEO, an example flash memory device would likely survive for several years, while our devices would not fail due to radiation damage in any meaningful timeframe. Meanwhile, at Europa, the example flash memory devices might survive for a few days, while our devices would likely survive for several years before radiation-induced failure. Even if radiation-induced failures occurred, most failures we observed were soft errors, and devices were able to continue switching. Our devices are similar in composition to devices made by Panasonic which are already commercially available. If those devices exhibit similar resilience to radiation effects as our own devices, they would be excellent candidates for radiation-hardened memory in space applications.
Acknowledgements

I am extremely grateful for the help and support I have received over the course of my graduate career. In particular, I would like to thank my advisor, Dr. Nathaniel Cady, for his constant support, encouragement, and feedback through more than 6 years of research. Dr. Cady’s input was instrumental in helping me apply for the NASA Space Technology Research Fellowship (NSTRF) which funded this project. Furthermore, his feedback over the next several years helped to shape me as both a scientist and a writer. Dr. Cady made sure he was always available to help with both my project and my professional development, encouraging me to attend conferences and produce publications from the very start of my project. The results of this work are in large part thanks to his continual efforts. I could not have asked for a more supportive or understanding advisor, and I was fortunate to be a part of his research group.

I would also like to thank Dr. Jean Yang-Scharlotta, my NSTRF mentor, for her substantial contributions to my work and my professional development. Dr. Yang-Scharlotta served as a mentor for me throughout the project, providing feedback and guidance, and working with me directly on many experiments. She helped to arrange collaborations with researchers at NASA and at Sandia National Laboratory, opening up many new research opportunities. Furthermore, she was willing to give frank criticism whenever I needed to improve my work, leading me to become a much more effective scientist. I am especially grateful for her patience, enthusiasm, and guidance throughout my graduate research career.

Furthermore, I am grateful to the NSTRF program for facilitating an excellent research experience through funding for the project and for visits to NASA and Sandia National Laboratory. The collaboration opportunities enabled by the program helped to strengthen my research and my professional development. The NSTRF team was incredibly understanding and supportive, especially when experiments did not always proceed according to the expected schedule. This program provided the
stability and resources for a successful graduate career, and enabled me to contribute toward space exploration, a cause I am personally passionate about.

I am especially grateful for the unwavering support and encouragement from my fiancé, Isabel Tian, throughout my graduate career. Her critical feedback of my writing and presentations greatly improved the quality of my work, and her support helped me to stay motivated through the most difficult parts of the project. Her artistic talent is evident in many of the figures in my publications and in this dissertation. She is wonderfully caring and talented, and I look forward to seeing the next step of each of our careers.

Finally, I am grateful to my parents, Tim and Sandy Holt, for their loving support. They have always gone above and beyond to help in any way they could, whether it be some home-cooked meals, introductions to professional colleagues, or simply being there to listen. Furthermore, they provided me with a tremendous advantage by covering the cost of my undergraduate education, greatly improving my financial security as I began my graduate career. I am deeply grateful for their unwavering support and care. I would also like to thank my sister, Lauren Holt, and my extended family for being supportive and always taking an interest in my work and my life. My accomplishments were made possible by the loving support of my family, for which I will always be grateful.
Copyright Permissions

Excerpts of several of our own published studies were included in this dissertation, with permission from the publishers:


Excerpts from an as-yet unpublished manuscript were included in Chapter 4. Those results are expected to be published under the working title “Comparison of Radiation Effects in Custom- and Commercially-Fabricated Resistive Memory Devices.”

- Excerpts from each of these articles were included with permission from the respective publishers.
- Excerpts of each of these articles were used in parts of the dissertation. In some cases, figures were adapted or updated to match formatting. Minor text changes were made within the excerpts, with some minor additions. The final wording of text in the unpublished manuscript may change after publication of this dissertation.
- These excerpts were included because they were part of the programmatic line of research that comprised this dissertation, and including them provided a coherent and appropriately sequenced investigation
- I, Joshua Holt, was the primary author and researcher on each of the excerpted works listed here.
- IEEE generally allows reproduction of materials for a thesis without a formal permission request. The following statement is required to be prominently displayed: “In reference to IEEE copyrighted material which is used with permission in this thesis, the IEEE does not endorse any of the University at Albany’s products or services. Internal or personal use of this material is permitted. If interested in reprinting/republishing IEEE copyrighted material for advertising or promotional purposes or for creating new collective works for resale or redistribution, please go to http://www.ieee.org/publications_standards/publications/rights/rights_link.html to learn how to obtain a License from RightsLink.” (https://www.ieee.org/content/dam/ieee-org/ieee/web/org/pubs/permissions_faq.pdf)
- MRS Advances extends automatic copyright permission for re-use of first-author publications. (http://www.cambridge.org/about-us/rights-permissions/permissions/permissions-requests-our-authors/)
# Table of Contents

1 Introduction
   1.1 Ionization effects in RRAM devices 6
      1.1.1 Ionization effects in HfO$_x$ RRAM devices 7
      1.1.2 Ionization effects in TaO$_x$ RRAM devices 9
   1.2 Displacement damage effects in RRAM devices 11
   1.3 References 16

2 Device Fabrication and Electrical Testing Procedures
   2.1 Shadow Mask Device Fabrication Process 24
   2.2 Photolithography Device Fabrication Process 29
   2.3 Inverted Liftoff Fabrication Process 35
   2.4 Conclusion 39
   2.5 References 40

3 Ionization Damage Effects in RRAM Devices 42
   3.1 Introduction 42
   3.2 TID Requirements for Space Missions 45
   3.3 TID Effects in Shadow Mask Devices 48
   3.4 TID Effects in Liftoff Devices 52
   3.5 Conclusion 56
   3.6 References 57

4 Displacement Damage Effects in RRAM Devices 61
   4.1 Introduction 61
   4.2 Review of Displacement Damage Effects in VCM-type RRAM Devices 66
   4.3 Displacement Damage Effects in Shadow Mask Devices 71
   4.4 Displacement Damage Effects in Photolithography-based Devices 72
4.5 Displacement Damage Effects in Inverted Liftoff Devices 77

4.6 Expected Displacement Damage Levels for Various Space Missions 88

4.7 Analysis of Radiation-induced Defects in TaO$_x$-based Devices 91

4.8 Conclusion 97

4.9 References 98

5 Conclusion 102

5.1 References 105
# List of Figures

1.1 VCM-type resistive switching 4
1.2 SRIM calculation of displacement damage 6
2.1 Circuit diagram for RRAM electrical characterization 21
2.2 Electrical testing setup for RRAM device testing 22
2.3 Pulsed set and reset waveforms 23
2.4 Shadow mask device layout 24
2.5 SEM cross-section of sputtered films 25
2.6 TaO<sub>x</sub> film composition 27
2.7 100 set/reset cycles of a shadow mask device 29
2.8 Top-down view of a photolithography-based device 30
2.9 Photolithography-based device fabrication process 31
2.10 Incomplete liftoff of the bottom electrode 33
2.11 Photoresist undercut for liftoff 33
2.12 Inverted photolithography process 37
2.13 Pinholes in TaO<sub>x</sub> layer 38
2.14 Retention of inverted devices 39
3.1 Shadow mask device design 48
3.2 TID effects on shadow mask device switching parameters 50
3.3 Breakdown of ion beam energy loss to ionization and displacements 51
3.4 Endurance and retention of inverted liftoff RRAM devices 53
3.5 Effect of gamma irradiation on inverted liftoff devices 55
3.6 IV characteristics of unformed inverted liftoff devices irradiated with gamma radiation 56
4.1 Example plot of displacement damage in a TaO<sub>2</sub> film 62
4.2 RRAM device fabrication flow 73
4.3 Effects of displacement damage on device resistance

4.4 Effects of displacement damage on switching resistance levels

4.5 Example reset and set curves for the inverted liftoff devices

4.6 Ar$^+$ ion bombardment of inverted liftoff devices

4.7 Forming of inverted liftoff devices after ion beam exposure

4.8 TEM cross-sections of non-irradiated and irradiated SUNY devices

4.9 Capacitance changes in SUNY devices due to displacement damage

4.10 XRD of irradiated TaO$_x$ blanket films

4.11 XPS O1s spectra of devices irradiated with Ar$^+$ ion beam

4.12 XPS Ta4f spectra

4.13 Varied vacancy concentration

4.14 Varied metal work functions

4.15 Varied vacancy concentration

4.16 Varied bandgap and electron affinity

4.17 Varied electron affinity

4.18 Fermi level pinning of defect band
# List of Tables

2.1  Sputtering conditions for RRAM device fabrication 26  
2.2  Shadow mask device switching characteristics 28  
2.3  Lift off process 32  
2.4  Sputtering conditions for photolithography device fabrication 34  
3.1  Shadow mask device switching parameters 49  
3.2  TID effects on shadow mask device switching parameters 50  
3.3  Switching parameters for inverted liftoff RRAM devices 54  
4.1  Ionization and displacements in shadow mask devices 71  
4.2  RRAM switching parameters 75  
4.3  Radiation-generated oxygen vacancies 75  
4.4  Inverted liftoff device switching parameters 78  
4.5  Heavy ion exposure of inverted liftoff devices 79  
4.6  Time to failure for devices in LEO and at Europa 90
Chapter 1

Introduction

There is a critical need for reliable electronic systems in space missions, as laid out in a NASA review for the X2000 program by Strauss and Daud (Strauss and Daud, 2000). In particular, as missions extend to more distant celestial targets, onboard systems need to be more resilient against failure and more able to self-correct when an error occurs. For missions to the inner planets, the average round-trip communication delay is 24 minutes, enabling many errors to be fixed through ground-based analysis and intervention. However, a mission to Jupiter has an average round-trip communication time of 86 minutes; if a fault occurs during a critical part of a mission, data collection might be heavily impacted before a ground-based intervention can be implemented. Even more distant targets would benefit even more from improved spacecraft reliability and decreased reliance on ground-based troubleshooting.

One of the priorities of NASA is to research the origins of life, including exploring environments that could possibly support life (NASA Strategic Plan 2018). Europa and Enceladus, moons of Jupiter and Saturn respectively, are prime candidates for exploration into the origins of life, due to the large oceans of water beneath the surface ice of both satellites (Manga and Wang, 2007). The long time-delay for any ground-based interventions for missions to these moons makes reliable spacecraft a necessity. For Europa, there is an even greater need for rad-hard systems, as Europa lies within a high-radiation zone surrounding Jupiter (Paranicas et al., 2007). The radiation guidelines in the X2000 program were developed specifically for a mission to Europa, and will serve as baseline requirements for rad-hard memory devices herein (Strauss and Daud, 2000).
One specific goal of the X2000 program was to develop rad-hard non-volatile memory to enable a mission to Europa (Strauss and Daud, 2000). In particular, memory devices would need to withstand \( > 1 \text{ Mrad(Si)} \) total ionizing dose (TID), retain data for \( > 10 \) years, and have cycle endurance on the order of \( 10^9 \). Additional benefits of developing novel non-volatile memory devices might also include improved memory density and speed, and reduced power requirements, depending on the technology used.

Currently, flash memory is widely used on spacecraft due to a number of advantages, including high memory density and low cost. Flash memory meets or exceeds the retention requirement of 10 years (Zhao et al., 2014). While flash memory cycle endurance only reaches \( \sim 10^6 \) cycles (Zhao et al., 2014), this endurance level is enough for many shorter space missions, or missions where a large amount of travel time is spent dormant, so that memory is only actively written during short experiment windows. However, flash memory is inherently vulnerable to radiation damage, due to its reliance on charge pumps to program and erase the memory cells (Nguyen et al., 1999). Radiation can also generate traps within the gate oxide of a floating gate, erasing the memory bit (Cellere et al., 2001; Duncan et al., 2016). Early versions of flash memory typically exhibited memory errors at TID \( < 100 \text{ kr}\text{ad(Si)} \) (Nguyen et al., 1999). A flash memory cell tested more recently exhibited memory errors at TID \( > 200 \text{ kr}\text{ad(Si)} \) when fully programmed (Duncan et al., 2016). However, without error correction or other radiation-hardening approaches, these cells do not come close to the \( 1 \text{ Mrad(Si)} \) radiation requirement set forth in the X2000 program (Strauss and Daud, 2000).

Several radiation-hardening approaches do exist, which may be able to improve the performance of flash memory or other on-board control circuitry. Silicon-on-insulator technology can minimize some types of current leakage and latchups (Schwank et al., 2003). Protection diodes and clamping circuits can be used to limit radiation-induced voltage spikes (Garg et al., 2006). Redundant circuitry and error correction are also used to mitigate radiation-induced errors (Garg et al., 2006). However, even if some of these approaches can make flash memory resilient
enough for shorter space missions, flash memory may still be a cause of system failure on longer missions or in high-radiation environments. For such high-radiation missions, the replacement of flash memory with an inherently radiation resistant memory technology will strongly decrease the likelihood of memory failures.

Resistive memory (RRAM) is a strong candidate for use in space, due to its inherent resistance to radiation effects, as well as favorable memory characteristics (Gonzalez-Velo et al., 2017). RRAM devices are expected to be inherently resistant to radiation damage, because they operate based on the movement of ions, rather than electrons. RRAM devices generally consist of a metal-insulator-metal structure, with some type of ion intentionally introduced into the insulator layer, which is often a transition metal oxide (Waser et al., 2009; Gonzalez-Velo et al., 2017). Regardless of the ion used, an electric field is applied to move the mobile cations through the insulator, producing a conductive filament and setting the device to a low resistance state (LRS) (Fig. 1.1). Another electric field, often a reverse bias, can be used to break the conductive filament, returning the device to a high resistance state (HRS). Alternating electric fields can then be applied to switch the device between HRS and LRS. Unipolar devices use the same polarity electric field for set and reset operations, while bipolar devices use opposite polarity fields. Some devices, referred to as electrochemical metallization memory (ECM), use metal cations from an active electrode (usually Cu or Ag) to produce a conductive metal filament. Other devices, referred to as valence change mechanism (VCM) devices, rely on movement of conductive oxygen vacancies, which are sometimes positively charged, to produce the conductive filament. Both ECM and VCM devices are expected to be relatively rad-hard, since both mechanisms rely on the movement of ions, rather than electrons, to change the resistance state of the device.

In this work, we focus on radiation effects in one implementation of VCM-type RRAM devices, made with tantalum oxide, based on several studies indicating especially favorable memory characteristics in TaO$_x$-based devices. In particular, TaO$_x$-based devices have exhibited retention > 10 years (Pan et al., 2014), up to $10^{12}$ cycle endurance (Kim et al., 2011), and sub-ns
switching speeds (Torrezan et al., 2011). Although these observations were made on different devices, they demonstrate the strong potential of TaO$_x$-based devices to meet or exceed the X2000 requirements for rad-hard non-volatile memory. HfO$_x$-based devices have also exhibited high retention and cycle endurance, making them another strong candidate for rad-hard memory (Lee et al., 2010; Chen et al., 2013). We chose to focus on TaO$_x$-based devices due to their strong resistive switching capabilities and relative lack of radiation effect studies.

![Figure 1.1. VCM-type Resistive Switching.](image)

Devices begin in an unformed state, with oxygen vacancies (or metal cations for ECM-type devices) distributed through the insulator. During forming, voltage is applied, causing vacancies (or metal cations) to migrate across the insulator, forming a conductive filament and setting the device to LRS. With the application of a reverse bias (for bipolar devices) vacancies (or metal cations) dissipate away from the conductive filament, breaking the filament and resetting the device to HRS. The device can then be switched between HRS and LRS repeatedly.

RRAM devices are typically not affected by single radiation events, but can be affected by cumulative effects, including ionization damage and displacement damage (Summers et al., 1995; Srour et al., 2003; Gonzalez-Velo et al., 2017). Ionization damage is the ejection of an electron, resulting in the generation of holes and free electrons. This is unlikely to cause major changes in RRAM devices, since ejection of an electron does not directly affect the location of oxygen
vacancies (or metal cations for ECM devices). Indeed, a number of studies have demonstrated radiation hardness > 1 Mrad(Si) in HfO$_x$- and TaO$_x$-based RRAM devices against ionization damage from $^{60}$Co gamma radiation (Morgan et al., 2014; McLain et al., 2014; Fang et al., 2014; Lin et al., 2015; Hu et al., 2016), 10 keV x-rays (Bi et al., 2013), and ion beam sources (Hughart et al., 2013; He et al., 2012). Although some of these devices exhibited changes around 5 Mrad(Si) (Fang et al., 2014; Lin et al., 2015), most HfO$_x$ and TaO$_x$ devices appear to easily exceed the 1 Mrad(Si) threshold for rad-hard devices from the X2000 program. Nevertheless, a few studies reported device failure at TID levels below this threshold (Zhang et al., 2011; McLain et al., 2014), making ionization damage effects important to consider in our own devices.

By contrast, displacement damage involves the physical displacement of atoms within a material (Summers et al., 1995; Srour et al., 2003; Gonzalez-Velo et al., 2017). In a TaO$_x$-based RRAM device, this will mostly result in the generation of oxygen vacancies and interstitials, with a lower number of tantalum vacancy-interstitial pairs (Fig. 1.2). This can result in an increase in the number of oxygen vacancies within a device, lowering resistance and possibly forming or strengthening a conductive filament. Indeed, resistance decrease due to heavy ion irradiation has been observed in numerous cases in TiO$_x$, HfO$_x$, and TaO$_x$ devices (Marinella et al., 2012; He, 2013; Hughart et al., 2013; Tan et al., 2013; Weeden-Wright et al., 2014). Several studies estimate that TaO$_x$-based RRAM devices switch to LRS when oxygen vacancy concentration exceeds $\sim 10^{21}$ vacancies/cm$^3$ (Kim et al., 2014; Prakash et al., 2015). In this work, displacement damage dose (DDD) will be measured as oxygen vacancy concentration (cm$^{-3}$) to facilitate comparison of effects between different devices and studies.

Although the X2000 program identified a TID threshold for ionization damage tolerance of memory devices, it did not specify a corresponding threshold for DDD resilience. Any discussion of DDD received by devices is complicated by many factors; in particular, any single heavy ion which strikes a spacecraft is likely to generate many secondary particles, which add to the received fluence of the device (Benton and Benton, 2001). DDD also depends heavily on the
number of over-layers above the active device area, along with the amount of spacecraft casing or shielding around the device, which is evident from simulations discussed later in this work (Ziegler et al., 2010). Finally, heavy ion fluence, and therefore DDD, varies with the solar cycle, further complicating DDD calculations (Benton and Benton, 2001). Therefore, any estimate of DDD is valid for a specific device and spacecraft configuration, and for a specific mission. However, for the sake of comparison, we will provide ballpark estimates of DDD that would be received for our devices on a few example missions.

![SRIM Calculation of Displacement Damage](image)

**Figure 1.2. SRIM Calculation of Displacement Damage.** SRIM was used to calculate the number of vacancies created in a Ta$_2$O$_5$ film within a device due to bombardment with 230 keV Ar$^+$ ions. Approximately twice as many O atoms were displaced compared to Ta atoms. Calculations of displacement-induced vacancy concentration in RRAM devices were based on these simulations.

### 1.1 Ionization Effects in RRAM Devices

Ionization damage effects in RRAM devices have been the focus of numerous studies over the past decade. The results from these studies have varied greatly, with some studies reporting device changes on the order of 1-10 Mrad(Si), while others report no changes up to 50 Mrad(Si) or more. In most cases, if a change was observed, devices in HRS were affected, sometimes switching to LRS. Although ionization damage involves the production of electron-
hole pairs, some atomic displacements could occur at high dose. In many cases, electrons generated by ionizing radiation escape from the oxide into the electrode of a device (Atanassova et al., 2001; Zhang et al., 2011). This can lead to a build-up of positive charge, as holes typically remain trapped in the oxide. This charge build-up could lead to localized electric fields, which might be able to move oxygen atoms, moving existing oxygen vacancies or creating new ones. Since this is a secondary effect of ionizing radiation, very high TID levels would be needed to observe changes in the devices. Moreover, devices in LRS would be nearly immune, as excess charge could escape through the conductive filament, and any additional vacancies formed far from the conductive filament would not affect the already-low device resistance. Based on this reasoning, if any radiation effects are observed, we expect them to occur in HRS or unformed devices, rather than devices in LRS. In this section, a selection of papers will be reviewed, examining this line of reasoning.

1.1.1 Ionization effects in HfO$_x$ RRAM devices

Several studies have examined ionization effects, from a variety of sources, on HfO$_x$-based devices (He et al., 2012; Bi et al, 2013; Morgan et al., 2014; Fang et al., 2014; Lin et al., 2015; Hu et al., 2016; Hu et al., 2018). None of these studies observed a decrease in resistance after irradiation. However, two studies observed increased susceptibility of the HRS to constant voltage stress (Fang et al., 2014; Hu et al., 2018). In one case, devices consisted of 50 nm TiN top electrode, 10 nm HfO$_x$ switching layer, and 50 nm Pt bottom electrode (Fang et al., 2014). In this case, gamma irradiation up to 5.2 Mrad(HfO$_2$) did not affect device resistance or switching voltage. However, irradiated devices switched from HRS to LRS under +0.9 V constant stress, and from LRS to HRS under -1.1 V constant stress, which did not occur in control devices. The second study tested devices consisting of 10 nm Ni bottom electrode, 80 nm HfO$_x$ switching layer, and 150 nm Au top electrode, irradiated to 20 Mrad(Si) with gamma irradiation (Hu et al., 2018). Again, no changes in resistance or switching voltage were observed. Switching from HRS to LRS
was observed under electrical stress test at a slightly lower voltage for irradiated devices than for non-irradiated controls. These two studies demonstrate that gamma irradiation from a $^{60}$Co source does cause damage to the switching oxide, even if evident only under constant electrical stress. Although the resistance states were not affected by irradiation, this “hidden” damage might affect retention or endurance at high TID.

Several more studies examined the effects of gamma radiation on HfO$_x$-based devices, none of which observed major changes in devices due to TID (Morgan et al., 2014; Lin et al., 2015; Hu et al., 2016). One of these studies found no changes in device resistance up to 10 Mrad(Si) from a $^{60}$Co gamma source (Morgan et al., 2014). Another study observed a slight decrease in resistance of the LRS, but in this case, LRS was on the order of 1 GΩ, with HRS around 10 TΩ, making both states similar to unformed states in other devices (Lin et al., 2015). The third study found that Ni/HfO$_x$/Ni devices in LRS increased from 100 Ω to 300 Ω after 100 krad(Si) of gamma radiation (Hu et al., 2016). LRS remained constant at ~300 Ω for the remainder of the experiment, up to 20 Mrad(Si). Retention and endurance were unaffected by this level of gamma irradiation, but they were only tested to $5 \times 10^4$ seconds and $10^4$ cycles respectively.

These studies illustrate the wide range of ionization effects reported in just HfO$_x$-based RRAM devices, underscoring how strongly radiation effects can vary due to changes in device composition, process flow, or experimental setup. Nevertheless, none of the reported ionization-induced changes switched a device to a new resistance state or interfered with further switching. The wide range of observations showing different, but small effects from radiation, indicate that these devices are generally rad-hard, and certainly capable of withstanding the 1 Mrad(Si) requirement of the X2000 program.

HfO$_x$ device performance has also been measured against several other sources of ionization damage, including 10 keV x-rays (Bi et al., 2013), 1 MeV protons (He et al., 2012), and 1.8 MeV protons (Bi et al., 2013). TiN/Hf/HfO$_x$/TiN devices exposed to 10 keV x-rays exhibited no changes up to 7 Mrad(SiO$_2$) (Bi et al., 2013). The same devices, when exposed in HRS to 1.8
MeV protons, increased in resistance from ~25 kΩ to ~50 kΩ. This gradual change was attributed to displacement damage, which will be covered in more detail in the next section. Based on our own simulations using Stopping and Range of Ions in Matter (SRIM), proton energy loss into devices is typically dominated by ionization damage, usually exceeding displacement damage energy loss by several orders of magnitude. That said, all ions have the potential to directly cause displacement damage, and the gradual change observed is more typical of displacement damage effects. Meanwhile, TiN/HfO₂/TiN devices were exposed to a 1 MeV proton beam (He et al., 2012). These devices did not exhibit a change in resistance or switching voltage up to an incredible 5 Grad(Si). Displacement damage was not calculated in this study, but maximum fluence was 1.7E15 ions/cm², compared to 1E14 ions/cm² in the study that observed HRS resistance increase due to proton beam exposure (Bi et al., 2013). Therefore, whether the devices from the first study increased resistance due to ionization or displacement effects, the same change did not occur in the second study at higher levels of both effects.

1.1.2 Ionization effects in TaOₓ RRAM devices

Meanwhile, a few studies have investigated ionization effects in TaOₓ-based devices, again with varying results (Zhang et al., 2011; Hughart et al., 2013; McLain et al., 2014). One study examined ionization effects from 180 krad(Si) gamma radiation (⁶⁰Co source) in TiN/TaOₓ/Pt devices with varying TaOₓ thickness and cell size (Zhang et al., 2011). They found that devices with 25 nm TaOₓ did not change resistance, but devices with 50 nm TaOₓ, irradiated in HRS exhibited large and varied changes in resistance, with some device resistances increasing up to two orders of magnitude, and other device resistances decreasing by two orders. The decrease in HRS resistance was attributed to charge accumulation in the thicker oxide, providing a conduction path. No explanation was given for the devices that increased in resistance. The dose required to observe resistance changes, 180 krad(Si), was much lower than in most other studies, which could suggest that device changes were caused by non-radiation effects, such as
electrostatic discharge (ESD) events. If this were the case, it could explain the wide range of device response in the study. However, without knowledge of the experimental setup, it is impossible to know if non-radiation effects might have contributed to the observations.

Another study investigated the ionizing effects of 28 MeV Si$_{2+}$ ions on Pt/Ta/TaO$_x$/Pt devices (Hughart et al., 2013). A device was exposed to increasing “shots” of ions until a transition from HRS to LRS was observed. This transition occurred between 60-120 Mrad(Si). The part was reset, and the transition occurred again in the same window, 5 more times. The part was sensitive to total dose in a single shot, but not accumulated dose, suggesting that reading the device removed built-up charge, eliminating ionization damage. Meanwhile, exposure to 10 keV x-rays did not cause any resistance changes in the devices, with a maximum uninterrupted dose of 18 Mrad(Si), and total accumulated dose of 63 Mrad(Si). Therefore, these particular TaO$_x$-based devices were highly resilient against ionization damage from both ion and x-ray sources.

A follow-up study examined the effects of ionization dose rate on TiN/TaO$_x$/Ta/TiN devices (McLain et al., 2014). Devices were exposed to 20 MeV electrons, at dose rates of approximately 1E8 and 4E8 rad(Si)/s. Some of the devices exposed to the higher dose rate experienced a decrease in resistance from HRS, with one device transitioning to LRS. No changes in resistance were observed for devices at the lower dose rate. To ensure that devices were being affected by dose rate, rather than TID, Pt/Ta/TaO$_x$/Pt devices were exposed to $^{60}$Co gamma radiation at dose rates of 1E8 and 4E8 rad(Si)/s. Again, some devices at the high dose rate transitioned from HRS to LRS, while devices at the low dose rate did not exhibit any changes in resistance up to 10 krad(Si). These two results suggest that device failure occurs when the ionization damage rate exceeds the rate of damage removal. Built-up charge from ionization damage could be removed through device electrodes, particularly if the terminals are grounded, or through charge recombination in the oxide.

Together, these studies illustrate the wide range of device responses to ionization damage. Many other material systems have been examined for radiation effects, including TiO$_x$.  

(Tong et al., 2010; Hughart et al., 2013; Agashe et al., 2017). However, the results of these other studies generally fall within the spectrum of radiation response discussed in HfO$_x$ and TaO$_x$ devices. In most cases, RRAM devices exceed the 1 Mrad(Si) requirement of the X2000 program, with some studies reporting device resilience above 50 Mrad(Si). One report of device failure at TID < 1 Mrad(Si) observed such failure only at very high dose rate (McLain et al., 2014). Results from another report (Marinella et al., 2012), which observed device changes at a dose of 10 krad(Si) from x-rays, were not able to replicated when the researchers upgraded test equipment and shielding (Hughart et al., 2013). However, several of the reports reviewed here observed device changes at TID < 10 Mrad(Si) (Fang et al., 2014; McLain et al., 2014; Lin et al., 2015). These studies report device changes at TID levels only slightly above the 1 Mrad(Si) target. There are enough examples of devices close to that target that new RRAM devices should be tested to determine their response to ionization damage.

1.2 Displacement Damage Effects in RRAM Devices

Unlike ionization damage, displacement damage is expected to cause changes in RRAM devices, due to the creation of new oxygen vacancies when an oxygen atom is displaced. Displacement damage is generally caused by ion bombardment, particularly heavy ions. The concentration of vacancies introduced into a device through ion bombardment can be calculated using Stopping and Range of Ions in Matter (SRIM), a Monte Carlo simulation which predicts ion energy loss to ionization and displacement damage processes (Ziegler et al., 2010). To facilitate comparison between different studies, all displacement damage dose (DDD) levels will be reported in oxygen vacancies per cm$^3$. If a study does not report vacancies/cm$^3$, SRIM will be used to calculate the DDD based on the details given in the paper. SRIM does not take into account vacancy-interstitial recombination, so the true concentration of vacancies will likely be lower than the values predicted by SRIM, especially at DDD levels approaching total atomic
disruption, since recombination rates increase as the concentration of vacancies and interstitial atoms increases.

Two studies used simulations to predict when RRAM devices would change resistance states (Kim et al., 2014; Prakash et al., 2015). In the first study, the COMSOL Multiphysics simulation suite was used to self-consistently solve three equations: a current continuity equation for oxygen vacancies, a current continuity equation for electrical conduction, and a Fourier equation for Joule heating (Kim et al., 2014). The simulation was used to solve for vacancy concentration, electrostatic potential, and localized temperature within a Pd/Ta$_2$O$_5$/TaO$_x$/Pd device. The simulated IV characteristics matched the experimental data well, predicting the shape of the reset process, as well as the voltage required. This transition occurred at a vacancy concentration of $5 \times 10^{20}$ vacancies per cm$^3$. Meanwhile, the second study used a Monte Carlo simulation, assuming a cylindrical conductive filament (Prakash et al., 2015). This study observed that some devices (Pt/TaO$_x$/TiN) in LRS had a linear IV characteristic, while other devices in LRS exhibited non-linear behavior. The simulation predicted that this transition would occur around $10^{21}$ oxygen vacancies per cm$^3$, representing an inter-vacancy distance of less than 1 nm. For comparison, there are $5.6 \times 10^{22}$ oxygen vacancies per cm$^3$ in Ta$_2$O$_5$, so this transition occurs when about 2% of oxygen sites are vacant. Based on these two studies, TaO$_x$-based devices seem likely to transition from HRS to LRS at a vacancy concentration in the range of $10^{20}$-$10^{21}$ vacancies per cm$^3$.

One study on TaO$_x$-based devices observed degradation of the HRS starting at $10^{19}$ vacancies per cm$^3$, completing the transition to LRS at $10^{20}$ vacancies per cm$^3$ (Hughart et al., 2013). In this study, Pt/Ta/TaO$_x$/Pt devices were irradiated with 800 keV Ta ions to introduce high levels of displacement damage within the TaO$_x$ layer. SRIM was used to tune the ion beam energy to minimize the rate of ionization damage relative to displacement damage. Devices in HRS began to exhibit a decrease in resistance at $\sim 10^{19}$ vacancies per cm$^3$. Resistance continued to decrease gradually with continued ion beam exposure up to $3 \times 10^{20}$ vacancies per cm$^3$. 
Devices were reset and exposed to the ion beam several more times, with the resistance decrease occurring at lower DDD with each subsequent run. Pt/TiO$_x$/Pt devices were also exposed to the Ta ion beam, exhibiting an abrupt decrease in HRS resistance around $1 \times 10^{20}$ vacancies per cm$^3$. The DDD level required to switch the TaO$_x$ and TiO$_x$ devices agrees well with the level predicted by the simulations (Kim et al., 2014; Prakash et al., 2015), with resistance changes occurring at slightly lower levels than predicted.

Another study investigated the effects of displacement damage from neutrons and protons on Pt/TiO$_x$/Pt devices (Delonno et al., 2013). No changes in device resistance or IV characteristics were observed from two separate exposures to a neutron beam, displacing up to 0.0017% of atoms within the TiO$_2$ layer. However, 350 keV protons, displacing 1% of TiO$_2$ atoms, caused an increase in current of devices irradiated in HRS. 1% displacement corresponds to $6.4 \times 10^{20}$ oxygen vacancies per cm$^3$, slightly higher than the threshold for switching of similar devices observed in Hughart et al., 2013.

Another pair of studies examined the response of TiN/HfO$_x$/Hf/TiN devices to a 1.8 MeV proton beam (Bi et al., 2013; Weeden-Wright et al., 2014). These studies observed somewhat different results over two experiments exposing devices to the proton beam. The first study observed an increase in HRS resistance up to a DDD level of $\sim 4 \times 10^{17}$ vacancies per cm$^3$, based on SRIM plots reported in the study (Bi et al., 2013). These devices measured 18 nm across, limiting the conductive filament to that size at most. With a small conductive filament, displacements of a few atoms might affect the resistance strongly, possibly explaining why resistance increased at relatively low DDD levels. The second study irradiated the devices to a higher fluence, switching the devices 50 times at each fluence level and reporting average HRS and LRS (Weeden-Wright et al., 2014). This study did not observe an increase in HRS resistance, likely because switching the device restored the size and shape of the conductive filament after each ion beam exposure. However, at $\sim 8 \times 10^{17}$ vacancies per cm$^3$, devices in this second study became stuck in LRS, unable to switch. Device function could be recovered by increasing the
reset pulse width to 125 ns, causing the devices to reach their former HRS level. After recovery, switching was possible using the original 5 ns reset pulses. In both studies, devices were also irradiated to 1 Mrad(SiO₂) with 10 keV x-rays to test whether ionization damage would cause changes in device behavior. No changes were observed from ionization damage, so the resistance changes due to proton bombardment were attributed to displacement damage. The devices reported in the second study became stuck in LRS at relatively low DDD levels, compared to the predicted range of $10^{20}-10^{21}$ vacancies per cm³. It is possible that the HfOₓ films in these devices were crystalline, and accumulated vacancies from displacement damage aggregated along grain boundaries, possibly adding to the filament or producing a new filament. The HfOₓ layer was deposited by atomic layer deposition (ALD), which has been shown to produce crystalline films at 300°C (Hausmann and Gordon, 2003). The studies do not specify ALD temperature, but they do mention that the process was kept below a thermal budget of 400°C, so it is possible the HfOₓ films were deposited at elevated temperature or annealed afterward, producing crystalline HfOₓ.

Another study investigated the effects of Br ion exposure on TiN/TaOₓ/Pt devices (Tan et al., 2013). At a DDD level of $1.25 \times 10^{15}$ oxygen vacancies per cm³, devices in HRS exhibited an inconsistent change in resistance; some devices exhibited a resistance decrease to LRS, while other devices increased resistance. The decrease in resistance of some devices was attributed to oxygen vacancies reconnecting the conductive filament, whereas the increase in resistance was explained as oxygen atoms filling in more of the vacancies within the filament after being displaced from elsewhere in the film. Which direction the resistance changes in a device may depend on how much of the filament was broken during reset. As discussed in the study, if only a few vacancies are needed to reconnect the filament, it is more likely to decrease in resistance. In the meantime, radiation-induced annealing will cause oxygen atoms to migrate into the filament, which could increase resistance. It is surprising that resistance changes were observed at such low DDD levels, 5 orders of magnitude lower than the predicted level for resistance state
switching. The change at low DDD levels, and the inconsistency of the resistance change, suggest that the filament is very narrow, so small changes can cause large changes in the devices.

Reports of the effects of displacement damage in RRAM devices vary widely. Although two studies predicted a transition from HRS to LRS on the order of $10^{20}$-$10^{21}$ displacement-induced oxygen vacancies per cm$^3$ (Kim et al., 2014; Prakash et al., 2015), all of the experimental studies observed resistance changes below this threshold. This discrepancy may be due to the simulation assumption of a cylindrical conductive filament. Real conductive filaments often have a pyramidal or hourglass shape, with a region that is narrower than the rest of the filament (Kwon et al., 2010; Gao et al., 2018). In these cases, small changes at the narrow portion of the filament could have an outsized impact on device performance which would not be captured by the simulations described here. Overall filament size can also vary between devices, which might also affect a device’s radiation response. A small filament with an average diameter of a few nm could be affected by the addition or subtraction of even a single oxygen vacancy, which might lead to the inconsistent resistance changes observed in Tan et al., 2013.

In this work, we produced TaO$_x$-based RRAM devices and characterized the response of those devices to ionization and displacement damage. The following sections in Chapter 1 discuss detailed radiation effects in RRAM devices. Chapter 2 provides an overview of the fabrication process used for each radiation experiment, and the evolution of our fabrication approach throughout the work. Chapter 3 details the effects of ionization damage in the devices, while chapter 4 covers displacement damage effects. A set of TaO$_x$-based vendor devices were used as a comparison to our own devices, reinforcing the potential for TaO$_x$-based RRAM devices to be used as rad-hard non-volatile memory.
1.3 References


Ninomiya, T., Wei, Z., Muraoka, S., Yasuhara, R., Katayama, K., & Takagi, T. (2013). Conductive Filament Scaling of TaOx Bipolar ReRAM for Improving Data Retention Under Low Operation Current, 60(4), 1384–1389.


Chapter 2

Device Fabrication and Electrical Testing Procedures

TaO$_x$-based RRAM devices were fabricated in-house on 100 mm Si wafers coated with 100 nm SiO$_2$. In general, devices were patterned using photolithography, and films were deposited by sputtering. The device fabrication process evolved over the course of the project, and each major iteration will be detailed within this chapter. In general, the fabrication process was optimized to improve data retention, device yield, and reproducibility. In particular, retention of both the high resistance state (HRS) and low resistance state (LRS) needed to be > 1 week to enable radiation testing.

In the following sections, each fabrication strategy that was used will be detailed. In the first process, a shadow mask was used to pattern the devices, rather than photolithography, providing a simple, high-throughput method to test many device compositions. However, the shadow mask introduced high variability among devices due to edge shadowing of the deposition. Because of this, a photolithography process was implemented, improving device yield and wafer-to-wafer reproducibility. Eventually, the photolithography process was truncated to a “short loop” process to once again enable high-throughput characterization of many device compositions. Throughout these processes, several parameters were optimized, including TaO$_x$ stoichiometry, electrode composition, and film thicknesses.

Process repeatability was achieved in part due to maintenance and care of the Kurt Lesker PVD75 sputtering tool used for all thin film depositions. Access to this tool was restricted to a few users with approximately 10 approved deposition materials. Most approved materials were fab-friendly, with the exception of Pt, which is relatively inert. Chimneys and shutters around each of the three sputtering sources were used to minimize cross-contamination of sputter materials. Built-up flakes were removed from the chimneys and shutters as needed. Gas flow was carefully metered using two mass flow
controllers, enabling repeatable reactive sputtering in a precisely-controlled Ar/O₂ environment. Process control was implemented using an electronic logbook to record and measure deviations of deposition parameters over time. Together, these strategies to improve reproducibility resulted in highly repeatable thin film depositions over the course of this work. Despite variations introduced from shared cleanroom use and seasonal humidity changes, the reproducibility of the deposited films enabled iterative process development, and the production of reliable devices.

Electrical testing was used to characterize the switching behavior of the RRAM devices. In all cases, device testing was performed using an Agilent B1500 parameter analyzer and a Cascade Microtech probe station. In most cases, a 2n4338 junction field effect transistor (JFET—Newark, SKU: 06J8861) was used in series (1T1R configuration) to limit current through the RRAM device during forming and set operations (Fig. 2.1). Current was limited by applying a gate voltage corresponding to the desired saturation current. The saturation current applied to forward bias, including forming and set, but did not apply to reverse bias (reset), where current could also flow out of the gate. However, RRAM devices typically do not need a current compliance for the reset operation, as the increase in resistance during reset decreases the current flowing through the device, preventing further reset.

High-speed pulses were applied using an Agilent B1530 waveform generator attachment installed in the B1500. The EasyExpert software, developed by the B1500 manufacturer, was used to drive the B1500 and B1530, defining parameters for current-voltage (IV) sweep and pulse-based switching of devices. IV sweep testing involves increasing voltage in a step-wise fashion over a relatively long time period, such that the current through the device reaches a steady state at each voltage step. Pulsed switching involves applying a voltage pulse with a defined ramp rate, voltage, and duration, limiting the amount of energy that passes through the device. Generally, pulsed switching is less damaging to a device, since the total energy is limited (Gonzalez-Velo et al., 2017). Pulsed switching also more closely resembles the switching process that would be implemented in a commercial RRAM chip. However, IV sweeps are
useful for observing switching behavior and conduction mechanism. Therefore, both types of testing are useful in characterizing devices.

Figure 2.1. Circuit diagram for RRAM electrical characterization. (a) Voltage was applied to the RRAM top electrode (bottom electrode for inverted devices). The RRAM bottom electrode (top electrode for inverted devices) was connected to ground through a JFET, which served to limit current through the circuit based on its saturation current at a given gate voltage during forming and set. (b) The saturation current was modified depending on the test by changing the gate voltage. The source of the JFET was connected to signal ground at the B1500.

The electrical connections used to apply voltage to the device can have a significant impact on read sensitivity and voltage pulse shape, particularly for high-speed pulse switching. In general, IV sweeps were conducted using source/measurement units (SMU) from the B1500. The SMU cables were attached to the Remote Sense/Switch Unit (RSU) designed to pair with the B1530 pulse generator. Pulsed measurements were made using the B1530 waveform generator / fast measurement unit (WGFMU) and associated WGFMU cables, which also attached to the RSU. The RSU has an SMA cable output and can pass through up to +/- 20 V direct current (DC), or up to +/- 10 V high-speed pulsing. This enables the use of both IV sweeps and high-speed pulses to switch a device without the need to rearrange wires. In most cases, the SMA output from RSU1 was connected to the device top electrode. Voltage was applied to the top electrode, returning through RSU2 and either SMU2 or WGFMU2, for IV sweeps or high-speed pulsing.
In most cases, the transistor was connected with triaxial cables in between the bottom electrode and ground (through RSU2). A diagram of the standard wiring setup can be found in Fig. 2.2.

Figure 2.2. Electrical testing setup for RRAM device testing. Voltage was applied to the device using a B1500, with B1530 pulse generator for high-speed pulsing. Voltage was applied through a source/measurement unit (SMU1) for IV sweeps, and through a waveform generator/fast-measurement unit (WGFMU1) for pulsed operation. In either case, the signal was passed through a remote sense/switch unit (RSU1), which senses which input is being used and transfers the signal to an output SMA port. An SMA cable was used to connect the RSU to the probe tips. Current returned through a similar pathway through RSU2, followed by either SMU2 or WGFMU2, where circuit ground was applied. In some cases, a JFET transistor (not pictured) was attached between RSU1 and the device using triaxial cables.

This wiring setup served for general-purpose testing of devices, enabling 100 ns set and reset pulses with little or no voltage overshoot, as measured with an Agilent Infinium DSO9254A oscilloscope (Fig. 2.3). However, some specific tests required different wiring setups. In particular, for IV characterization of device conduction mechanisms, the SMU cables were connected directly to the probe tips to minimize noise, with no transistor, RSU, or SMA cables in the signal path (the probe tips used an SSMC connection). For high-speed pulsed switching without the transistor, current was supplied through WGFMU1, then RSU1, then SMA to the SSMC connection on the probe tip. The return path was a mirror image, with ground supplied at WGFMU2. The testing procedure and wiring setup for each device type will be detailed in the appropriate sections below.
2.1 Shadow Mask Device Fabrication Process

The first process used to produce RRAM devices utilized a shadow mask to pattern the devices (Fig. 2.4). Metal films were deposited using direct current (DC) sputtering, while the TaO$_x$ layer was deposited using radio frequency (RF) reactive sputtering. Reactive sputtering involves introducing a reactive gas, O$_2$ in this case, into the Ar sputtering atmosphere. In our case, TaO$_x$ was sputtered from a metallic Ta target in an O$_2$/Ar environment, producing a TaO$_x$ film on the substrate. All sputter targets were 2” diameter targets, and depositions took place in a Kurt Lesker PVD75 sputtering system with three sources, enabling up to three different materials to be deposited without breaking vacuum. This process produced very smooth films, as evident from scanning electron micrograph (SEM) cross-sections (Fig. 2.5).

Figure 2.3. Pulsed set and reset waveforms. High-speed pulses were used to set (a) and reset (b) RRAM devices. No overshoot was observed in the pulse shape for set or reset.
Figure 2.4. Shadow mask device layout. The shadow mask consisted of a metal plate with square holes through which the oxygen getter layer and top electrode were deposited. This resulted in square devices with a side length ranging from 20 µm to 100 µm.

Figure 2.5. SEM cross-section of sputtered films. SEM cross-section of a device stack revealed that sputtered Pt and TaO$_x$ films were very smooth. Although not pictured, HfO$_x$, Hf, Ti, and W were also very smooth, generally with sub-nm rms roughness measured using atomic force microscopy (AFM).

Shadow mask devices were fabricated on pieces of Si wafers (approx. 1” x 1” squares) with a coating of 100 nm SiO$_2$. A blanket 5 nm layer of Ti was deposited onto the wafer pieces as an adhesion
layer, followed by a blanket 100 nm layer of Pt, which served as the bottom electrode. A dummy wafer piece was then used to cover up one edge of the Pt bottom electrode, preventing deposition on that edge so that electrical contact could later be made to the bottom electrode. The dummy wafer piece covered ~5-10% of the Pt. A 10 nm TaO$_x$ layer was deposited over the exposed Pt area in a sputtering atmosphere of 7% O$_2$:Ar. Finally, the wafer piece was affixed to a shadow mask using Kapton tape, and 5 nm Ti was deposited through the shadow mask pattern, followed by 100 nm Pt. Ti served as an oxygen getter layer, removing oxygen from the TaO$_x$ layer and introducing additional oxygen vacancies into the oxide, as well as an expected gradient of vacancies to give the devices a defined polarity, and Pt served as the top electrode. The sputtering conditions for each material in the final shadow mask devices are detailed in Table 2.1.

**Table 2.1. Sputtering conditions for RRAM device fabrication.**

<table>
<thead>
<tr>
<th>Film</th>
<th>Target Material</th>
<th>RF/DC</th>
<th>Power (W)</th>
<th>O$_2$:Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>Pt</td>
<td>DC</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>TaO$_x$</td>
<td>Ta</td>
<td>RF</td>
<td>125</td>
<td>7%</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti</td>
<td>DC</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>W</td>
<td>W</td>
<td>DC</td>
<td>50</td>
<td>0</td>
</tr>
</tbody>
</table>

Throughout the development of this process, the O$_2$:Ar ratio during TaO$_x$ deposition and the material used for oxygen getter layer were optimized to produce devices with repeatable switching. The effect of O$_2$:Ar ratio during sputtering on TaO$_x$ stoichiometry was measured using x-ray photoelectron spectroscopy (XPS) (Fig. 2.6). Although XPS is a surface characterization technique, depth profiling is possible by sputtering the sample with an Ar ion beam, removing layers of material and enabling measurement of material composition of buried layers. However, Ar sputtering in XPS has been shown to selectively remove oxygen in oxides, particularly for heavier metals such as Ta (Hofmann, 1998), complicating measurement of buried film composition. Because of the potential for preferential sputtering, XPS was used to characterize the surface of blanket TaO$_x$ layers, rather than buried layers. Because of this, it is possible that the samples oxidized further in atmosphere, and that the buried layers
have less oxygen than the surface layers. However, since the most oxidized film was measured to have a stoichiometry of TaO$_2$ (compared to Ta$_2$O$_5$ fully oxidized), any native oxidation that may have taken place did not completely oxidize the surface layer.

Figure 2.6. TaO$_x$ film composition. XPS was used to measure the relative atomic percent of Ta and O in sputtered TaO$_x$ films with increasing O$_2$:Ar ratio in the sputtering atmosphere. The sputtered TaO$_x$ approaches a stoichiometry of Ta$_2$O$_3$, indicating the presence of many oxygen vacancies.

Devices were produced using a range of O$_2$:Ar ratios, from 1% up to 10% O$_2$. Of these, devices at 6% O$_2$ and below were in LRS upon fabrication and were unable to reset. Devices made with 7% or more O$_2$:Ar ratio began in an insulating state with resistance $> 1$ MΩ. These devices were able to be electroformed, reset, and switched between HRS and LRS repeatedly. Devices deposited in a 7% O$_2$:Ar environment showed initial promise, and eventually switched more than 1,000 times using current-voltage (IV) sweeps after further process optimization.

The other major parameter that was optimized in these devices was oxygen getter layer material. The purpose of this material was to remove some oxygen from the TaO$_x$ layer, introducing more oxygen vacancies and a switching polarity in the device. The use of an oxygen getter layer is common in RRAM devices, and often improves switching stability and yield (Fang et al., 2014; Alamgir et al., 2018). An
Ellingham diagram can be used to choose an appropriate oxygen getter material, showing the Gibbs free energy of formation for various oxides (Howard, 2006). In general, the oxide with the most negative energy of formation is the most stable, and that material will absorb oxygen from the surrounding materials.

Several different oxygen getter layers were tested in the RRAM device stack, including Ti, Al, Zr, and W. Of these, TiO$_2$, Al$_2$O$_3$, and ZrO$_2$ all have more negative energies of formation than Ta$_2$O$_5$. Although all three of these had similar energies of formation, a Ti layer resulted in more stable switching than Al or Zr. Because of this, the final device composition for the shadow mask devices included a 5 nm Ti layer.

Devices made with a Ti oxygen getter layer, and TaO$_x$ deposited in 7% O$_2$:Ar switched for more than 1,000 cycles in IV sweep mode (Fig. 2.7). These devices were used in gamma radiation experiments at the NASA Jet Propulsion Laboratory (JPL), detailed in chapter 3. These devices were switched using IV sweeps, with SMU cables attached directly to triaxial connectors on the probe manipulator, with a transistor in series between the RRAM device and ground. Switching voltage was on the order of 1 V, and the HRS/LRS resistance ratio was ~4 (Table 2.2). For comparison, devices intended for memory are recommended to have a resistance ratio > 10 (Waser et al., 2010).

<table>
<thead>
<tr>
<th>Film</th>
<th>7% O$_2$ *</th>
<th>7.5% O$_2$ *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vform (V)</td>
<td>2.28 +/- 0.33</td>
<td>2.31 +/- 0.04</td>
</tr>
<tr>
<td>Vset (V)</td>
<td>0.73 +/- 0.05</td>
<td>0.75 +/- 0.03</td>
</tr>
<tr>
<td>Vreset (V)</td>
<td>-0.80 +/- 0.06</td>
<td>-0.78 +/- 0.10</td>
</tr>
<tr>
<td>LRS (kΩ)</td>
<td>3.04 +/- 0.75</td>
<td>2.86 +/- 0.34</td>
</tr>
<tr>
<td>HRS (kΩ)</td>
<td>13.0 +/- 3.5</td>
<td>10.7 +/- 2.0</td>
</tr>
<tr>
<td>HRS/LRS</td>
<td>4.8 +/- 1.4</td>
<td>4.1 +/- 1.0</td>
</tr>
<tr>
<td>Yield</td>
<td>11/29 = 38%</td>
<td>5/8 = 63%</td>
</tr>
</tbody>
</table>

*Table values are mean +/- standard deviation

However, the more pressing concern was that retention of the HRS was on the order of a few hours, making radiation experiments more difficult to design and interpret. This, combined with the low device yield (~10-40% varying by sample), led us to explore other avenues for device fabrication. The
shadow mask caused a shadowing of the deposition close to the pattern sidewalls due to the thickness of the shadow mask, which led to thinner Ti and Pt being deposited around the outer edges of each device. Devices also ranged in size from squares with 100 µm side length down to 25 µm side length. The smallest devices, with 25 µm side length, received less deposited material overall compared to larger devices due to this edge shadowing effect. Therefore, an alternative patterning approach using photolithography was developed to improve uniformity and yield across multiple wafers.

**Figure 2.7. 100 Set/reset cycles of a shadow mask device.** Voltage sweeps were used to switch a shadow mask device 100 times. Although there was some variation in both the HRS and LRS, the resistance ratio remained consistent across the 100 cycles.

### 2.2 Photolithography Device Fabrication Process

Development of the photolithography process required optimization of several key processes, including photolithography-based liftoff, reactive ion etch (RIE), and wet etch. The eventual result of these process optimizations was a well-controlled device fabrication process which produced devices
capable of switching up to 100,000 times, with 100% device yield. The final device composition in this process consisted of 50 nm Pt bottom electrode, 10 nm TaOₓ switching layer, 2.5 nm Hf oxygen getter layer, and 50 nm W top electrode, with an additional 5 nm Ti adhesion layer and 50 nm W top contact pad, enabling contact with probe tips far from the device area (Fig. 2.8).

Figure 2.8. Top-down view of a photolithography-based device. Photolithography-based devices were designed at the intersection of two electrode contact pads. The contact pads were far from the device area so that bonded wires would not shield the device from the ion beam.

The optimized device fabrication process included several key steps, which will be detailed in the following paragraphs (Fig. 2.9). The process was carried out on 4” diameter Si wafers with a 100 nm SiO₂ surface layer. Photoresist was spun onto the wafer and patterned for liftoff. 50 nm Pt was deposited by DC sputtering, and the excess photoresist was removed, leaving behind the patterned Pt bottom electrodes. Blanket layers of 10 nm TaOₓ, 2.5 nm Hf, and 50 nm W were deposited atop the Pt bottom electrodes. TaOₓ was deposited in 30% O₂:Ar, and Hf was used as the oxygen getter layer, since the energy of formation of HfO₂ is much lower than Ta₂O₅, as shown on an Ellingham diagram (Howard, 2006). Photoresist was spun onto the wafer and patterned to cover just the device areas. Reactive ion etch (RIE) was used to etch away the W, Hf, and TaOₓ everywhere except for the device areas. RF sputtering was
then used to deposit 15 nm of SiO$_2$ as an insulating layer to isolate the electrodes and protect the device sidewalls. The photoresist was stripped, lifting off the SiO$_2$ over the device area and exposing the W top electrode. Another liftoff step was used to pattern an additional 5 nm Ti adhesion layer and 50 nm W top contact pad to produce contact pads for the probe tips to land on that were removed from the device area. This step was necessary because some of the planned radiation experiments required switching the devices within the radiation chamber, and a bonded wire directly overtop the device area would have shielded the device from the ion beam. A final photolithography step followed by wet etch was used to remove the SiO$_2$ layer from the bottom electrode contact pads, enabling electrical contact to be made to both electrodes. Further details of the optimization of each step of the process will be covered in the following paragraphs.

Photolithography-based liftoff was performed using liftoff resist (LOR3A) and Shipley 1813 resist. LOR3A was deposited onto the wafer, followed by S1813. The purpose of liftoff resist was to produce an undercut in the resist profile. If liftoff is performed with vertical resist sidewalls, the lifted-off material sometimes includes “wings” which can interfere with device function (Fig. 2.10). An undercut sidewall in the resist profile prevents these wings from forming. LOR3A assists in forming this undercut by etching away in the photoresist developer solution. 1813 is a positive photoresist, meaning it is removed from the wafer by developer solution wherever it is exposed to UV light. LOR3A is not photoactive but is removed by the developer. Therefore, during development, 1813 is removed from the patterned area, and then LOR3A is removed from that area and begins to undercut the non-exposed 1813, producing an undercut resist sidewall (Fig. 2.11). Both resists were developed using AZ 300 MIF, a basic solution containing tetramethylammonium hydroxide (TMAH). After sputter deposition of Ti/Pt or Ti/W, S1813 resist was stripped in a sonicating bath of acetone, and LOR3A was removed overnight using Microposit Remover 1165. The complete liftoff process can be found in Table 2.3.
Figure 2.9. Photolithography-based device fabrication process. Devices were fabricated using a combination of liftoff-based and etch-based photolithography. (1) The first photoresist layer was patterned, and the Pt bottom electrode was deposited. (2) The photoresist was removed in a liftoff process, leaving behind the patterned bottom electrode. (3) The Ta₂O₅ switching layer, oxygen getter layer, and W top electrode were deposited in one step, without breaking vacuum. (4) Photoresist was patterned atop the W top electrode to define the active device area. (5) Reactive ion etching was used to remove the top electrode, oxygen getter, and oxide, stopping on the Pt bottom electrode. (6) An insulating layer of SiO₂ was deposited to isolate the bottom electrode from the top electrical contacts. (7) The photoresist was stripped, exposing the W top electrode over the active device area. (8) Photoresist was patterned, and Ti and W were deposited, to form the top contact pads. (9) The photoresist was stripped in a liftoff process, leaving the top W contact pads. Not pictured: A final photolithography + etch step was used to remove the SiO₂ insulating layer from the bottom electrode contact pads, allowing electrical probes to make contact.

Table 2.3. Liftoff process.

<table>
<thead>
<tr>
<th>Step Number</th>
<th>Step Name</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dehydrate</td>
<td>Bake 150C for at least 5 min</td>
</tr>
<tr>
<td>2</td>
<td>HMDS</td>
<td>Apply P20 (HMDS) to wafer – wait 10 s – spin 4,000 RPM for 40 s</td>
</tr>
<tr>
<td>3</td>
<td>LOR3A</td>
<td>Apply to wafer – spin 300 RPM for 10 s – 3000 RPM for 30 s Bake 150C for 3 min</td>
</tr>
<tr>
<td>4</td>
<td>S1813</td>
<td>Apply to wafer – spin 4000 RPM for 40 s Bake 110C for 180 s</td>
</tr>
<tr>
<td>5</td>
<td>Expose</td>
<td>Expose resist to 365 nm UV to 65 mJ/cm²</td>
</tr>
<tr>
<td>6</td>
<td>Develop</td>
<td>Develop in AZ 300 MIF 25 s – Bake 110C 1 min – Develop 1 more min</td>
</tr>
<tr>
<td>7</td>
<td>Deposition</td>
<td>Deposit films to be lifted off</td>
</tr>
<tr>
<td>8</td>
<td>Removal</td>
<td>Strip 1813 resist in sonicated acetone bath 10 min Soak in Microposit Remover 1165 overnight</td>
</tr>
</tbody>
</table>
Figure 2.10. **Incomplete liftoff of the bottom electrode.** Atomic force microscopy (AFM) revealed incomplete liftoff of a bottom electrode, leaving behind “wings” which could short a device.

Figure 2.11. **Photoresist undercut for liftoff.** Photoresist overhang for liftoff is evident in SEM cross-section. LOR3A liftoff resist was used to undercut the photoactive 1813 resist. The overhang prevents wings forming during liftoff, as shown in Fig. 2.9.
Sputter deposition of the various layers followed a similar approach to the shadow mask devices. DC sputtering was used for metals, and RF sputtering was used for oxides. Details of the deposition conditions for each material can be found in Table 2.4. Sputter deposition of SiO₂ was particularly challenging, likely due to the high hardness of Si and SiO₂ (Insepov et al., 2000). SiO₂ deposition was attempted using RF sputtering from a SiO₂ target and from a Si target in O₂/Ar sputtering atmosphere. In both cases, the deposition rate was very low, and the oxide was sub-stoichiometric. Sputtering from a SiO₂ target caused the target to crack, possibly due to thermal stress and structural defects from sputtering. Therefore, SiO₂ deposition was carried out using a Si target in an O₂/Ar sputtering atmosphere. Chemical vapor deposition (CVD) is a better approach for SiO₂ deposition. However, the films we produced using PVD were insulating, and their quality was not of major concern, since they were to be used as an insulating layer only. Therefore, no further process development was needed for the SiO₂ layer.

**Table 2.4. Sputtering conditions for photolithography device fabrication.**

<table>
<thead>
<tr>
<th>Film</th>
<th>Target Material</th>
<th>RF/DC</th>
<th>Power (W)</th>
<th>O₂:Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>Pt</td>
<td>DC</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>Ir</td>
<td>Ir</td>
<td>DC</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>TaOₓ</td>
<td>Ta</td>
<td>RF</td>
<td>125</td>
<td>30%</td>
</tr>
<tr>
<td>Hf</td>
<td>Hf</td>
<td>DC</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>W</td>
<td>W</td>
<td>DC</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

The RIE process was optimized to remove the W top electrode through a chemical etch, and a small amount of any oxygen getter material through an anisotropic physical etch. An etching atmosphere was sustained with flow rates of 40 sccm SF₆ and 10 sccm O₂ for the W etch, with pressure of 15 mTorr. The power of the inductively-coupled plasma (ICP) was set to 500 W, and the RIE power was set to 100 W. An etch time of 55 seconds was required to remove 50 nm of W. Since many of our oxygen getter layers do not form volatile compounds suitable for reactive etching, an anisotropic physical etch process was developed. This process was carried out at 5 mTorr, with flow rates of 5 sccm SF₆, 5 sccm O₂, and 40
sccm Ar. The Ar sputtered away surface layers of any thin film oxygen getter layer. For a 5 nm film, 10 seconds of etching were required, with ICP power of 500 W and RIE power of 100 W. This process can coat the chamber with a small amount of re-deposited material, so an aggressive chamber clean afterward was necessary to prevent material build-up in the chamber. The clean involved a physical etch process, using 50 sccm SF$_6$, 20 sccm O$_2$, and 10 sccm Ar at 50 mTorr for 40 minutes, with ICP power of 1000 W and RIE power of 0 W. This physical etch was followed by an O$_2$ clean using 100 sccm O$_2$ at 50 mTorr for 1 hour, with ICP power of 1000 W and RIE power of 0 W.

The devices produced using this method were able to switch up to 100,000 times, with up to 100% device yield. In most cases, device retention was > 1 day. However, in some cases, retention was as short as 5 minutes, after which some devices in HRS transitioned to LRS. Despite this occasional retention problem, the effects of displacement damage were investigated in these devices, using an Ar$^+$ ion beam at the University at Albany. The results of those experiments were reported at the Materials Research Society meeting in Phoenix, AZ in spring 2017 (Holt et al., 2017).

### 2.3 Inverted Liftoff Device Fabrication

A final round of device development was undertaken to eliminate the intermittent retention problem observed in the devices made from the photolithography process. Without a clear indication of what might cause some devices to fail after a few minutes, when others retained data for more than one week, it seemed worthwhile to revisit the material composition of the devices. After all, some of the film characterizations and optimizations had been completed more than a year prior, and several process changes had been implemented in the meantime. Since there was no clear cause of the retention problem, several device compositions were tested for resistive switching using a streamlined photolithography-based process which enabled high-throughput fabrication and testing.
The streamlined photolithography process involved a single liftoff patterning step (Fig. 2.12). The bottom electrode, oxygen getter layer, and TaO\textsubscript{x} switching layer were deposited as blanket films on a 4” Si wafer with 100 nm SiO\textsubscript{2}. Photoresist (LOR3A/S1813) was used to pattern the top electrodes. The top electrode was deposited overtop the patterned resist, and the resist was removed, lifting off the excess metal. This process produced top electrode pads atop a blanket switching layer and blanket bottom electrode. To make electrical contact to the bottom electrode, the probe tips were connected to two adjacent top electrode contact pads, and a constant voltage of -20 V was applied until breakdown occurred, typically within 5-30 seconds. Those two top electrode pads were then shorted semi-permanently to the bottom electrode, and served as bottom electrode contacts for device testing. Over several days or weeks, the resistance between these pads sometimes rose from ~30 Ω to as high as 10 kΩ. If this occurred, an IV sweep to -20 V was performed, shorting the contacts once again.

One possible cause of retention problems was contamination, especially water vapor, at the TaO\textsubscript{x}/Pt interface. This interface is expected to form a Schottky-like contact, where the barrier height can be modulated by the presence of oxygen vacancies, contributing to the high resistance and low resistance states (Sawa, 2008; Marchewka et al., 2016). TaO\textsubscript{x} has a high electron affinity, and as such, is more likely to form a Schottky-like contact with a high-work function metal such as Pt or Ir (Marchewka et al., 2016). In our devices, the use of Pt or Ir as the electrode contacting the TaO\textsubscript{x} layer was necessary, as devices made with a W or Ru electrode typically failed to reset after forming. This suggests that a Schottky-like interface is indeed being formed at the TaO\textsubscript{x}/Pt interface, and oxygen vacancies are modulating the barrier height.
Figure 2.12. Inverted photolithography process. Inverted devices were produced using a single photolithography-based liftoff step. The W bottom electrode, Hf oxygen getter layer, and TaO$_x$ switching layer were deposited onto the substrate as blanket films. Photoresist was patterned on the wafer, and the Ir or Pt top electrode was deposited. The resist was stripped, leaving behind the patterned top electrode, which defined each device area. The device stack is inverted compared to the other fabrication process reported in this chapter.

In light of the possible sensitivity to the TaO$_x$/Pt interface to water vapor, a humidity chamber was installed in the sputter tool to deliver air with a controlled humidity to the wafer between the TaO$_x$ and Pt layers. Wafers were baked at 300C for 1 hour in the sputter chamber using a heating lamp to desiccate the surface. Then, the wafers were exposed to the appropriate humidity level for 1 hour at 600 Torr. Devices exposed to humidity levels of 0%, 10%, or 20% humidity failed to reset after forming. Devices exposed to 30%, 40%, 50%, and 60% humidity were able to switch, with no obvious differences in
switching characteristics. Ambient humidity ranged from 20% to 50%, so it is possible that devices made on the driest days might have been more prone to failure. This humidity experiment required inversion of the device stack, as humidity treatment immediately before TaOₓ deposition caused pinholes to appear in the TaOₓ layer (Fig. 2.13). Because of these pinholes, the device stack was inverted, and humidity treatment was applied to the TaOₓ layer, just before Pt electrode deposition. Because the stack was inverted, voltage was applied to the blanket bottom electrode and the top electrode was connected to ground through the JFET, opposite all other devices described above.

Figure 2.13. Pinholes in TaOₓ layer. Pinholes appeared in the TaOₓ layer when a humidity treatment was applied to the Pt electrode before TaOₓ deposition.

Meanwhile, devices were fabricated with an Ir top electrode, instead of Pt. Both metals have a high work function, and are expected to form a Schottky-like contact with TaOₓ (Marchewka et al., 2016). However, Ir serves as a better barrier to diffusion of oxygen and water vapor, which might help to improve device retention (Ebisuzaki, Kass, and O’Keefe, 1968; Velho and Bartlett, 1972; Noring et al., 1981; Mumtaz et al., 1993). Indeed, devices made with an Ir top electrode retained data for more than 1 week (Fig. 2.14), and device yield increased from ~25% with a Pt electrode to ~70% with Ir top electrode.
Additionally, several combinations of TaO$_x$ and Hf were tested for device retention, varying the O$_2$:Ar ratio in the sputtering atmosphere for TaO$_x$, and the thickness of Hf, both of which contribute to the number and distribution of vacancies within the TaO$_x$ layer. The combination of 20 nm TaO$_x$ (30% O$_2$:Ar) and 5 nm Hf yielded devices with > 1 week data retention of the HRS and LRS, for both Pt and Ir top electrodes.

The devices produced using this inverted liftoff-based fabrication process were used in final radiation experiments. Devices with a Pt top electrode were exposed to gamma radiation at JPL, while devices with Ir top electrode were exposed to a heavy ion beam for displacement damage experiments at the University at Albany. Those experiments will be detailed in chapters 3 and 4 respectively.

![Figure 2.14. Retention of inverted devices.](image)

Retention of inverted devices in the LRS (a) and HRS (b) was measured over 5 days. Devices exhibited minimal resistance changes over this time period.

2.4 Conclusion

Each of the fabrication processes detailed in this chapter had benefits and drawbacks. The shadow mask process had a fast turnaround time enabling rapid testing of many device compositions. However, the shadow masks caused shadowing of the deposition near the edges of the mask and throughout the entire device area for the smaller patterns. This shadowing introduced variability in the devices which led to low overall device yield and repeatability. By contrast, the photolithography process produced very repeatable devices with high device yield. However, this process had a much slower turnaround, making it more difficult to test many compositions of devices. The inverted liftoff process was developed as a best-of-both-worlds process, combining the repeatability of photolithography with
the fast turnaround time of the shadow mask process. However, this process involved spinning photoresist directly onto the TaO$_x$ switching layer, which could introduce contaminants into the device. We were able to produce repeatable devices despite this possible contamination source. However, an ideal approach would involve deposition of all device layers and the top electrode without breaking vacuum. Devices from each of these processes were used in radiation experiments detailed in the next chapters.

2.5 References


Chapter 3

Ionization Damage Effects in RRAM Devices

3.1 Introduction

Ionization damage, which generates electrons and holes in a target material, is a major concern for electronics in space. High total ionizing dose (TID) levels can cause insulating oxides to become leakier, degrading device performance over time (Nguyen et al., 1999; Cellere et al., 2003; Duncan et al., 2016). This problem is compounded by the fact that both electromagnetic radiation and cosmic rays cause ionization damage (Fang et al., 2014; Summers, Burke, and Xapsos, 1995). Electrons, light ions, and heavy ions can each impart a mixture of ionization and displacement damage within a device, but typically the contribution from ionization damage is much higher than the contribution from displacement damage (Summers, Burke, and Xapsos, 1995). As particle mass increases, the relative contribution of displacement damage increases (Arnold, Krefft, and Norris, 1974). However, even for heavy ions, ionizing energy loss typically exceeds non-ionizing energy loss by at least a factor of 10 except for near the tail end of the ion’s path through a material (Arnold, Krefft, and Norris, 1974).

The generation of electron-hole pairs from ionization damage can degrade flash memory performance by making oxides in the charge pumps and floating gates leakier, making it more difficult to store charge (Nguyen et al., 1999; Cellere et al., 2003; Duncan et al., 2016). However, resistive memory (RRAM) devices are less susceptible to the generation of charge since information is stored as resistance instead of charge and depends on the location of oxygen vacancies. Despite this, RRAM devices could still be affected by ionization damage through electromigration or lattice relaxation, which might cause atomic displacements. Additionally, with enough localized charge build-up, vacancies could migrate due to the electric field, possibly switching the device state. As detailed in chapter 1, there is significant variation in
RRAM device susceptibility to ionization damage; however, most devices can withstand a total ionizing dose > 1 Mrad(Si), meeting the requirement of the X2000 program for a mission to Europa (Strauss and Daud, 2000), an example of a mission with high radiation requirements.

Ionization effects can be further divided into two categories: single event effects (SEE) and total ionizing dose (TID). SEE occur when a single particle imparts a large amount of ionization damage into a device, generating enough charge to cause a change in the device (Bennett et al., 2014). Flash memory, DRAM, and logic are all vulnerable to SEE, exhibiting a wide range of effects, including soft errors and hard errors, depending on the location and angle of the incident particle, as well as the amount of energy imparted by the particle (Cellere et al., 2006; Irom and Nguyen, 2007; Irom, Nguyen, and Allen, 2013). Several studies indicate that ECM-type RRAM devices in 1T1R configuration can be affected by SEE (Mahalanabis et al., 2014; Mahalanabis et al., 2015; Chen et al., 2015). Meanwhile, one study observed SEE and multiple event upsets (MEU) in 1T1R VCM-type RRAM (Bennett et al., 2014). MEU was defined as small changes in device resistance with repeated single events, eventually adding up to a functional change in resistance state. Another study investigated SEE in the Panasonic MN101L microcontroller, which contains TaOx-based RRAM devices (Chen et al., 2014). Although SEE were observed in the Panasonic chip, all events were attributed to errors in the peripheral control circuitry, rather than the RRAM array.

In another case, ionization damage dose rate due to electron bombardment was observed to cause device failure, and grounded electrodes resulted in lower failure rates compared to floating electrodes (McLain et al., 2014). Above the critical dose rate, devices failed at ~100 rad(Si), far below the 1 Mrad(Si) threshold observed for those devices in TID tests with a 60Co gamma source. It seems likely that the dose rate-related failure observed in this study falls under SEE or MEU. The combination of these studies indicates that RRAM devices have at least some susceptibility to SEE, generally higher with
increasing linear energy transfer (LET) or with applied voltage (Bennett et al., 2014; Chen et al., 2014; Chen et al., 2015).

Meanwhile, recall from chapter 1 that several studies have investigated TID effects in RRAM devices, observing device failures ranging from 180 krad(Si) (Zhang et al., 2011) up to 60 Mrad(Si) (Hughart et al., 2013), with several studies not observing any failures up to their highest tested TID level of 10 Mrad(Si) (Morgan et al., 2014) or 20 Mrad(Si) (Hu et al., 2016; Hu et al., 2018). Since there is such high variation in TID susceptibility, and since at least one study reports device failure below the 1 Mrad(Si) threshold for a mission to Europa, TID effects are an important consideration for devices intended for aerospace applications.

It may be possible to mitigate TID effects, and even SEE, by designing a memory access protocol with radiation effects in mind. According to several studies, SEE are more likely to be observed when the event occurs during a write pulse, with high applied voltage (Bennett et al., 2014; Mahalanabis et al., 2015). Therefore, SEE could be minimized by minimizing the need to write to the devices, and by designing devices to switch using shorter pulse lengths. Meanwhile, TID effects have been shown in at least one case to be mitigated by applying a read pulse to the device (Hughart et al., 2013). A read pulse applies enough electric field to remove built-up charge due to TID effects, but generally not enough field to greatly increase susceptibility to SEE. Therefore, addressing the memory with intermittent reads throughout a mission could both mitigate TID, and help to catch errors when they occur. The expected TID threshold for the specific devices used in a mission can be used to determine how often a read pulse should be applied. Finally, when device terminals are grounded or shorted together and allowed to float, the devices are more resilient against TID and dose rate-based failure (McLain et al., 2014). Although it is common to float memory devices in crossbar arrays while specific devices are addressed, an entire array could be grounded when not in use to improve resilience to ionization effects.
In this study, we focused on TID effects in TaO$_x$-based RRAM devices. Our devices have a similar composition to the devices in the Panasonic MN101L microcontroller, providing a possible comparison to a commercial implementation of RRAM devices (Chen et al., 2014). In particular, the TaO$_x$/Ir interface in the Panasonic devices and the TaO$_x$/Pt interface in our own devices likely form Schottky-like barriers that can be modified by the introduction of oxygen vacancies, contributing to resistive switching (Sawa, 2008; Marchewka et al., 2016). In the next section, TID requirements for various space missions will be outlined. Then, each TID experiment on our devices will be detailed in its own section, including device composition, electrical testing configuration, and radiation experiment results.

3.2 TID Requirements for Space Missions

TID requirements for space missions can vary widely based on the destination, duration, and solar cycle. Missions to Jupiter have much higher TID requirements than missions in low earth orbit (LEO), as the trapped radiation belts of Jupiter greatly increase the received dose (Benton and Benton, 2001; Paranicas et al., 2007). Meanwhile, devices in LEO often remain at lower altitude than Earth’s radiation belts, as long as the South Atlantic Anomaly is avoided (Hiertzler, 2002). Because of this, satellites in LEO are often protected from a significant amount of solar and cosmic radiation, as this radiation is trapped or deflected by Earth’s magnetic field, decreasing radiation hardness requirements. Mission duration has an obvious effect on TID-hardness requirements, as longer missions will be exposed to greater TID levels. Furthermore, fluence of galactic cosmic ray ions is decreased during a solar maximum, more than offsetting the increase in fluence of solar ions (Ferrari, Pelliccioni, and Rancati, 2001; Benton and Benton, 2001). However, high-dose solar particle events (SPE) are more common during a solar maximum, so devices that more sensitive to dose rate than TID might be at higher risk during a solar maximum, even with a lower average TID. Finally, missions that orbit a celestial body, such as a moon or planet, are
generally protected from a significant amount of incoming radiation due to shielding from the celestial body (Paranicas et al., 2007).

Recall that ionization damage can be caused by many different sources of radiation, including electromagnetic (x-ray, gamma), electrons, neutrons, light ions (protons, alpha particles), and heavy ions (e.g. iron). In general, gamma radiation from cosmic sources is a ubiquitous source of ionization damage in space (Fichtel, Simpson, and Thompson, 1978). However, enough gamma radiation is absorbed by Earth’s atmosphere that ground-level gamma exposure comes predominantly from terrestrial sources (Evrard et al., 2006). Earth’s trapped radiation belts primarily consist of trapped electrons and protons (Benton and Benton, 2001). These charged particles typically produce mostly ionization damage in devices, with a minimal but non-zero contribution from displacement damage, although the exact relative contributions depend on the target material (Arnold, Krefft, and Norris, 1974). Solar radiation also consists almost entirely of electrons and protons (Benton and Benton, 2001). By contrast, galactic cosmic radiation consists of charged particles which can include electrons, light ions, and many heavy ions (Benton and Benton, 2001). Generally, the prevalence of an ion in cosmic radiation decreases with increasing ion mass. However, iron is particularly abundant compared to most other ions because of its high binding energy per nucleon (Benton and Benton, 2001). Of these, the only radiation sources that typically introduce significant amounts of non-ionizing (displacement) damage in devices are the heavy ions in cosmic rays. Therefore, ionization damage is an ever-present concern for electronics in space.

A mission to Europa, in the vicinity of Jupiter, represents a relatively high dose mission, with strict radiation hardness requirements, due to the trapped radiation belts of Jupiter (Paranicas et al., 2007). Recall that the X2000 program called for an ionizing radiation hardness of 1 Mrad(Si) for a mission to Europa (Strauss and Daud, 2000). This requirement is based on a 10-year mission lifetime. The ionizing dose rate experienced by a spacecraft in orbit around Europa is significantly higher than in open space, but the mass of Europa does shield against approximately half of the incident radiation for an orbiting
spacecraft (Paranicas et al., 2007). The requirement of 1 Mrad(Si) could likely apply to any mission of 10-year duration, since incoming dosage will be lower in open space than near Jupiter. However, as discussed by Strauss and Daud (2000), the further a mission travels from Earth, the more important device reliability becomes, as the communication delay becomes too great for effective ground-based monitoring and intervention.

By contrast, a 10-year mission in LEO can have much lower radiation hardness requirements, and ground-based intervention can help to recover errors that do arise. A summary of more than 20 early US space missions in cis-lunar space recorded average dose rates of ~200-300 µGy/day, which translates to ~70-110 rad per decade (Benton and Benton, 2001). The highest reported dose rates, approximately 3,000 µGy/day, correspond to 1 krad in a decade, assuming such a high dose rate remained steady for 10 years, and was not the result of a high-fluence SPE during a short mission. Units of absorbed dose (e.g. Gy or rad) are often specified for the specific material absorbing the radiation, as different materials absorb energy at different rates. While this summary did not specify the irradiated material, it is clear that TID is not a major concern in cis-lunar space, with the possible exception of missions that remain within Earth’s trapped radiation belts. Therefore, SEE, particularly during periods of high solar activity, are the major concern for spacecraft orbiting Earth.

Although TID is not a concern for missions in LEO, there is enough scientific and commercial interest in more distant and longer missions to warrant investigation of TID effects in devices. Europa and Enceladus are primary scientific targets due to their sub-surface water oceans, which could provide clues to the origins of life (Shapiro and Schulze-Makuch, 2009). Both Europa and Enceladus are far enough from Earth that the communication delay for ground-based intervention is greater than 1 hour, which could jeopardize a mission in the case of an ill-times failure (Strauss and Daud, 2000). Meanwhile, longer-term missions to establish a permanent presence on the moon, Mars, or asteroids for commercial mining could require high TID-hardness due to the open-ended duration and scope. A mission to Europa or Enceladus
is one of NASA’s near-term scientific goals (NASA Strategic Plan, 2018). A permanent presence on a celestial body is a more distant but equally important goal. Therefore, investigation of TID effects is an important part of radiation-hardness qualification of devices intended for space applications.

### 3.3 TID Effects in Shadow Mask Devices

In the first experiment on TID effects, the shadow mask devices were exposed to ionization damage from gamma radiation, protons, N⁺ ions, and Ar⁺ ions, and the results were presented at the International Integrated Reliability Workshop (Holt, Yang-Scharlotta, and Cady, 2015). Recall that the shadow mask devices consisted of Pt top and bottom electrodes, with a TaOₓ switching layer and Ti oxygen getter layer (Fig. 3.1). The TaOₓ layer was deposited by reactive sputtering in 7% O₂:Ar sputtering atmosphere. The Pt bottom electrode and TaOₓ layer were deposited as blanket films, and the Ti and Pt top electrode were deposited through a shadow mask. Square devices with a 30 µm side length were used for this experiment.

![Figure 3.1. Shadow mask device design.](image)

(a) Top-down pattern of shadow mask devices top electrode pads. Since the bottom electrode was a blanket layer, each top electrode pad defined a device area. (b) Devices consisted of a blanket Pt bottom electrode (with Ti adhesion layer), TaOₓ switching layer, Ti oxygen getter layer, and Pt top electrode.

The devices were switched in series with a JFET, as described in chapter 2, to limit current during forming and set based on the saturation current of the transistor. Devices were formed and switched using IV sweeps (Table 3.1). These devices had data retention on the order of 1 hour, after which, devices in HRS would transition to LRS. The duration of radiation exposure was longer than 1 hour, so it was not
possible to observe changes in resistance due to TID. Instead, devices were irradiated in the unformed state, and then switching characteristics were measured over 100 IV sweeps after irradiation and forming. Non-irradiated control devices were formed and switched at the same time as the irradiated devices.

Table 3.1. Shadow mask device switching parameters. (Adapted with permission from Holt, Yang-Scharlotta, and Cady, 2015 © 2015 IEEE)

<table>
<thead>
<tr>
<th>IV Sweep</th>
<th>Bi-directional Voltage Sweep</th>
<th>JFET Gate Voltage</th>
<th>JFET Saturation Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>Form</td>
<td>+6 V</td>
<td>-500 mV</td>
<td>70 µA</td>
</tr>
<tr>
<td>Set</td>
<td>+2 V</td>
<td>-250 mV</td>
<td>220 µA</td>
</tr>
<tr>
<td>Reset</td>
<td>-1 V</td>
<td>0 V</td>
<td>N/A</td>
</tr>
<tr>
<td>Read</td>
<td>-100 mV</td>
<td>0 V</td>
<td>N/A</td>
</tr>
</tbody>
</table>

For the gamma radiation experiment, devices were exposed to gamma radiation at the NASA Jet Propulsion Laboratory using a $^{60}$Co source, which generates gamma radiation at $E = 1.1732$ and 1.3325 MeV. The devices were irradiated to a TID of 64.7 Mrad(Si), at a dose rate of 38 rad(Si)/s. No radiation-induced changes were observed in set voltage ($V_{\text{set}}$), reset voltage ($V_{\text{reset}}$), LRS resistance ($R_{\text{on}}$), HRS resistance ($R_{\text{off}}$), or resistance ratio ($R_{\text{off}}/R_{\text{on}}$) for irradiated devices compared to non-irradiated controls (Fig. 3.2).

Ion beam experiments were carried out at the University at Albany, State University of New York (SUNY). Devices were exposed to separate ion beams of protons, $N^+$ ions, and $Ar^+$ ions, each at 1 MeV. Calculations using the Monte Carlo simulation Stopping and Range of Ions in Matter (SRIM—Ziegler, Ziegler, and Biersack, 2010) indicate that at such high beam energy, the majority of ion energy loss is to ionization rather than displacements, even for $Ar^+$, which causes a relatively high number of displacements (Fig. 3.3). Nevertheless, the displacement damage dose (DDD) applied to the TaO$_x$ layer during $N^+$ and $Ar^+$ ion beam exposure is comparable to the DDD level required to switch our other TaO$_x$-based devices, as detailed in chapter 4. Those devices which were affected by DDD increased in resistance to a state similar to unformed, which may explain why no changes were observed in these experiments. Since these devices were irradiated in the unformed state, displacement damage might not have made a clear change
to the devices. Furthermore, since the devices were formed and switched after irradiation, the nature of the newly-formed filament might be similar in irradiated and non-irradiated devices, obscuring the effects of displacement damage.

Figure 3.2. TID effects on shadow mask device switching parameters. Shadow mask devices were exposed to four sources of ionizing radiation: $^{60}$Co gamma radiation (64.7 Mrad(Si)), an H$^+$ ion beam (1 MeV, $10^{15}$ ions/cm$^2$), a N$^+$ ion beam (1 MeV, $10^{15}$ ions/cm$^2$), and an Ar$^+$ ion beam (1 MeV, $5 \times 10^{14}$ ions/cm$^2$). No significant changes were observed in set voltage (a), reset voltage (b), LRS resistance (c), or HRS resistance (d) for any of the radiation conditions tested. Plots are adapted with permission from Holt, Yang-Scharlotta, and Cady, 2015, © IEEE 2015.

Table 3.2. Ionization and displacements in TaO$_x$ switching layer from ion beam exposure.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Fluence</th>
<th>TID (Mrad(Si))</th>
<th>DDD ($10^{20}$ vac/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>$1 \times 10^{15}$</td>
<td>1500</td>
<td>0.02</td>
</tr>
<tr>
<td>N$^+$</td>
<td>$1 \times 10^{15}$</td>
<td>25000</td>
<td>20</td>
</tr>
<tr>
<td>Ar$^+$</td>
<td>$1 \times 10^{15}$</td>
<td>12000</td>
<td>175</td>
</tr>
</tbody>
</table>
Figure 3.3. Breakdown of ion beam energy loss to ionization and displacements. SRIM was used to calculate the relative ion energy loss to ionization (red) and displacement (blue) processes for a 1 MeV H\(^+\) ion beam (a) and a 1 MeV Ar\(^+\) ion beam (b) in the shadow mask devices. In both cases, the energy loss to ionization was much larger than energy loss to displacement within the TaO\(_x\) switching layer. However, displacement damage made up a significant fraction of Ar\(^+\) ion energy loss.

As is evident from Table 3.2, the devices in this study withstood an extremely high TID level with no observed changes in switching characteristics. A similar resistance to extreme TID was observed in previous ion beam experiments at SUNY Albany (He et al., 2012). One study found that TaO\(_x\)-based devices with a 25 nm TaO\(_x\) layer were much less susceptible to TID effects from gamma irradiation than devices with a 50 nm TaO\(_x\) layer (Zhang et al., 2011). They attributed the susceptibility of the thicker devices to increased charge trapping in the thicker oxide. If the same relationship holds true for our own devices, the 10 nm TaO\(_x\) layer of the shadow mask devices may be thin enough that nearly all charges that build up in the oxide are quickly compensated by the electrodes. Another possible reason no TID effects were observed is that devices were formed and switched after irradiation. If, as suggested in Hughart et al. (2013), the application of even a small voltage can mitigate built-up charge in a device, forming and switching these devices would immediately remove nearly all built-up charge.

The short retention and high device-to-device variability of the shadow mask devices limited the type of radiation experiments that could be carried out. Several studies have reported a shift in device
resistance during irradiation for both TID and DDD (Gonzalez-Velo et al., 2017). Many RRAM devices have a continuum of possible resistance states (Bai et al., 2014; Alamgir et al., 2017), so static device resistance is an important parameter to measure during radiation studies. The short data retention of these devices prevented measurement of resistance changes, since the typical device retention was shorter than the duration of the radiation experiments. Meanwhile, forming and switching the devices might cause them to quickly converge to similar filament shapes and sizes, obscuring any radiation effects. As discussed in chapter 2, these limitations drove us to develop a photolithography-based process to improve device retention and uniformity. In the next section, TID experiments on the inverted photolithography liftoff-based devices will be covered in detail.

3.4 TID Effects in Inverted Liftoff Devices

The inverted liftoff devices (see Fig. 2.11) were exposed to gamma radiation at JPL in a follow-up to the TID experiments on shadow mask devices. The purpose of these experiments was to investigate TID effects in devices with longer retention and better device-to-device uniformity, compared to the shadow mask devices. With data retention longer than 1 month, and endurance greater than $10^6$ cycles, these devices are a better representation of commercial devices (Fig. 3.4). The results of these experiments are expected to be published, along with experiments on displacement damage detailed in chapter 4.

As in the previous TID experiment, devices were switched in series with a JFET to limit current during forming and set operations. Due to the fabrication process for these devices, there was no exposed contact to the blanket W bottom electrode. Instead, electrical contact was made to the bottom electrode by applying constant 20 V between two adjacent device pads until both of those devices pads became shorted to the bottom electrode. After this process, a resistance of $\sim30$ Ω separated the two pads, indicating that very good contact was made to the bottom electrode. The resistance between the two
pads was checked at the start of device testing each day. Rarely, the resistance between the pads drifted up to 1-10 kΩ; however, a voltage sweep to +20 V restored the 30 Ω resistance each time this occurred.

![Figure 3.4. Endurance and retention of inverted liftoff RRAM devices.](image)

The inverted liftoff devices retained data for at least 12 days in both the HRS (a) and LRS (b). Each device switched for at least 100,000 times before failure, with HRS (c) plotted separately from LRS (d) for clarity. Some devices switched more than 1,000,000 times. Devices were tested to a maximum of 3,000,000 cycles, and the two devices that made it to this level would likely have continued to switch with further testing.

Once electrical contact was made with the bottom electrode, devices were formed using a voltage sweep. For all device testing, voltage was applied to the bottom electrode so that positive voltage was the set direction and negative voltage was the reset direction, following the same convention used for the shadow mask devices. Device forming voltage varied from 12-18 V, so forming sweeps were applied with ascending voltage until forming occurred. During forming the transistor gate voltage was set to -700 mV, corresponding to 1 µA saturation current. After forming, devices were reset by applying -2.5 V, increasing to -3.5 V if reset did not occur. The first reset often required more voltage than a standard reset, and led to a wide range of HRS levels in the devices. Devices that reset to 10 kΩ < R < 1 MΩ were used for radiation
experiments. Devices that reset to $R > 1 \, \text{M\Omega}$ were formed and reset again until reaching $10 \, \text{k\Omega} < R < 1 \, \text{M\Omega}$. Devices that failed to reset to $R > 10 \, \text{k\Omega}$ were not used in the study. Switching was attempted on a few of the devices that reset to $R > 1 \, \text{M\Omega}$, but these devices only switched up to 30 times, and had high variation in resistance states, as the entire filament was likely dissociated during reset, and each set might even establish a new filament in a different location. Therefore, devices with an intermediate HRS level of 10-1000 kΩ were required for stable switching. After forming and first reset, devices were switched 20 times using IV sweeps, followed by 20 times using high-speed pulses (Table 3.3). Devices were then set to either the HRS or LRS for radiation experiments.

Table 3.3. Switching parameters for inverted liftoff RRAM devices.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Voltage</th>
<th>Transistor Gate Voltage</th>
<th>Transistor Saturation Current</th>
<th>Pulse Width / Edge Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forming</td>
<td>+12-20 V</td>
<td>-700 mV</td>
<td>1 µA</td>
<td>N/A</td>
</tr>
<tr>
<td>IV Sweep Set</td>
<td>3 V</td>
<td>-350 mV</td>
<td>200 µA</td>
<td>N/A</td>
</tr>
<tr>
<td>IV Sweep Reset</td>
<td>-2.5 V</td>
<td>0 V</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Pulsed Set</td>
<td>2.5 V</td>
<td>0 V</td>
<td>1 mA</td>
<td>100 ns / 100 ns</td>
</tr>
<tr>
<td>Pulsed Reset</td>
<td>-3 V</td>
<td>0 V</td>
<td>N/A</td>
<td>100 ns / 100 ns</td>
</tr>
<tr>
<td>Pulsed Read</td>
<td>-0.4 V</td>
<td>0 V</td>
<td>N/A</td>
<td>100 µs / 100 µs</td>
</tr>
<tr>
<td>CV Sweep</td>
<td>-2 V to +2 V</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Devices were exposed to gamma radiation from a $^{60}$Co gamma source at JPL. Device terminals were left floating during irradiation, but the substrate was grounded. Electrostatic discharge (ESD) precautions, including a dissipative wrist strap and conductive gown were used to minimize the chances of ESD events affecting device resistance. Resistance was measured after each dose level, up to a TID of 31 Mrad(Si) (Fig. 3.5). Non-irradiated control devices were measured over a similar duration as the irradiated devices so that any natural drift in resistance over the one-week TID experiment would be accounted for. No significant changes in resistance were observed in control devices or irradiated devices for either LRS or HRS.

IV sweep analysis was performed on irradiated unformed devices to determine whether physical changes were taking place in the TaO$_x$ that might not be observed by resistance measurements of formed
devices. IV reads at JPL showed that unformed device resistance increased after gamma irradiation (Fig. 3.6). However, when the same devices were measured again at SUNY, the resistance of both irradiated and non-irradiated devices had greatly increased, and no differences between the devices were detected (Fig. 3.6). The current measured at SUNY was on the order of 10 pA, compared to 10 nA at JPL. This difference is likely not due to the sensitivity of the measurements, as both measurements were above the noise floor of their respective setups. Therefore, it seems likely that the electrical characteristics of the devices shifted during the ~1 week time between measurements at JPL and measurements at SUNY. In irradiated devices, radiation-generated traps or holes might anneal away at room temperature over the course of a week (Diebold et al., 1998; Fujitsu et al., 1999). The voltage sweeps might also fill in some traps or holes due to charge injection (Chiu, 2014). The decrease in current of the non-irradiated devices suggests that some room temperature annealing might be taking place that would affect both irradiated and non-irradiated devices. However, since the non-irradiated devices had already had a month to anneal at room temperature, one more week seems unlikely to cause such a large effect.

![Figure 3.5. Effect of gamma irradiation on inverted liftoff devices.](image)

(a) Device resistance was measured at each dose level of exposure to gamma radiation for devices in HRS (a) and LRS (b). No significant changes in resistance were observed due to irradiation for either device type. The time axis represents time since the beginning of the experiment, underscoring the similar timescale of resistance measurements for control and irradiated devices.
3.5 Conclusions

Overall, our devices were relatively resistant to TID effects from gamma radiation compared to other reported devices. Several other studies have reported RRAM device failure below the level tested here (Zhang et al., 2011; Fang et al., 2014; Agashe et al., 2017), although devices have been reported to survive up to 60 Mrad(Si) before failure (Hughart et al., 2013). Our devices easily exceed the 1 Mrad(Si) TID requirement of the X2000 program for a mission to Europa, and are likely suitable for missions with even higher radiation requirements. Since Europa is an example of a high-radiation mission target, our devices would likely be suitable for most or all rad-hard applications in space. Further experiments would be useful to examine the effects of SEE on an array of these devices, since other RRAM devices were reported to be vulnerable to SEE during write operations (Bennett et al., 2014; Mahalanabis et al., 2014; Mahalanabis et al., 2015; Chen et al, 2015). Furthermore, displacement damage, especially from heavy ion cosmic rays could be a potential source of failure for these devices due to direct modification of the conductive filament. In the next chapter, displacement damage effects in our devices will be detailed,
along with the outlook for these devices in the high-radiation environment of Europa from a displacement damage perspective.

3.6 References


Chapter 4

Displacement Damage Effects in RRAM Devices

4.1 Introduction

Displacement damage, caused by incident light and heavy ions, is another major concern for devices in space, and is particularly complex due to the many associated physical changes that can occur after an ion strike (Srou, Marshall, and Marshall, 2003). Initially, displacement damage creates new vacancy and interstitial defects in a target material. However, defect reordering can quickly lead to many other types of defects, depending on the target material. Furthermore, different sources of displacement damage can lead to different distributions of defects within a material. For example, 1 MeV electrons produce relatively diffuse defects, while 1 MeV neutrons produce concentrated regions full of defects by ejecting a lattice atom, producing additional defects as that atom comes to rest. (Srou, Marshall, and Marshall, 2003)

Analysis of displacement effects in space is further complicated by the diversity of the space radiation environment, which includes electrons, neutrons, light ions, and heavy ions (Benton and Benton, 2001). This range of damage sources is likely to have unpredictable effects on devices; for example, electron exposure might slowly build up defects distributed evenly through a material, while a single heavy ion which produces a localized region of high defect density might lead to a single event effect (SEE) or multiple event effect (MEE). However, analysis of displacement damage is even further complicated by spacecraft design and composition. When an incident ion strikes a spacecraft hull, it typically ejects several particles, which eject even more particles, producing a cascade of secondary radiation (Benton and Benton, 2001). This secondary radiation might well contribute most of the displacement damage introduced into a device, since displacement damage is more prevalent for heavier atoms, and for atoms
that are closer to their final resting point (Arnold, Krefft, and Norris, 1974). Therefore, the displacement damage visited on a device depends on the incident particle type, particle energy, target composition, and spacecraft composition and configuration.

Due to these confounding factors, it is very difficult to replicate the space radiation environment in ground-based studies (Srour, Marshall, and Marshall, 2003). Therefore, a general physical characteristic must be chosen to represent displacement damage effects within devices, enabling extrapolation of monoatomic ion beam experiments to the diverse radiation environment of space. We have chosen to represent displacement damage as the number of oxygen vacancies per cm$^3$ introduced into the devices. By definition, displacement damage creates vacancies and interstitials of atoms within the target material. For high-Z transition metal oxides, preferential displacement of the lighter oxygen atoms is common (Hofmann, 1998), which is evident as well in our own simulations of displacement damage using the Monte Carlo simulation Stopping and Range of Ions in Matter (Fig. 4.1) (SRIM—Ziegler, Ziegler, and Biersack, 2010).

Figure 4.1. Example plot of displacement damage in a Ta$_2$O$_5$ film. SRIM was used to calculate atomic displacements in a Ta$_2$O$_5$ film within a device. Approximately twice as many oxygen atoms are displaced as tantalum atoms in this example.
Oxygen vacancies were chosen as the displacement effect of interest in our devices since VCM-type RRAM devices switch based on the movement of oxygen vacancies (Waser et al., 2009; Gonzalez-Velo, Barnaby, and Kozicki, 2017). Typically, though not always, the oxide is a bulk insulator, with a conductive filament of oxygen vacancies connecting the electrodes to form a low resistance state (LRS). In this case, the high resistance state (HRS) is usually reached by dissociating part of the conductive filament, leading to a higher resistance that is still lower than an unformed device.

Since the conductive filament in these cases is made up of oxygen vacancies, a radiation-induced change in oxygen vacancies within the device could have a significant effect on device performance. Indeed, devices in one study were observed to sometimes increase, and sometimes decrease, in resistance from heavy ion bombardment (Tan et al., 2013), an effect which was attributed to radiation-induced displacements near the conductive filament. Although gamma radiation primarily causes ionization damage, it can also cause displacements (Srour, Marshall, and Marshall, 2003) or amplify coincident displacement damage (EerNisse and Norris, 1974). In particular, ionization of a material produces charged sites which might facilitate defect formation or rearrangement (Arnold, Krefft, and Norris, 1974). It is therefore possible that gamma radiation caused displacements, some of which broke the conductive filament, while other displacements added to the conductive filament of devices in the study.

However, the majority of studies report only a decrease in resistance due to displacement damage in devices (Hughart et al., 2013; Tan et al., 2013; Delonno et al., 2013; Weeden-Wright et al., 2014; Holt et al., 2017). Indeed, a decrease in resistance seems intuitive, since the introduction of new oxygen vacancies is likely to increase the overall concentration of vacancies within the film, even if some vacancies recombine with the radiation-generated oxygen interstitial atoms. An increase in overall vacancy concentration should generally cause resistance to decrease. However, displacement might increase device resistance if a critical vacancy within a narrow portion of the filament recombines with an oxygen atom, breaking the filament.
This discussion has so far been limited to instantaneous effects of displacement damage. Although we generally focus on instantaneous effects in our own work, there are several mechanisms that can change the final concentration of defects of an irradiated material which warrant discussion. Short-term and long-term annealing, involving vacancy-interstitial recombination and defect reordering, can significantly decrease defect concentration, but may also increase it if more defects lead to a more favorable state (Srour, Marshall, and Marshall, 2003). Injection annealing, the recombination or reordering of defects due to charge injection, can also lead to a decrease or increase in vacancy concentration (Srour, Marshall, and Marshall, 2003). Of course, elevated temperature can also facilitate either of these annealing mechanisms. Therefore, the radiation response of devices in a real-world application could possibly be mitigated (or exacerbated) by applying voltage or raising device temperature. The effects of annealing are specific to a given material set and device composition, so device-specific testing must be done to determine whether annealing could improve the radiation tolerance in a given application. An example of possible charge injection annealing in our own devices will be discussed later in this chapter.

Finally, it should be noted that the radiation environment in space is mostly steady-state, with defects being continually generated within devices. Therefore, although an equilibrium concentration of defects might be reached, the defects within a device will not reach a permanent resting state. The effects of annealing after a high-fluence ion beam exposure may or may not translate to similar effects in a steady-state radiation environment. For example, an application of voltage might facilitate defect recombination, but it might also make devices more likely to change resistance if an ion strike occurs while voltage is being applied. Indeed, several studies found that devices are more likely to change resistance when struck by ions while a bias is applied (Gonzalez-Velo, Barnaby, and Kozicki, 2017). The threshold of voltage required to switch a specific device at a specified DDD level should be considered for devices bound for steady-state radiation environments. This threshold voltage for switching during irradiation
should be well above the read voltage, and ideally as close as possible to the voltage required to write to the device (i.e. no observed change in write voltage during irradiation).

Despite these complications, the non-ionizing energy loss (NIEL) has emerged as a standard of comparison for displacement damage effects across experiments and devices (Summers, Burke, and Xapsos, 1994). However, since our devices are expected to be affected most strongly by the generation or movement of oxygen vacancies, we opt to use DDD, measured in oxygen vacancies per cm$^3$, as a basis of comparison for VCM-type RRAM devices. Since switching is based on a conductive filament of oxygen vacancies, changes in oxygen vacancy concentration or distribution could directly affect device performance. Annealing can affect oxygen vacancies through recombination with oxygen interstitials (Srour, Marshall, and Marshall, 2003). Although it might be useful to distinguish between generation of point defects and localized clusters of defects (per Srour, Marshall, and Marshall, 2003), a merging of these into one average vacancy concentration is a reasonable first pass at investigating displacement damage effects in the devices, particularly at the very high DDD levels required to cause changes in our own devices, as will be reported herein. At extremely high DDD levels, the defect concentration is effectively uniform, even when individual ion strikes produce localized defect clusters, as will be evident from simulations of defect generation in the devices. It should be noted that comparison of oxygen vacancy concentration among studies of ECM-type devices might be less useful, since the conductive filament in those cases is made of metal ions (Waser et al., 2009; Gonzalez-Velo, Barnaby, and Kozicki, 2017).

In the following sections, displacement damage effects observed in VCM-type RRAM devices will be reviewed. Our own experiments on DDD effects will then be detailed for each device configuration, as described in chapter 2. An analysis of total ionizing dose (TID) will be presented for each DDD experiment, to consider the possibility that TID, rather than DDD, caused any observed changes in device behavior.
Finally, an analysis of possible conduction mechanisms, and radiation effects on those conduction mechanisms, will be presented.

4.2 Review of Displacement Damage Effects in VCM-type RRAM Devices

When comparing various studies of displacement damage effects on RRAM devices, DDD was used as a standard of comparison, with units of radiation-induced oxygen vacancies per cm$^3$, as previously described. Many studies already reported DDD level; however, for any that did not report it, an attempt was made to estimate the DDD based on information from the study. DDD was calculated using Transport of Ions in Matter (TRIM), a calculation within the SRIM software suite (Ziegler, Biersack, and Ziegler, 2015). The TRIM calculation is a Monte Carlo simulation of ion transport and energy loss through a target material. Two major assumptions are made in the TRIM calculation to improve simulation time while maintaining accuracy: the use of an analytic formula to determine atom-atom collisions, and the use of a “Free-Flight-Path” to focus on only the most important collisions for the calculation (Ziegler, Biersack, and Ziegler, 2015). Calculations of DDD (and TID in some cases) were made using the Monolayer Collision option, which ignores the free flight path assumption, calculating a collision for each monolayer of the target material. Aside from this change, the Monolayer Collision option is identical to the Detailed Calculation with Full Damage Cascades option, which calculates the energy loss from displaced recoil atoms until their energy drops below the lowest displacement energy of any atom in the target material. TRIM does not consider recombination of vacancies with interstitial atoms, so the calculated concentration may overestimate the true vacancy concentration within a device. However, the vacancy concentration calculated by TRIM indicates the number of vacancies that were originally created by ion bombardment, making it a useful measurement of damage to the target material.

As described in chapter 1, two studies simulated the resistance state of VCM-type TaO$_x$-based RRAM devices and calculated the oxygen vacancy concentration required to switch the devices from HRS.
to LRS (Kim, Choi, and Lu, 2014; Prakash et al., 2015). The first of these studies examined switching in a Ta$_2$O$_5$/TaO$_x$ bi-layer device, where switching occurs in the Ta$_2$O$_5$ layer due to the formation and rupture of a vacancy-based conductive filament (Kim, Choi, and Lu, 2014). Resistive switching was simulated by considering oxygen vacancy migration due to the local electric field, the vacancy concentration gradient, and the temperature gradient due to Joule heating. Partial differential equations were self-consistently solved to determine vacancy movement when a bias was applied to the device. This model captured the gradual reset process exhibited by actual devices using a range of reset voltages. Therefore, the model appears to reflect the physical resistive switching process in those specific devices very well. They attributed the HRS to a gap in the conductive filament with a low vacancy concentration, defined as $< 5 \times 10^{20}$ vacancies per cm$^3$. In their model, there is a steep drop-off of vacancy concentration after this threshold. Therefore, it is not clear whether a device at $5 \times 10^{20}$ vacancies per cm$^3$ would be conductive or insulating. However, based on their vacancy profile plots, a lower bound for the switching threshold in these devices might be $10^{20}$ vacancies per cm$^3$.

The second study (Prakash et al., 2015) used a previously developed model (Larentis et al., 2012) to solve for the conduction mechanism of RRAM devices. Specifically, the model was solved for the threshold of vacancy concentration required to switch from trap-assisted tunneling conduction to ohmic conduction. This threshold was found to be around $10^{21}$ vacancies per cm$^3$ for the TaO$_x$-based devices examined in the study. The distribution of the LRS resistance was computed and verified experimentally for a range of compliance currents, filament sizes, and vacancy concentrations. Devices were still able to switch even if the LRS did not reach a fully ohmic state, but there was greater variation in the LRS resistance in those cases.

In both of the above studies, the LRS was defined as a metallic state with ohmic conduction. However, resistive switching can occur at much higher resistance levels with fewer available oxygen vacancies. In one example, the LRS was on the order of 1 GΩ, with HRS of $\sim 10$ TΩ (Lin et al., 2015).
Because of this, the vacancy concentration threshold required for resistive switching in these studies may be an upper bound, since ohmic conduction requires a relatively large vacancy concentration. Devices which have a non-linear LRS current-voltage (IV) characteristic might switch at a lower vacancy concentration threshold. Of course, both studies investigated TaO$_x$-based devices, whereas different materials might also have different vacancy concentration thresholds for ohmic conduction. Our own TaO$_x$-based devices reported herein had relatively low-resistance non-ohmic conduction in the LRS, with relatively high variation in LRS as predicted for non-ohmic resistance states (Prakash et al. 2015). Because of the many factors that could affect the oxygen vacancy concentration threshold required for resistive switching, these studies serve as a general guideline, not a rule, for the RRAM resistive switching threshold. The range of $10^{20}-10^{21}$ vacancies per cm$^3$ will be tentatively considered to be the expected threshold for radiation-induced switching; however, individual studies may report much higher or lower thresholds. Fortunately, both studies discussed here simulated resistive switching in TaO$_x$-based devices, which will provide a comparison to our own TaO$_x$-based devices.

As previously described in chapter 1, there have been several studies on displacement damage effects in VCM-type RRAM devices (Marinella et al., 2012; Hughart et al., 2013; Bi et al., 2013; Delonno et al., 2013; Tan et al., 2013; Weeden-Wright et al., 2014). Two studies on the same TaO$_x$-based devices observed a gradual decrease in resistance of the HRS beginning at a DDD of $\sim10^{19}$ vacancies per cm$^3$, as calculated by TRIM (Marinella et al., 2012; Hughart et al., 2013). This decrease in resistance continued with increasing DDD up to $3 \times 10^{20}$ vacancies per cm$^3$, the highest DDD level tested, and was consistent over multiple devices and multiple irradiation runs per device (with a reset in between each run). An example IV curve for the devices indicated a linear IV characteristic in LRS, so these devices appear to reach ohmic conduction at a vacancy concentration slightly lower than predicted for TaO$_x$ devices (Prakash et al., 2015). By contrast, TiO$_x$ devices tested alongside the TaO$_x$ devices exhibited a sudden, instead of gradual decrease in resistance from HRS to LRS at $\sim10^{20}$ vacancies per cm$^3$, highlighting how different
device compositions and materials can have very different responses to displacement damage. The breakdown of ion energy loss to ionizing and non-ionizing process was not revealed; however, the authors used TRIM to optimize the ion beam energy to produce displacement damage within the TaO$_x$ or TiO$_x$ layers, so the observed effects are likely due to displacement damage.

Another study observed a decrease in resistance of TiO$_x$ devices in HRS at 6.4 x 10$^{20}$ vacancies per cm$^3$ (Delonno et al., 2013). This change in resistance is on the same order of magnitude as the TiO$_x$ devices reported in Hughart et al. (2013). However, the radiation source in this case was a 350 keV proton beam. Protons, like all light ions generally lose a large fraction of their energy to ionizing processes, and only a small fraction to non-ionizing processes such as atomic displacements (Arnold, Krefft, and Norris, 1974), so it is possible that ionization damage contributed to the observed change in resistance. Neutron bombardment was also investigated, but only up to a DDD level of 6 x 10$^{17}$ vacancies per cm$^3$. No changes in device resistance were observed due to neutron bombardment, but at such a low DDD level, a resistance change would not be expected, based on the other studies reviewed so far.

A pair of studies on HfO$_x$ devices observed opposite effects from proton beam irradiation (Bi et al., 2013; Weeden-Wright et al., 2014). In the first study, the HRS resistance increased by a factor of 2-3, a change which was attributed to displacement damage (Bi et al., 2013). This change occurred at 4 x 10$^{17}$ vacancies per cm$^3$, a relatively low threshold for displacement damage compared to the other studies discussed so far. Meanwhile, in the second study, devices became stuck in the LRS (or switched with a very low $R_{off}/R_{on}$ ratio) after proton beam irradiation to 8 x 10$^{17}$ vacancies per cm$^3$. In the first study, device resistance was read before and after irradiation to observe changes in static resistance; however, in the second study, average LRS and HRS during 50 set/reset cycles was measured after irradiation, so the results are an indirect comparison. Again, a proton beam produces a substantial amount of ionization damage in devices, which might contribute to the observed results. Both studies investigated TID effects up to 1 Mrad(SiO$_2$) (Weeden-Wright et al., 2014) and 7 Mrad(SiO$_2$) (Bi et al., 2013), and observed no
changes in device resistance or dynamic HRS and LRS due to TID. The proton beam produced approximately 10 Mrad(HfO$_2$) TID in the HfO$_2$ switching layer, according to our own TRIM calculations. This TID level is not much higher than the 7 Mrad(Si) level which did not affect the devices, so the observed changes are likely due to displacement damage, not TID.

One study observed a decrease in HRS resistance of TaO$_x$ devices at a low DDD threshold of $10^{17}$ vacancies per cm$^3$ (Tan et al., 2013). This study was particularly remarkable, as an increased resistance was observed in some HRS devices, even while other devices decreased in resistance at the same DDD level. The authors attribute this to atomic displacements of a very thin filament. If the filament is very thin, the addition (removal) of one critical vacancy could significantly decrease (increase) device resistance. The overall filament need not even be very thin, as long as the thinnest part of the filament, where switching takes place, is thin enough for a small atomic change to cause a large change in resistance. If the filament does indeed have such a thin region, it might explain the resistance changes observed at very low DDD levels. Although TID could again possibly contribute to the results, the use of heavy bromine ions favors displacement damage, unlike the proton beam experiments previously reviewed.

There is no consensus on the effects of displacement damage in VCM-type devices. While most studies observed a decrease in resistance, as would be expected from an increase in oxygen vacancies, some studies observed the opposite effect. The DDD thresholds required to elicit changes in device resistance or switching behavior vary over 4 orders of magnitude, even among devices made from one switching oxide, TaO$_x$. It is unclear to what extent TID contributed to the radiation effects attributed to DDD. In almost all cases, DDD-induced changes in device resistance occurred below the threshold predicted for TaO$_x$ devices of $10^{20}$-$10^{21}$ vacancies/cm$^3$ (Kim, Choi, and Lu, 2014; Prakash et al., 2015), although this range might be an overestimate since it corresponds to devices with ohmic LRS behavior, where high vacancy concentrations are required. As will be seen in the following sections, our own TaO$_x$-
based devices were more resilient to DDD than the devices reviewed so far, with radiation effects observed at or above the predicted threshold of $10^{21}$ vacancies per cm$^3$. It is unclear why our devices were more resilient to DDD, but a combination of electrical and material characterization, as well as conduction mechanism analysis was used to attempt to address this difference.

### 4.3 Displacement Damage Effects in Shadow Mask Devices

An initial characterization of displacement damage was carried out on the shadow mask devices using various ion beams, including protons, N$^+$, and Ar$^+$ ions. These experiments were detailed in chapter 3 due to the high TID introduced into the devices. However, each of the ion beams produced displacement energy as well, so DDD effects should also be considered (Table 4.1). Again, these results were presented at the International Integrated Reliability Workshop (IIRW 2015) and published in that conference’s proceedings (Holt, Yang-Scharlotta, and Cady, 2015).

#### Table 4.1. Ionization and displacements in shadow mask devices. (Same as Table 3.2)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Fluence</th>
<th>TID (Mrad(Ta$_2$O$_5$))</th>
<th>DDD ($10^{20}$ vac/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>1E15</td>
<td>1500</td>
<td>0.02</td>
</tr>
<tr>
<td>N$^+$</td>
<td>1E15</td>
<td>25000</td>
<td>20</td>
</tr>
<tr>
<td>Ar$^+$</td>
<td>1E15</td>
<td>12000</td>
<td>175</td>
</tr>
</tbody>
</table>

Recall from chapter 3 that no significant changes were observed in the set voltage, reset voltage, HRS, LRS, or HRS/LRS ratio for any of the ion beam exposures, despite the high levels of TID and DDD introduced into the devices. The short data retention precluded investigation of static resistance changes in the devices due to irradiation. However, at such high DDD levels, it is surprising that the N$^+$ ion beam, and especially the Ar$^+$ ion beam, did not cause any changes in switching voltage or average resistance states over 50 set/reset cycles. It is possible that switching the devices facilitated recombination of oxygen vacancies and interstitials, quickly recovering any built-up damage through injection annealing (Srour, Marshall, and Marshall, 2003). It is also possible that the use of a very thin (10 nm) switching oxide limited the number of defects that could become trapped within the oxide (Zhang et al., 2011). Static resistance
measurements before and after irradiation might help to distinguish between these two mechanisms. Moreover, static resistance measurements give a strong indication of whether the switching region of the conductive filament changed in size or shape, as small changes in the filament could cause large changes in device resistance. Therefore, the next set of experiments focused on devices with longer data retention, enabling static resistance measurements.

4.4 Displacement Damage Effects in Photolithography-based Devices

Recall from chapter 2 that a photolithography-based process was developed for fabricating RRAM devices with longer data retention and higher device yield. The devices produced with this process typically exhibited data retention > 1 day, which was long enough to enable ion beam experiments to investigate DDD. For these experiments, device resistance was measured using IV sweeps, with a JFET in series to limit current during forming and set, as previously described in chapter 2. The results of this study were presented at the Materials Research Society meeting in April, 2017, and presented in that conference’s proceedings (Holt et al., 2017). The remainder of this section is an excerpt from that publication with minor textual and formatting changes, reprinted here with permission (MRS Advances © 2017 Materials Research Society).

Excerpt from Holt et al., 2017

Devices (12 x 12 µm) were fabricated using a combination of photolithography-based additive and subtractive processes, including liftoff, reactive ion etch (RIE), DC and RF sputtering (Fig. 4.2). Electrical measurements were performed using an Agilent B1500 parametric analyzer, using a one transistor, one resistor (1T1R) setup. An off-chip JFET was connected to the RRAM device in series to limit current during the electroforming and set operations. The switching parameters, including current compliance (transistor saturation current) are listed in Table 4.2.
Ion irradiation experiments were carried out using an Extrion ion implanter at the State University of New York at Albany to deliver a 170 keV Ar⁺ ion beam. Ion energy was chosen to minimize ionization damage, as simulated using Stopping and Range of Ions in Matter (SRIM). This enabled observation of displacement damage effects with minimal contribution from ionization damage. Fluences were calculated using SRIM to generate at least $10^{21}$ vacancies per cm$^3$ in the TaO$_x$ layer so that device switching from HRS to LRS would likely occur (Table 4.3). SRIM 2013 was used to calculate vacancies/Å/ion using the Monolayer Collision Steps option, to 5,000 ions.

Devices were formed and switched 50 times, leaving half in HRS and half in LRS. Device resistance was read once more approximately one hour before irradiation, and again approximately one hour after
irradiation. Finally, devices were switched 50 times post-radiation, enabling measurement of average resistance states for each device.

The pre-rad and post-rad reads were used to determine whether radiation caused any immediate disruption in resistance states. The resistance of devices left in the LRS was not affected by ion bombardment, but several devices left in HRS exhibited radiation-induced decreases in resistance (Fig. 4.3). Five out of nine devices subjected to the highest fluence decreased in resistance by >50%, with some of these devices fully reaching the LRS (p < 0.001). One device irradiated at the lower fluence level also switched from HRS to LRS during irradiation, although there was no significant change in resistance for the lower fluence group overall (p > 0.05).

The average resistance level of HRS and LRS for each device was measured before and after irradiation for 50 set/reset cycles. The goal was to determine whether irradiation had a lasting effect on device resistance states. As previously discussed, cycling of the devices might facilitate vacancy-interstitial recombination, eliminating some of the radiation damage. As would be expected if this were the case, no significant changes in average resistance states during switching were observed for either irradiated group compared to the non-irradiated controls (Fig. 4.4). Although a slight decrease in resistance (~30%) was observed in the average HRS, this was observed in all devices, including the controls.

Figure 4.3. Effects of displacement damage on device resistance. Device resistance was read before and after irradiation. More than half of devices irradiated in HRS at the highest fluence exhibited a large decrease in resistance during irradiation (p < 0.001).
Table 4.2. RRAM switching parameters

<table>
<thead>
<tr>
<th>Switching Operation</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Form</td>
<td>5V IV sweep, 40 uA current compliance</td>
</tr>
<tr>
<td>Set</td>
<td>3V IV sweep, 1 mA current compliance</td>
</tr>
<tr>
<td>Reset</td>
<td>-2.5V IV sweep, 200 uA current compliance</td>
</tr>
<tr>
<td>Read</td>
<td>-100 mV pulse: 10 ms pulse, 100 ms edge time</td>
</tr>
</tbody>
</table>

Table 4.3. Radiation-generated oxygen vacancies

<table>
<thead>
<tr>
<th>Fluence (ions/cm²)</th>
<th>Number of Devices in HRS</th>
<th>Number of Devices in LRS</th>
<th>Generated Oxygen Vacancies (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>1.43E12</td>
<td>8</td>
<td>9</td>
<td>10²¹</td>
</tr>
<tr>
<td>1.43E13</td>
<td>9</td>
<td>8</td>
<td>10²²</td>
</tr>
</tbody>
</table>

Figure 4.4. Effects of displacement damage on switching resistance levels. Devices were switched 50 times before and after irradiation, and average resistance levels of LRS and HRS were measured. No significant changes in either resistance state were observed compared to non-irradiated controls.

Our findings support the hypothesis that displacement damage produces oxygen vacancies which contribute to the conductive filament. The lower fluence level used was calculated using SRIM to deliver more than enough vacancies to switch a device to LRS. However, SRIM does not account for any oxygen vacancy-interstitial recombination, some of which likely occurs immediately. Therefore, the true radiation-induced vacancy concentration is expected to be somewhat lower than the simulation values. It is therefore unsurprising that only one device in the lower fluence group was affected strongly enough to switch the device. Meanwhile, the higher fluence, which delivered 10x the dose, caused more than half of devices to decrease in resistance by more than 50%.
The hypothesis that oxygen vacancy-interstitial recombination could be accelerated by switching the devices was also supported. When the irradiated devices were cycled, the shift in resistance disappeared, indicating that many of the generated vacancies had recombined away. However, this does not indicate the filament has been restored to its original shape and size. There is a distinct possibility the filament is broadened during irradiation, both by radiation-accelerated diffusion of vacancies and by generation of new vacancies in the vicinity of the conductive filament. While device switching likely facilitates recombination of many of these vacancies, the final filament is likely broader than the original.

Interestingly, the recovery of device resistance after switching is similar to the “fading memory” effect discussed in Ascoli et al., 2016. In this study, device resistance states were consistent across devices with different forming conditions, indicating that the filaments of all devices converged to a single switching mode after just a few set/reset cycles. Our results indicate that a radiation-induced disturbance in resistance can likewise be eliminated by switching the devices. Meanwhile, the ~30% decrease in the HRS of control devices is within normal variation for these devices over a period of one day. This effect could be due to room temperature annealing of the conductive filament, stabilizing part of the filament and resulting in a narrower switching window.

Further metrology experiments, using X-ray photoelectron spectroscopy (XPS) or Rutherford backscattering (RBS) to measure vacancy concentration, or in situ transmission electron microscopy (TEM) to measure changes in filament size and shape, are needed to determine the overall effect of high levels of displacement damage on the conductive filament. This effect is important to understand, as it has implications for devices operating in constant low fluence rate environments such as space. Although the typically low fluence rates found in space might never switch the devices, they might still alter filament shape over time, resulting in long-term changes in these devices.

End of Excerpt from Holt et al., 2017
Further analysis of SRIM/TRIM calculations revealed that the devices in the above study received approximately 6 Mrad(Ta$_2$O$_5$) TID from Ar$^+$ ion beam irradiation. As discussed in chapter 3, this TID level is high enough to cause some devices reported in the literature to change in resistance. However, no resistance changes were observed due to TID in any experiments on our own devices tested to at least 20 Mrad(Si). Furthermore, ion beam experiments on the shadow mask devices reached TID levels > 1 Grad(Si) without causing any observed change in switching voltage or average resistance states. Since the DDD in this study was 1-2 orders of magnitude higher than the predicted level for forcing a TaO$_x$-based device from HRS into LRS (Kim, Choi, and Lu, 2014; Prakash et al., 2015), it seems very likely that the observed decrease in resistance was due to displacement damage effects in the device. Indeed, there are $\sim$5.6 x $10^{22}$ oxygen atoms per cm$^3$ in fully stoichiometric Ta$_2$O$_5$, so this DDD level represents displacement of $\sim$20% of oxygen atoms within the film. As will be discussed further in a later section, it is unlikely this DDD level would be reached in most space applications, and if it was, other devices would likely fail due to radiation damage before these RRAM devices.

4.5 Displacement Damage Effects in Inverted Liftoff Devices

Another DDD experiment was carried out, this time on the inverted liftoff devices described in chapter 2, to serve as a comparison to the photolithography devices. These new devices exhibited data retention > 1 month, which enabled additional experimental options, such as multi-day radiation experiments. The following section is an excerpt of an as yet unpublished manuscript on these experiments, with some additional unpublished data included which is not found in the manuscript.

Excerpt from unpublished manuscript

Electrical testing was performed using an Agilent B1500 analyzer with B1530 high-speed pulse generator attachment. Devices were formed and switched with a transistor in series to limit current through the circuit based on the saturation current of the transistor at a given gate voltage. Voltage was
applied to the blanket bottom electrode, and ground was applied to the patterned top electrode. The device forming process varied somewhat from device to device. All devices were formed using a current-voltage (IV) sweep until forming occurred, up to a maximum of +20 V, with a gate voltage of -700 mV on the transistor, which corresponds to a saturation current of approximately 1 µA. Devices were reset at -2.5 V, which led to a wide range of resistance states. Devices capable of resetting to a HRS of 10 kΩ < R < 1 MΩ were used for switching. Devices that reset to R > 1 MΩ were formed and reset again, until they reached a HRS of 10 kΩ < R < 1 MΩ. Devices which did not reset or failed to reach R > 10 kΩ after reset were not used for radiation testing. During SET operations, the transistor was used to limit current to approximately 200 µA. The transistor remained in series during RESET operations but does not limit current under reverse bias, which is reflected in Table 2. All resistance measurements reported here include a contribution from the series transistor, which is approximately 700 Ω for low drain voltage and a gate voltage of 0 V.

Following forming and first reset, the devices were subjected to 10 set/reset cycles using direct current (DC) sweeps, followed by 20 set/reset pulses, with the transistor in series in both cases (Table 4.4, Fig. 4.5). A subset of devices was switched to LRS with one more set pulse, to be irradiated in the LRS. Devices were divided into three irradiation groups: LRS, HRS, and unformed, and each resistance was read using a read pulse. After ion beam irradiation, device resistance was read again using a read pulse at each dose level. Commercial devices were formed, then switched 20 times using high-speed pulsing. Again, a subset of devices was set to LRS for irradiation. Both device types were irradiated in a floating state (substrate grounded), and device resistance was read after each ion beam exposure using a read pulse.

Devices with Ir top electrode were used for heavy ion experiments, carried out at the State University of New York at Albany Ion Beam Laboratory. Devices were irradiated using an Ar⁺ ion beam, introducing primarily displacement damage in the TaOₓ switching layer, as calculated using Stopping and Range of Ions in Matter (SRIM; Ziegler et al, 2010). Ion energy and fluence was varied, as shown in Table
4.5. For each fluence level, the concentration of oxygen vacancies introduced into the TaO$_x$ layer was estimated using SRIM. Pristine Ta$_2$O$_5$ contains ~5.6 x 10$^{22}$ oxygen atoms per cm$^3$, based on the density of Ta$_2$O$_5$. Therefore, at the highest radiation fluence, the TaO$_x$ film experienced near-total atomic disruption, as 3 x 10$^{23}$ atomic displacements of oxygen occurred per cm$^3$ (Table 4.5). This fluence level represents the upper extreme of displacement damage, since nearly every oxygen atom has been displaced at such a high fluence.

Table 4.4. Inverted liftoff device switching parameters.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Voltage</th>
<th>Transistor Gate Voltage</th>
<th>Transistor Saturation Current</th>
<th>Pulse Width / Edge Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forming</td>
<td>+12-20 V</td>
<td>-700 mV</td>
<td>1 µA</td>
<td>N/A</td>
</tr>
<tr>
<td>IV Sweep Set</td>
<td>3 V</td>
<td>-350 mV</td>
<td>200 µA</td>
<td>N/A</td>
</tr>
<tr>
<td>IV Sweep Reset</td>
<td>-2.5 V</td>
<td>0 V</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Pulsed Set</td>
<td>2.5 V</td>
<td>0 V</td>
<td>1 mA</td>
<td>100 ns / 100 ns</td>
</tr>
<tr>
<td>Pulsed Reset</td>
<td>-3 V</td>
<td>0 V</td>
<td>N/A</td>
<td>100 ns / 100 ns</td>
</tr>
<tr>
<td>Pulsed Read</td>
<td>-0.4 V</td>
<td>0 V</td>
<td>N/A</td>
<td>100 µs / 100 µs</td>
</tr>
<tr>
<td>CV Sweep</td>
<td>-2 V to +2 V</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 4.5. Example reset and set curves for the inverted liftoff devices. Example current-voltage (IV) sweeps are shown for reset (a) and set (b) operations on the inverted liftoff devices. In these examples, the transistor is connected in series limiting current during the set operation.

Table 4.5. Heavy ion exposure of inverted liftoff devices.

<table>
<thead>
<tr>
<th>Ion Species</th>
<th>Fluence (ions/cm$^2$)</th>
<th>DDD (vacancies/cm$^3$)</th>
<th>TID (Mrad(Ta$_2$O$_5$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>170 keV Ar$^+$</td>
<td>1.67 x 10$^{13}$</td>
<td>1 x 10$^{21}$</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>1.67 x 10$^{14}$</td>
<td>1 x 10$^{22}$</td>
<td>800</td>
</tr>
<tr>
<td>230 keV Ar$^+$</td>
<td>4.35 x 10$^{14}$</td>
<td>3 x 10$^{22}$</td>
<td>4,000</td>
</tr>
<tr>
<td></td>
<td>4.35 x 10$^{15}$</td>
<td>3 x 10$^{23}$</td>
<td>40,000</td>
</tr>
</tbody>
</table>

Devices in LRS or HRS that were exposed to displacement damage from an Ar$^+$ ion beam exhibited an increase in resistance at high fluence (Fig. 4.6). This increase in resistance was observed regardless of
resistance state of the devices, with only a few device resistances remaining below 1 MΩ. Despite this increase in resistance of formed devices, unformed devices decreased in resistance, as would be expected from an increase in defects within the oxide. Furthermore, the voltage required to form irradiated devices was much lower than for non-irradiated devices, and the resistance upon forming was much more varied than for non-irradiated control devices (Fig. 4.7). Another study noted a decrease in forming voltage after displacement damage (Tan et al., 2013), indicating that ion bombardment may be a way to lower forming voltage in these devices. This decrease in forming voltage is likely due to the increased concentration of vacancies after ion beam exposure, decreasing the number of additional vacancies needed to form a filament.

Figure 4.6. Ar⁺ ion bombardment of inverted liftoff devices. Devices were irradiated with Ar⁺ ions, and resistance was measured at each fluence level. At the highest fluence levels, resistance of devices in HRS (a) and LRS (b) increased to greater than 1 MΩ. Non-irradiated control devices measured alongside the test devices did not exhibit a change in resistance. ( *** p < 0.001; **** p < 0.0001)
Figure 4.7. Forming of inverted liftoff devices after ion beam exposure. Irradiated devices required a much lower forming voltage compared to non-irradiated controls (p < 0.01). Device resistance immediately after forming (no reset) varied over a wide range for irradiated devices (p < 0.0001). By contrast, control devices formed to a consistent resistance ~ 1kΩ.

Transmission electron microscopy (TEM) cross-section of a device exposed to Ar⁺ ion bombardment revealed an increase in roughness of each interface within the film stack (Fig. 4.8), providing a possible explanation for the varied resistance of irradiated devices after forming. Additionally, the Hf layer, visible as two distinct layers in the non-irradiated control device, merged into a single layer after irradiation. The two Hf layers in the non-irradiated control are likely an oxidized HfOₓ layer near the TaOₓ, and a metallic Hf layer near the W electrode. Displacement damage caused these two layers to mix, possibly allowing Hf to extract more oxygen from the TaOₓ region. The extreme level of displacement damage predicted by SRIM is evident in the changes observed under TEM cross-section. Although not clear from the TEM, a possible explanation for the increased resistance of both sets of devices at extremely high damage levels is the formation of localized voids at the TaOₓ/electrode interfaces due to displacement damage. If such a void formed over the conductive filament, it would break the conductive path, causing the resistance to increase to an unformed state with R > 1 MΩ.

Capacitance of unformed devices increased at the highest level of Ar⁺ irradiation, measured at 10 kHz and 1 MHz (Fig. 4.9). This increase was much more pronounced at lower frequencies, indicating that a major contributor to the increased capacitance comes from slower processes, such as ionic conduction.
or polarization (Izgorodina et al., 2009). This increase in capacitance likely reflects the increase in oxygen vacancies and free oxygen atoms within the devices due to displacement damage.

![Figure 4.8](image_url)

**Figure 4.8.** TEM cross-sections of non-irradiated and irradiated SUNY devices. (a) TEM cross-section of a non-irradiated device revealed smooth films and well-defined interfaces throughout the device. (b) TEM cross-section of an irradiated device (1 x 10^23 vac/cm^3) revealed roughening of the interfaces and a change in apparent morphology of the TaO_x switching layer.

![Figure 4.9](image_url)

**Figure 4.9.** Capacitance changes in SUNY devices due to displacement damage. Capacitance-voltage measurements (CV sweeps not pictured) were taken of non-irradiated controls and irradiated devices at AC frequencies of 10 kHz (a) and 1 MHz (b). At both frequencies, capacitance increased at the highest radiation dose (p < 0.0001).
Meanwhile, XRD and XPS measurements of irradiated blanket TaO$_x$ films did not reveal changes in film composition due to irradiation. XRD revealed that the TaO$_x$ films were amorphous before and after irradiation (Fig. 4.10). This was expected, since sputtered TaO$_x$ needs to be annealed to at least 600° C to transition from amorphous to poly-crystalline (Joshi and Cole, 1999; Park et al., 1992). Displacement damage would be expected to make films more amorphous, so a film that is already amorphous is unlikely to exhibit noticeable changes in crystallinity due to irradiation.

XPS was used to measure the O1s (Fig. 4.11) and Ta4f (Fig. 4.12) spectra of the blanket films. There was no difference in binding energy, peak shape, or O:Ta atomic ratio due to irradiation. Two peaks are evident in the O1s spectrum, the smaller of which has previously been attributed to “non-bridging” oxygen (Fang et al., 2014). In this previous study, an increase in non-bridging oxygen was observed after gamma irradiation, likely from the breaking of Hf-O bonds (Ta-O bonds in our case). Displacement damage from ion bombardment should be even more likely to break atomic bonds than gamma radiation. However, since our TaO$_x$ films were amorphous, they may have already been saturated with non-bridging oxygen sites, with further atomic displacements merely moving atoms around, without changing the overall bonding structure of the film. If non-bridging oxygens and oxygen vacancies did indeed reach saturation in our devices, as appears to be the case, any further displacements would serve only to accelerate diffusion of those species, leading to dissolution of the vacancy-based conductive filament.
Figure 4.10. XRD of irradiated TaO$_x$ blanket films. No crystalline peaks associated with Ta$_2$O$_5$ were present in the XRD spectra of irradiated or non-irradiated blanket TaO$_x$ films, indicating the TaO$_x$ films were amorphous. Several crystal peaks associated with W were present in both spectra. One unidentified peak (blue arrow) did not correspond to any crystal peaks for Ta, Ta$_2$O$_5$, Hf, HfO$_2$, or W. (Djerdj et al., 2005; Lee et al., 2002; Yu et al., 2013)
Figure 4.11. XPS O1s spectra of devices irradiated with Ar⁺ ion beam. No differences were observed in the XPS O1s spectra of irradiated TaOₓ films at the highest radiation dose when compared to non-irradiated controls. The overall spectrum (blue curve) is comprised of two smaller oxygen peaks (orange curves). The larger O1s peak at 530 eV binding energy corresponds to bridging oxygen atoms connected to two or more Ta atoms. The smaller O1s peak at 531 eV binding energy corresponds to non-bridging oxygen atoms (Fang et al., 2014). The residuals of the fit are plotted above the spectra.
Figure 4.12. XPS Ta4f spectra. No differences in peak binding energy or shape were observed in the Ta4f spectra of irradiated and control devices.

Overall, the inverted liftoff devices were more resilient to displacement damage effects than other devices reported in the literature. TiO$_x$-based devices have been reported to fail at a threshold of 1 x 10$^{20}$ radiation-induced oxygen vacancies per cm$^3$ (Hughart, et al., 2013), while HfO$_x$-based devices have been reported to fail at around 4 x 10$^{17}$ vacancies per cm$^3$ (Bi et al., 2013), and at 8 x 10$^{17}$ vacancies per cm$^3$ (Weeden-Wright, 2014). Meanwhile, the photolithography-based devices from the previous section
showed a failure threshold of \( \approx 1 \times 10^{22} \) vacancies per \( \text{cm}^3 \) (Holt et al., 2017). The most likely explanation for this high resilience to displacement damage in our devices is that the as-deposited TaO\(_x\) films have a large concentration of oxygen vacancies to begin with. The XPS measurements previously described revealed a TaO\(_x\) stoichiometry close to TaO\(_2\), rather than stoichiometric Ta\(_2\)O\(_5\), indicating that \( \approx 20\% \) of the oxygen sites are already occupied by a vacancy before irradiation. This stoichiometry corresponds to \( 10^{22} \) vacancies per \( \text{cm}^3 \), while our devices in this study exhibited resistance changes at \( 4 \times 10^{22} \) vacancies per \( \text{cm}^3 \). This suggests that devices which are very sub-stoichiometric might be more tolerant of displacement damage effects. Indeed, one study on displacement damage in zirconia observed that damage accumulation slowed once the radiation-induced defects surpassed a critical threshold (Sickafus et al., 1999). A high initial concentration of defects is likely to cause a similar effect.

Another possible explanation for this high resilience to displacement damage is that oxygen vacancies have an unusually low energy barrier of migration (\( \approx 0.4 \) eV) within Ta\(_2\)O\(_5\) (Jiang and Stewart, 2016). Consequently, oxygen vacancies and interstitials may be more likely to spontaneously recombine in Ta\(_2\)O\(_5\) than in other oxides, mitigating some of the accumulated damage, and since the TaO\(_x\) films were amorphous, the disorder of the films cannot be increased by ion bombardment. However, one study observed a transition from HRS to LRS at \( 1 \times 10^{17} \) displacement damage-induced oxygen vacancies per \( \text{cm}^3 \) (Tan et al., 2013). A transition from HRS to LRS at such a low damage threshold seems unexpected, given the simulations indicating that such a transition should occur around \( 1 \times 10^{21} \) vacancies per \( \text{cm}^3 \) (Kim et al., 2014; Prakash et al., 2015).

Finally, it is possible but unlikely that TID contributed to the observed change in resistance. Ionization damage has been reported to increase device resistance in one case (Zhang et al., 2011), and the TID delivered in the highest Ar\(^+\) fluence was \( \approx 40 \) Grad(Ta\(_2\)O\(_5\)), which is an extremely high TID. However, the extremely high levels of displacement damage likely outweigh any TID effects. Since each atom was displaced an average of \( \approx 6 \) times at the highest fluence, there was ample opportunity for built-up charge
to recombine or escape through the electrodes, particularly with a TaO$_x$ film as thin as 25 nm. Furthermore, the shadow mask devices previously reported did not exhibit TID effects when irradiated up to 12 Grad(Ta$_2$O$_5$) (Holt, Yang-Scharlotta, and Cady, 2015), and previous HfO$_x$-based devices did not exhibit resistance changes up to 5 Grad(Si) from a 1 MeV proton beam (He et al., 2012). Therefore, it seems likely that the observed resistance, capacitance, and morphology changes in the devices at high Ar$^+$ fluence were primarily due to displacement damage, rather than ionization damage.

End of excerpt of unpublished manuscript

4.6 Expected Displacement Damage Levels for Various Space Missions

Given the extremely high DDD required to cause radiation-induced changes in our devices, it is very unlikely these devices would experience a radiation-induced failure in a real space application. In this section, estimates of realistic DDD levels from various space missions will be calculated. Due to the dependence of DDD on spacecraft configuration, incident ion type and energy, and device composition, these DDD estimates are specific to these devices, and not broadly applicable. However, they should give a reasonable estimate of how long these specific devices might survive in various space environments.

The first environment we will consider is low Earth orbit (LEO), which generally remains below the altitude of Earth’s trapped radiation belts, shielding it from some lower energy ions (Benton and Benton, 2001). LEO is an attractive orbit for many satellites, including the International Space Station (ISS), due to the low altitude (i.e. low cost) and partial radiation shielding from the trapped radiation belts. Although the radiation environment is not strong enough to prohibit the use of flash memories, rad-hardened devices generally need to be used even in LEO (Oldham et al., 2006). SPE’s are very frequent during a solar maximum, which occurs every 11 years (Benton and Benton, 2001). Therefore, missions expected to coincide with a solar maximum should be designed with radiation tolerance and single event effects in mind.
Dosimetry from LEO indicates a range of energetic ion types, energies, and prevalence (Benton and Benton, 2001). For our purposes, the overall fluence of ions will be 10 ions/(m²*sr*s), where sr stands for steradian, the unit of solid angle, with 12.57 sr in a solid sphere. All ions will be assumed to have an energy of 400 MeV/amu, and all ions will be assumed to be oxygen, with a mass of 16 amu and energy of 6.4 GeV. Each of these assumptions should significantly overestimate the actual radiation environment in LEO based on the dosimetry in Benton and Benton (2001). Furthermore, to account for unpredictable secondary ion cascades, we will assume that 10% of the original ion energy is introduced into the switching layer as displacement damage. This assumption likely overestimates the displacement damage by several orders of magnitude. Therefore, our estimate of time to failure is an absolute worst case scenario, and no devices would be expected to fail before that time has elapsed. Furthermore, devices will likely survive for several orders of magnitude longer than the estimates put forth here. The minimum DDD level at which a device failure was observed in our devices was $10^{21}$ vacancies per cm³, so that level will be used to calculate time to failure. For comparison, an example flash memory device failed at $10^{15}$ vacancies per cm³ (Claeys et al., 2002), 6 orders of magnitude below our own devices.

Calculations for time to failure at Europa were based on dosimetry from Cooper et al., 2001. Ions were assumed to have an energy of 1 MeV, and a total fluence of $10^4$ ions/(cm²*sr*s), both of which are again overestimates. Note that this fluence was measured in cm², while the LEO fluence was measured in m². Therefore, there is a difference in energetic ion fluence of 11 orders of magnitude between Europa and LEO! The most prevalent particles have a lower energy at Europa than in LEO, likely due to shielding of LEO by Earth’s trapped radiation belts. However, the lower energy is more than made up for by the extreme fluence levels.

Time to failure was calculated for both our devices and the example flash memory devices in LEO and at Europa (Table 4.6). The calculations clearly overestimate damage in the devices, as flash memory would not be used in LEO at all if it failed after just 10 hours. This suggests that the values are
underestimated by at least 3 orders of magnitude, which would put flash time to failure at ~1 year. Since this time to failure estimate is from ion bombardment of single devices, memory longevity could be improved by using error correction, redundancy, and other rad-hardening techniques discussed in chapter 1. Nevertheless, it is clear that the example flash memory devices would be unsuitable for use at Europa. Meanwhile, our own devices would not fail from displacement damage in LEO, and would last at least 2 days at Europa. Moreover, if time to failure is in fact underestimated by 3 orders of magnitude, our devices would survive for several years at Europa. Even if the timescale is on the order of months, the devices would be resilient enough that error correction would be able to fix errors as they came up. Our devices do not exhibit effects from displacement damage until at least 2% of oxygen atoms have been displaced, and even then, most devices did not exhibit any change in resistance. The control circuitry and other onboard devices would likely fail at much lower DDD levels.

Table 4.6. Time to failure for devices in LEO and at Europa.

<table>
<thead>
<tr>
<th>Orbit</th>
<th>RRAM Time to Failure</th>
<th>Example Flash Memory Time to Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Earth Orbit</td>
<td>&gt; 1,000 years</td>
<td>&gt; 10 hours</td>
</tr>
<tr>
<td>Europa</td>
<td>&gt; 2 days</td>
<td>&gt; 1 second</td>
</tr>
</tbody>
</table>

Although the estimated time to failure is clearly an underestimate of ~3 orders of magnitude, it provides both a worst case scenario for device performance in different radiation environments and a comparison of our device performance to an example flash memory device. In LEO, the fluence is low enough that our devices would not fail in any meaningful timeframe due to DDD. Meanwhile, rad-hardened devices, such as RRAM devices, are a requirement for missions to Europa. As commercial RRAM devices become more widely available, the options for rad-hardened memory devices will increase, benefitting missions from LEO to Europa to permanent installations.
4.7 Analysis of Radiation-induced Defects in TaO\textsubscript{x}-based Devices

In order to further understand the physical processes of displacement damage in our devices, device IV behavior was modeled using the MDLsoft Ginestra simulation software. Ginestra simulates conduction by self-consistently solving the Poisson equation and a charge continuity equation (Ginestra User Manual). The Poisson equation is used to calculate local electric field; meanwhile a separate charge continuity equation is computed for each type of carrier, including “electrons, holes, and the ones trapped at defect sites.” The Fourier equation can optionally be solved to determine local temperature. These equations are solved on the scale of individual atoms and defects, providing granular detail of device composition and electrical function. Electrical conduction is simulated by stepping the time forward in small increments, enabling the simulation of current transients if desired. IV sweep behavior is simulated by incrementing the voltage as well as time. In this section, experimental data will be overlaid onto simulated IV sweeps using the Ginestra software to form tentative conclusions of likely device conduction behavior. This analysis is incomplete, but provides some hints as to possible effects of displacement damage on electrical conduction in the devices.

As a first attempt at modeling displacement damage in our RRAM devices, the oxygen vacancy concentration was varied over several orders of magnitude and compared to the experimental data (Fig. 4.13). For this simulation, the device consisted of a W top electrode, 8 nm HfO\textsubscript{x} layer, 25 nm TaO\textsubscript{x} layer, and Ir bottom electrode. This device stack is inverted compared to our physical devices because the software always applies voltage to the top electrode, while we applied voltage to the W bottom electrode during device testing. The Hf layer in our devices was assumed to be a sub-stoichiometric HfO\textsubscript{x} oxide layer, based on TEM cross-section of an irradiated device (Fig. 4.8). The oxygen vacancy concentration of both oxides was varied, with several configurations matching the experimental data (Fig. 4.13). In particular, when HfO\textsubscript{x} vacancies were held at $10^{20}$ per cm\textsuperscript{3}, a vacancy concentration of $10^{22}$ per cm\textsuperscript{3} in the TaO\textsubscript{x} layer matched the experimental IV data very well. However, when the HfO\textsubscript{x} vacancy concentration
was raised to $10^{21}$ per cm$^3$, a TaO$_x$ vacancy concentration of $10^{21}$ per cm$^3$ matched the experimental data the best. Additionally, devices which had previously been heated to 75C had lower current density than devices which had never been heated above room temperature, indicating that some annealing of radiation damage occurred at 75C.

Figure 4.13. Varied vacancy concentration. Simulated vacancy concentration was varied in the TaO$_x$ and HfO$_x$ layer of a simulated unformed device bombarded with heavy ions using the Ginestra software. In both plots, the labels indicate TaO$_x$ vacancy concentration. (a) HfO$_x$ vacancy concentration was held constant at $10^{20}$ per cm$^3$. The experimental data matched very well with a TaO$_x$ vacancy concentration of $10^{22}$ per cm$^3$. (b) HfO$_x$ vacancy concentration was held constant at $10^{21}$ per cm$^3$. The experimental data matched very well with a TaO$_x$ vacancy concentration of $10^{21}$ per cm$^3$. Meanwhile, experimental devices which had previously been measure at 75C had a lower current density than devices which had never been exposed to elevated temperature, indicating that annealing of radiation-induced defects took place at 75C. Experimental data is shown as large blue or orange symbols, while simulated devices are shown as small blue or green symbols.

Since several configurations of defect levels seemed to fit the experimental IV curves in the positive direction, IV sweeps in the negative direction were included in the experimental data. The vacancy concentrations were set to $10^{21}$ per cm$^3$ in both TaO$_x$ and HfO$_x$ layers, and the work functions of the W and Ir electrodes were varied to match the asymmetry of the experimental data (Fig. 4.14). Since work function depends on the interface characteristics of a metal, it can vary due to contamination, defects, or crystal structure (Chelvayohan and Mee, 1982; Greiner et al., 2012). The difference in work function between the two electrodes produces a built-in potential in the device, which controls the
asymmetry, or rectification, of the IV characteristic. A W work function of 5 eV, with an Ir work function of 6 eV appeared to most closely match the slight asymmetry of the experimental data.

Figure 4.14. Varied metal work functions. The work functions of the W and Ir electrodes were varied to modify the built-in potential, which contributes to IV asymmetry. In this example, the W work function was set to 5 eV, while the Ir work function was varied. When the Ir work function was set to 6 eV, the simulated IV curve seemed to match the slight asymmetry of the experimental data. Experimental data is shown as a set of three curves (blue, green, and red) with large symbols, while simulated curves are represented by small symbols connected by lines.

However, the simulated current density was much lower than the experimental data. The IV characteristics were simulated up to $10^{22}$ oxygen vacancies per cm$^3$ in the TaO$_x$ layer, keeping the metal work functions constant at 5 and 6 eV respectively (Fig. 4.15). Changes in vacancy concentration had very little effect on simulated current density, indicating that an interface-limited conduction mechanism might be dominant. Indeed, if vacancy concentration is high enough, the oxide might be leaky compared to an interface with a high energy barrier, in which case Schottky emission, or another interface-limited mechanism might dominate. The bandgap and electron affinity of both the TaO$_x$ and HfO$_x$ layer were varied, effectively varying the barrier heights of each interface in the device stack (Fig. 4.16). When TaO$_x$ bandgap and electron affinity were set to 3.45 and 2.45 eV respectively, and HfO$_x$ bandgap and electron affinity were set to 4.8 and 1.8 eV, the magnitude of the simulated current density matched the experimental data very well, although the shapes of the curves did not match perfectly. The fact that
modification of interface barrier heights led to a large change in simulated current density, while changes in defect concentration had minimal effect on current density, strongly suggests that an interface-limited conduction mechanism was dominant in the simulated devices.

Figure 4.15. Varied vacancy concentration. TaO$_x$ vacancy concentration was varied to increase simulated current density, with W work function set to 5 eV and Ir work function set to 6 eV. HfO$_x$ vacancy concentration was held constant at $10^{21}$ per cm$^3$. Vacancy concentration in the TaO$_x$ layer had minimal effect on current density, indicating that the dominant conduction mechanism is more likely interface-limited, rather than bulk-limited. As in the previous plots, experimental data is represented by large symbols, while simulations are represented by small, connected symbols.

Figure 4.16. Varied bandgap and electron affinity. Bandgap and electron affinity of the TaO$_x$ and HfO$_x$ layers were varied, effectively varying the energy barrier heights at each interface. In this example, TaO$_x$ bandgap and electron affinity were varied around 3.45 and 2.45 eV respectively, while HfO$_x$ bandgap and electron affinity were varied around 4.8 and 1.8 eV respectively. The simulated current density was on the same order of magnitude as the experimental data, although the IV curve shapes did not match. Experimental data is represented by large blue symbols, while simulations are represented by small, connected symbols.
At this point, the current density was on the correct order of magnitude, but the simulated IV curve needed to be flattened. To do this, the simulated 25 nm TaO\textsubscript{x} layer was split into three 8-nm TaO\textsubscript{x} layers, and the electron affinity of each layer was varied, varying the barrier height at each interface. Close to metal-oxide interfaces, the oxide defect band can become pinned to the Fermi level (Singhamahapatra et al., 2016). This was simulated by increasing electron affinity, bringing the conduction band of the interface TaO\textsubscript{x} layer and HfO\textsubscript{x} layer close to the work function of their respective electrodes, thereby lowering the barrier at these interfaces. The electron affinity of all four layers (3 TaO\textsubscript{x} layers and 1 HfO\textsubscript{x} layer) was varied, with the best match to experimental data when the electron affinities of the interface TaO\textsubscript{x} and middle TaO\textsubscript{x} layer were 4.5 eV and 3 eV respectively (Fig. 4.17). However, once again, the simulated current density was lower than the experimental data. To attempt to increase current density, the dielectric constant of the interface oxides (HfO\textsubscript{x} and first TaO\textsubscript{x} layer) was increased to 100, ensuring that most of the voltage drop across the device was in the middle TaO\textsubscript{x} layers (Fig. 4.18). This step was taken because the Ginestra software sometimes underestimates the conductivity of layers with a strong defect band.

**Figure 4.17. Varied electron affinity.** The electron affinities of all four layers (3 TaO\textsubscript{x} layers and 1 HfO\textsubscript{x} layer) were varied, modifying the energy barrier heights of each interface. This example shows the closest fit, with 4.5 eV electron affinity of the TaO\textsubscript{x} layer adjacent to the Ir electrode, and 3.0 eV electron affinity for the next TaO\textsubscript{x} layer. The third TaO\textsubscript{x} layer and the HfO\textsubscript{x} layer electron affinities were varied between 2.7 to 3.7 and 2 to 4.5 eV respectively, with minimal effect on the simulated IV characteristics. Experimental data is represented by large blue symbols, while simulations are represented by small, connected symbols.
Figure 4.18. Fermi level pinning of defect band. The dielectric constant of the TaO$_x$ layer adjacent to the Ir electrode, and HfO$_x$ layer (which is adjacent to the W electrode) was increased to 100, so that most of the voltage drop would occur over the middle TaO$_x$ layers. This modification was made to simulate pinning of the defect sub-band to the Fermi level. The simulated IV curve covers the same approximate range as the experimental data, although the shapes still differ. Experimental data is represented by large blue symbols, while simulations are represented by small, connected symbols.

Although the simulations did not completely match the experimental data, the modifications at each step brought the simulated current density incrementally closer to the data. As the simulated current magnitude and shape approaches the experimental data, it seems likely that at least some of the assumptions made in the simulations are accurate representations of our ion-bombarded devices. In particular, an interface-limited conduction mechanism is a strong possibility given the high concentration of oxygen vacancies within the devices. Given that a Schottky-like interface is expected to form at the TaO$_x$-Ir interface, and that it likely is modified by vacancy concentration (Sawa, 2008; Marchewka et al., 2016), an interface-limited mechanism is plausible. Meanwhile, the slight asymmetry observed in the data is likely due to the difference in work function of the electrodes, as the asymmetry would likely be more pronounced if it stemmed from a rectifying interfacial energy barrier (Yoon et al., 2014).

Further conduction mechanism analysis with IV sweeps at a greater range of temperatures could help to solidify some of these conclusions. In particular, Schottky emission is highly temperature
dependent (Chiu, 2014), and could be verified by measuring IV sweeps at a wider range of temperatures. We took IV sweep measurements at 25C, 50C, and 75C, as well as at 77K; however, measuring up to 100C or even 150C would make a stronger case for or against Schottky emission. However, care should be taken when heating to 75C or higher, as we observed annealing of radiation damage, measured as a slight increase in resistance, in devices measured at 75C. Based on our measurements up to 75C, the conduction mechanism of unformed devices exposed to high DDD levels seems somewhat temperature-dependent, which favors Schottky emission or Poole-Frenkel emission, while making tunneling mechanisms such as trap-assisted tunneling less likely (Chiu, 2014).

4.8 Conclusion

Overall, our devices were extremely tolerant of DDD effects. The minimum DDD level required to cause a resistance change in any device was $10^{21}$ vacancies per cm$^3$, which corresponds to displacement of 2% of the oxygen atoms in the device. Most devices exhibited a change in resistance at $10^{22}$ vacancies per cm$^3$, corresponding to displacement of 20% of oxygen atoms. XPS revealed that the as-deposited TaO$_x$ films are close to TaO$_2$ in stoichiometry, which corresponds to oxygen vacancies in 20% of oxygen sites. This high initial concentration of vacancies is the most likely explanation for the high tolerance of DDD effects in our devices. A radiation-induced change in resistance is only likely to occur once the radiation-induced vacancy concentration rivals the intrinsic vacancy concentration. It is therefore expected that our devices would start to fail around $10^{22}$ vacancies per cm$^3$, exactly as observed.

This DDD failure threshold is extremely high relative to other electronic devices, and high even compared to other RRAM devices. The RRAM devices reviewed here from other studies failed at DDD levels in the range of $10^{17}$-$10^{21}$ vacancies per cm$^3$. Our devices likely tolerate higher DDD levels due to their high intrinsic vacancy concentration. An example flash memory device failed at a DDD level of $10^{15}$ vacancies per cm$^3$. If our devices were incorporated into space applications in low Earth orbit, our devices
would not be expected to fail due to displacement damage for at least 1,000 years. Even at Europa, our devices would likely survive for several years before failing due to displacement damage, enabling extended investigation of the icy moon and its sub-surface ocean. Our results indicate that our devices, and RRAM devices in general, could be an important part of a successful and extended mission to Europa or other high-radiation targets.

4.9 References


Chapter 5

Conclusion

Our TaO\textsubscript{x}-based RRAM devices were found to be very tolerant of radiation effects, both from total ionizing dose (TID) and displacement damage dose (DDD). Compared to other RRAM devices, our devices were highly resistant to TID effects, surviving at least 20 Mrad(Si) of gamma radiation exposure without any device failures. While some studies reported device failure around 5 Mrad(Si) (Fang et al., 2014; Agashe et al., 2017), other studies observed no device failures up to the tested level of 10 Mrad(Si) (Morgan et al., 2014) or 20 Mrad(Si) (Hu et al., 2016), and one study observed failures only above 60 Mrad(Si) (Hughart et al., 2013). Generally, devices with thinner oxides appear to be more resistant to TID effects (Zhang et al., 2011), as expected from TID studies on CMOS gate oxides (Schwank et al., 2008). The X2000 program laid out by NASA required that memory devices be radiation-hardened up to 1 Mrad(Si) TID (Strauss and Daud, 2000), a requirement which almost all reported RRAM devices satisfy, and which our own devices greatly exceed. Therefore, RRAM devices in general, and our devices in particular, are strong candidates for radiation-hardened non-volatile memory devices in space applications.

Meanwhile, our devices were found to be exceptionally resistant to displacement damage effects. DDD, measured in radiation-generated oxygen vacancies per cm\textsuperscript{3}, was used to compare displacement damage levels between devices and studies. Again, RRAM devices appear to be generally tolerant to damage compared to comparable flash-based memory. Example flash memory devices failed at a DDD level of $10^{15}$ vacancies per cm\textsuperscript{3} (Claeys et al., 2002). Meanwhile, the lowest reported failure of VCM-type RRAM devices due to DDD occurred at $10^{17}$ vacancies per cm\textsuperscript{3} (Tan et al., 2013; Weeden-Wright et al., 2014). The lowest DDD level at which any of our devices failed was $10^{21}$ vacancies per cm\textsuperscript{3} (Holt et al., 2017). Although this is approximately the predicted failure threshold for TaOx-based RRAM devices (Kim,
Choi, and Lu, 2014; Prakash et al., 2015), most other reported devices failed at DDD levels 1-4 orders of magnitude lower than our devices. This high tolerance to DDD effects is likely due to the high initial concentration of oxygen vacancies in our devices. X-ray photoelectron spectroscopy (XPS) revealed that TaOₓ stoichiometry was close to TaO₂, instead of a fully stoichiometric Ta₂O₅. This corresponds to an intrinsic oxygen vacancy concentration of ~10²² per cm³. Most of our devices exhibited displacement damage effects once the DDD level reached this intrinsic vacancy concentration. This strongly suggests that the high intrinsic vacancy concentration is responsible for the high DDD tolerance, as lower levels of radiation-induced vacancies would be a small fraction of the overall vacancies within the devices.

The MDLsoft Ginestra simulation software was used to simulate current-voltage (IV) sweep behavior of irradiated devices, providing some further insight into displacement damage effects in the devices. IV sweep data from unformed, irradiated devices were compared to the simulation results to evaluate the likely mechanisms of damage. Displacement damage was modeled primarily as an increase in oxygen vacancy concentration in the devices. At high oxygen vacancy concentration (10²¹ vacancies per cm³), the simulations indicated that an interface-limited conduction mechanism was dominant, rather than a bulk-limited mechanism. This is expected, given that the TaOₓ/Ir interface should form a Schottky-like contact whose barrier can be modified by changes in oxygen vacancies (Sawa, 2008; Marchewka et al., 2016). Furthermore, at such high oxygen vacancy concentration, the bulk oxide might well be conductive, so energy barriers at the interfaces could be the greatest barrier to current flow. However, Schottky emission does not appear to be the dominant conduction mechanism in the devices, as Schottky emission typically leads to current rectification (Yoon et al., 2014), which was only minimally observed in our devices. It is possible that energy barriers formed at multiple interfaces, and that the highest barriers in each direction were approximately the same, which might lead to the mostly-symmetric IV characteristics in our devices. IV sweep analysis at 25 °C, 50 °C, and 75 °C did not clearly indicate Schottky emission, and IV sweeps at 77 K did not clearly indicate Fowler-Nordheim tunneling, as might be expected.
if Schottky emission dominates at room temperature (Chiu, 2014). Therefore, further IV sweep analysis at a wider range of temperatures is needed to confirm or refute specific conduction mechanisms in the irradiated devices.

Regardless of the exact mechanism of displacement damage in our devices, the devices were extremely tolerant to displacement damage. The DDD levels required to cause device failure corresponded to displacement of nearly every atom in the TaOx switching layer. If this level were reached in a real application, peripheral circuitry and other devices would likely fail before our own devices. A Fermi estimate indicates that this level would not be reached in low Earth orbit (LEO) on any meaningful timescale. However, this level might be reached after a few years at Europa, highlighting the critical need for radiation-hardened technologies to enable scientific exploration of the icy moon and its sub-surface ocean. Fortunately, our devices were able to continue switching after radiation-induced errors (Holt et al., 2017), indicating the possibility of error recovery and improved mission longevity in high-radiation environments. Several other studies have observed device switching after a radiation-induced failure, so soft errors may be more common than hard errors in these devices. Indeed, the movement of oxygen vacancies during set or reset might facilitate recombination of vacancies and interstitial atoms, mitigating displacement damage. Similar mitigation of TID effects has been directly observed (Hughart et al., 2013), so it may be possible to develop a standard operating procedure that involves periodically switching, or at least reading, devices even when not in use for long stretches of time to mitigate cumulative radiation effects. Specific procedures would need to be developed for specific devices, as the details of radiation response vary with the type and composition of device tested.

The outlook for commercial adoption of RRAM technology is promising. Panasonic has released a commercial implementation in its MN101L microcontroller (Chen et al., 2014). The Panasonic devices also consist of a TaOx switching layer with Ir electrode, and therefore might exhibit similar radiation effects to our own devices. If so, Panasonic’s devices would be well-positioned for high-radiation applications,
based on the very high tolerance to radiation effects observed in our devices. Panasonic is also working on a second-generation RRAM technology at the 40 nm node. Meanwhile, Crossbar Inc. is developing an ECM-type RRAM technology expected to be used as a storage-class memory. If these companies continue to successfully develop RRAM-based memories at ever-smaller nodes, RRAM devices will become a viable and promising option for rad-hard memory on space missions. Based on our results, and the range of results already published on radiation effects in RRAM devices, these devices could eliminate radiation concerns in LEO and significantly improve mission lifetime in high-radiation environments, furthering NASA’s goals of scientific exploration and commercial development (NASA Strategic Plan 2018).

5.1 References


