A Comparison of the Radiation Response of TaO_x and TiO_2 Memristors

David R. Hughart, *Member, IEEE*, Andrew J. Lohn, Patrick R. Mickel, Scott M. Dalton, Paul E. Dodd, *Fellow, IEEE*, Marty R. Shaneyfelt, *Fellow, IEEE*, Antoinette I. Silva, Edward Bielejec, Gyorgy Vizkelethy, Michael T. Marshall, Michael L. McLain, *Member, IEEE*, and Matthew J. Marinella, *Member, IEEE*

***Abstract*—The effects of radiation on memristors created using tantalum oxide and titanium oxide are compared. Both technologies show changes in resistance when exposed to 800 keV Ta ion irradiation at fluences above 10^{10} cm^{-2}. TaO_x memristors show a gradual reduction in resistance at high fluences whereas TiO_2 memristors show gradual increases in resistance with inconsistent decreases. After irradiation TaO_x devices remain fully functional and can even recover resistance with repeated switching. TiO_2 devices are more variable and exhibit significant increases and decreases in resistance when switching after irradiation. Irradiation with 28 MeV Si ions causes both technologies to switch from the off-state to the on-state when ionizing doses on the order of 60 Mrad(Si) or greater (as calculated by SRIM) are reached without applying current or voltage to the part. Irradiation with 10 keV X-rays up to doses of 18 Mrad(Si) in a single step show little effect on either technology. TaO_x and TiO_2 memristors both show high tolerance for displacement damage and ionization damage and are promising candidates for future radiation-hardened non-volatile memory applications.**

***Index Terms*—Displacement damage, ionization, memristor, radiation effects, resistive memory, RRAM, tantalum, titanium.**

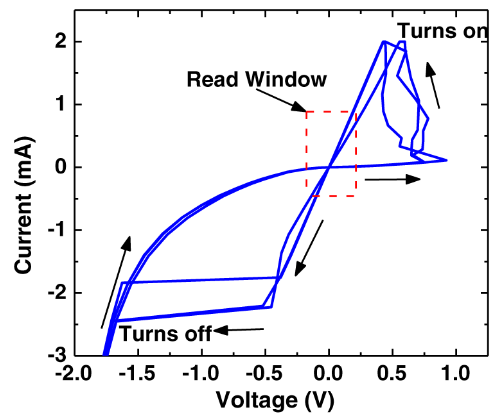

Fig. 1. Typical I-V curve with multiple loops for a TaO_x memristor with an example "read window" drawn [11].

I. Introduction

MEMRISTORS are of great interest for their potential applications as resistive RAM (ReRAM), one of the leading candidates to replace current non-volatile memory technologies as they become increasingly limited by scaling [1][2]. There are a variety of memristor structures, commonly consisting of two metal terminals with an insulator between them. Popular material choices for the insulator include oxides formed from tantalum, titanium, and hafnium. Memristors can change resistance based on applied current and voltage, forming resistance hysteresis loops. It is believed that this resistance change is the result of a change in radius [3]–[5] and/or concentration of a nanometer-scale conducting filament composed of an increased density of oxygen vacancies. The resistance state of the device can be determined without changing the resistance by applying a voltage lower than that required to alter the resistance. This is often called the "read window." Fig. 1 plots example loops for tantalum based memristors.

Recently, there has been interest in evaluating the radiation response of memristors for potential use as memories in radiation-hard electronics. Experiments on TiO_2 memristors reported that Co^{60} gamma rays and 941 MeV Bismuth ions had only minor effects on resistance values [6]. Memristor performance was also relatively unaffected by alpha particle irradiation up to a fluence of 10^{14} cm^{-2}, with a reduction in the off state resistance at a fluence of 10^{15} cm^{-2} but switching functionality still intact [7]. Tantalum oxide, TaO_x, has become a popular material choice for memristors lately due to impressive performance in the areas of endurance, switching speed, and power consumption [8]–[10]. Initial radiation experiments on TaO_x devices showed gradual resistance degradation when irradiated with 800 keV silicon ions, likely due to oxygen vacancy creation due to displacement damage [11]. Exposure to 10 keV X-rays caused switching from high resistance states to low resistance states when exposed to as little as 10 krad(Si) but Co^{60} irradiation showed little effect up to a dose of 500 krad(Si) [11]. HfO_2 memristors have also shown promising results, showing few changes to Co^{60} and 1 MeV proton irradiation [12][13].

In this paper we examine the effects of radiation-induced ionization and displacement damage from 28 MeV Si ions, 800 keV Ta ions, and 10 keV X-rays on TaO_x and TiO_2 memristors. Both materials show little change from 10 keV X-rays in doses

Manuscript received July 06, 2013; revised September 10, 2013; accepted October 04, 2013. Date of publication December 03, 2013; date of current version December 11, 2013. This work was supported in part by Sandia National Laboratory's Laboratory Directed Research and Development (LDRD) Program and the Defense Threat Reduction Agency. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

The authors are with Sandia National Laboratories, Albuquerque, NM 87185 USA (e-mail: dhughar@sandia.gov).

Color versions of one or more of the figures in this paper are available online at http://ieeexplore.ieee.org.

Digital Object Identifier 10.1109/TNS.2013.2285516

up to 18 Mrad(Si) in a single step. Ionization-induced switching occurs under 28 MeV Si ion irradiation after reaching a critical dose threshold on the order of 60 Mrad(Si) or higher, depending on the part. Displacement damage caused by both 800 keV Ta ions and 28 MeV Si ions cause resistance to degrade as the oxygen vacancy concentration increases beyond $\sim 10^{19}$ cm^{-3}. TiO_2 parts continue to show effects like degrading resistance and variability in off-state resistance after irradiation.

II. Experimental Details

The memristors for these experiments were fabricated using a "random shadow mask" technique to create isolated individual crossbars, resulting in about 30% of the bars crossing. A functional memristor is formed when a vertical and horizontal "dogbone" electrode cross, serving as the top and bottom electrodes respectively. The nominal device dimensions were 10 μm $\times$ 10 μm. The approximate TaO_x insulating layer thickness was 10 nm. There was a 10 nm layer of platinum and 50 nm of tantalum above the oxide layer and a 30 nm platinum contact on the bottom, the same structure as presented in [11]. However, the devices used in this work are from a different manufacturing batch. For TiO_2 devices, the TiO_2 layer thickness was approximately 28 nm with a 30 nm platinum electrode on top and a 15 nm platinum electrode on the bottom. The TaO_x parts irradiated with 800 keV Ta ions and 28 MeV Si ions come from the same wafer and the TiO_2 devices irradiated with those ions come from the same wafer. For the X-ray irradiation the parts include devices taken from the same wafers used in the ion irradiations, as well as some additional TaO_x devices from another wafer.

For radiation measurements, several memristor die were packaged in standard 28 and 40 pin DIPs; a typical sample had six devices bonded. Some memristors can wear out over time, where off resistance changes over time until it is similar to the on resistance [14]. In order to make sure failures were due to irradiation, devices were switched numerous times prior to experiments, and only devices without significant degradation of the off resistance were chosen for use in radiation experiments.

The parts used in this study were research devices and there was variation between the parts. Primarily, this was a difference in the off-state resistance, which could range from a few kilo-ohms, to tens of kilo-ohms for the TaO_x parts. On-state resistances were generally one hundred to two hundred ohms. Typical TaO_x devices showed hysteresis loops similar to Fig. 1, though there was some variation between parts due to differences in off-state resistance. Devices that failed had loops that showed significant changes in resistance (generally much larger than a 10% change) from loop to loop and would fail within five to ten loops. Devices that did not exhibit this characteristic were looped for numerous cycles, typically about twenty to thirty times (though some parts were cycled more than fifty times), and there were no such changes (though off-state resistances often showed $\sim 10\%$ variation). Additionally, these devices did not wear out during the testing. The devices that were tested in these experiments showed stable and consistent (within 10% variation) off-state resistance values during hysteresis loops prior to irradiation.

TiO_2 devices showed larger variation in off-state resistance (stable parts could vary by up to 20%) and sometimes exhibited off-state resistance degradation. In those cases, the off-state resistance would be lower after each loop, degrading one to two orders of magnitude over five to ten loops. Typical starting off-state resistance values for TiO_2 devices were tens of kilo-ohms to hundreds of kilo-ohms and on-state resistances were four hundred to five hundred ohms. The TiO_2 devices tested in this work showed consistent off-state resistance values that did not vary more than 20% and did not show pre-rad off-state resistance degradation.

Electrical measurements were made using an Agilent 4156C Semiconductor Parameter Analyzer. Typically, a read measurement was made after each shot, whereas a full set/reset characterization was performed following a series of irradiations. Read measurements consisted of a 50 mV sweep and resistance values were taken at a voltage of 25 mV. The 4156C was in voltage force mode for the read sweeps. For the hysteresis loops, the 4156C was in current force mode and devices were set into the on-state using 3 mA and reset to the off-state using -4 mA for TaO_x devices. The TiO_2 devices were set into the on-state using 2 mA and reset to the off-state using -3 mA.

A four point measurement setup was used due to the high series resistance of the crossbar structure. The resistance introduced by the elongated electrodes was often several kΩ. One set of electrodes supplied the current through the device and the other set measured the voltage drop across the device. This is necessary because the voltage applied across the current sourcing contacts is higher than the voltage across the device due to the added electrode resistance.

III. Results

TaO_x and TiO_2 memristors were irradiated using 800 keV Ta ion and 28 MeV Si ions at the SNL Ion Beam Laboratory (IBL) to investigate the effects of displacement damage and ionization. To study the effects of displacement damage we used an 800 keV Ta beam, for which we expected 4.83 vacancies/ion/A in the critical oxide region of the devices compared to 8.9×10^{-3} vacancies/ion/A for the 28 MeV Si beam. For ionization studies we used a 28 MeV Si beam producing significantly more ionization than the 800 keV Ta beam. This combination allows us to start understanding and separating the effects due to ionization and displacement damage. The beam was focused to a 0.032 cm^2 spot size which covered the entire 10 μm$\times$10 μm device. The irradiation was performed in vacuum at approximately 10^{-6} torr. The device was cycled (put through the full set/reset loop) pre-rad prior to pumping down to vacuum and then reset to a high resistance state. Electrical measurements were made *in situ*, with read measurements taken between each irradiation without disturbing the chamber vacuum. Pins were floating during irradiation. The devices were not cycled in vacuum, as previous devices sometimes failed under those conditions.

A. 800 keV Ta Ion Irradiation–TaO_x

Five TaO_x memristors were irradiated with 800 keV Ta ions to study the effects of displacement damage. Fluence values

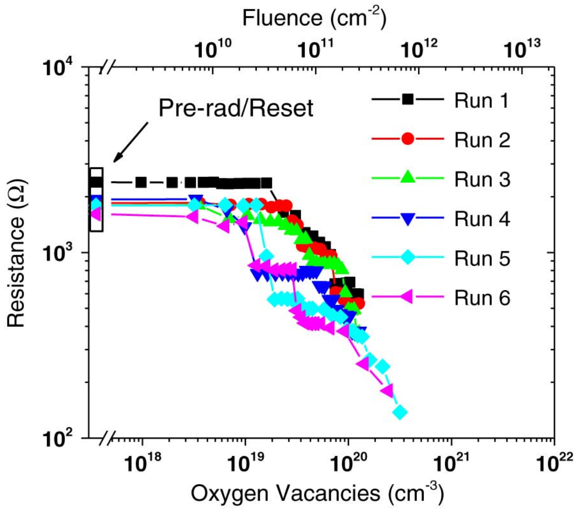

Fig. 2. Resistance versus calculated average oxygen vacancy concentration (bottom x-axis) and fluence (top x-axis) for a $\mathrm{TaO_x}$ memristor irradiated with 800 keV Ta ions. The part was reset between each run.

have been converted to the average concentration of oxygen vacancies created in the insulating layer, and ionizing dose delivered to the insulating layer. Conversions were calculated using SRIM assuming an oxide layer of $\mathrm{Ta_2O_5}$ [15]. The calculations were performed using SRIM 2012 with full cascade calculations for 10,000 particles. The ionizing dose calculation was calculated in rad(Si) and we note that the actual value will be lower since charge yield effects were not taken into account. This means that some percentage of the electron-hole pairs created will recombine immediately, so the actual dose will be lower than the calculated dose. Without further experiments the magnitude of the effect is difficult to estimate. However, the current results provide a useful relative indication of ionizing dose to facilitate comparison between devices tested with 800 keV Ta and 28 MeV Si ions.

Fig. 2 plots $\mathrm{R_{OFF}}$, the off state resistance, for a $\mathrm{TaO_x}$ memristor irradiated with 800 keV Ta ions versus the calculated average concentration of oxygen vacancies created as a result of the irradiation on the bottom x-axis and the fluence on the top x-axis. All runs in the figure are for a single device, with read sweeps applied between each shot and a set/reset cycle applied after each run in the irradiation sequence. The off-state resistance gradually degrades when the average oxygen vacancy concentration reaches roughly 10^{19} cm^{-3}, corresponding to a rather high fluence of 2×10^{10} cm^{-2}. After each run, the device is able to be reset, but the reset process does not completely restore the original off-state resistance. Later runs tend to start to degrade at lower fluence values. Runs four, five, and six begin to degrade at roughly half the fluence of earlier runs and show larger initial drops in resistance. At higher fluences the resistance curves for all runs tend to show similar behavior. The differences between runs may indicate that there is cumulative damage occurring. The decreases in initial off-state resistance from run to run also suggest cumulative damage is occurring and resetting the device does not return it to its original condition. Possible reasons for this will be explored in the discussion section.

B. 28 MeV Si Ion Irradiation - $\mathrm{TaO_x}$

$\mathrm{TaO_x}$ memristors were also irradiated with 28 MeV Si ions. As before, a read sweep was applied between each individual shot unless otherwise noted, and a full set/reset cycle was applied between each run in the irradiation sequence. Compared to 800 keV Ta, 28 MeV Si ion irradiation produces more electron-hole pairs that can potentially be trapped at defects (like oxygen vacancies) and build up in insulating regions. Since applying a read sweep may remove charge that is building up in the devices, Fig. 3(a) plots off-state resistance versus the calculated dose delivered per shot (which may be viewed as the dose delivered between read sweeps since a sweep was performed after every shot for the data plotted). When the dose delivered between sweeps reaches roughly 120 Mrad(Si) as calculated by SRIM, the resistance changes dramatically. This indicates that once these devices reach a certain dose per shot threshold, the device switches to the on-state. The threshold for this device appears to be in the range of 60-120 Mrad(Si), shown in Fig. 3(a) as the critical dose threshold. This is significantly higher than what has been required for several space vehicles and payloads [16] and what is considered significant radiation requirements ($>$ 100 krad(Si)) [17] and rad-hard from a total dose perspective (100-1000 krad(Si)) [18]. Resetting the device returns it to the initial off state with fairly little apparent accumulated damage. Unlike the resistance degradation attributed to displacement damage, the resistance change in this case is abrupt and consistently changes to the same resistance six times ($\sim 80\Omega$). This change does not appear to be affected by the total dose delivered, only the dose between read sweeps. Fig. 3(b) plots $\mathrm{R_{OFF}}$ versus calculated total dose for each run (each run is a set of shots that end after the device resistance changes and the part is reset) for the same data plotted in Fig. 3(a). The total dose per run ranges from 120 Mrad(Si) to 1.2 Grad(Si), demonstrating that there is not a clear threshold for accumulated dose. The resistance only changes once the dose delivered between read sweeps is equal to or greater than 120 Mrad(Si). A sixth run was also performed and the final three shots were all 60 Mrad(Si) (i.e. less than the critical dose per shot threshold), however, there was no read sweep applied between the final two shots. The first 60 Mrad(Si) shot showed no change in resistance when a read sweep was applied. After two consecutive shots of 60 Mrad(Si) with no read sweep between them, the device had switched on, just as in the cases when 120 Mrad(Si) was delivered in a single shot. This suggests that applying a read sweep can prevent this resistance change, likely by removing charge from the device. Additionally, the time between shots is on the order of minutes, so there is no apparent time dependence on that time scale.

While we are using 28 MeV Si ions primarily for ionization effects, displacement damage is still present. The oxide region of the device is relatively shallow compared to the range of the typical 28 MeV Si ion, as a result the energy loss of the ions is primarily in electronic stopping power (or ionization) with a small fraction of the ions generating recoils (or displacement damage). The effects of both mechanisms are demonstrated in Fig. 4, which plots $\mathrm{R_{OFF}}$ versus the calculated average concentration of oxygen vacancies created on the bottom x-axis and

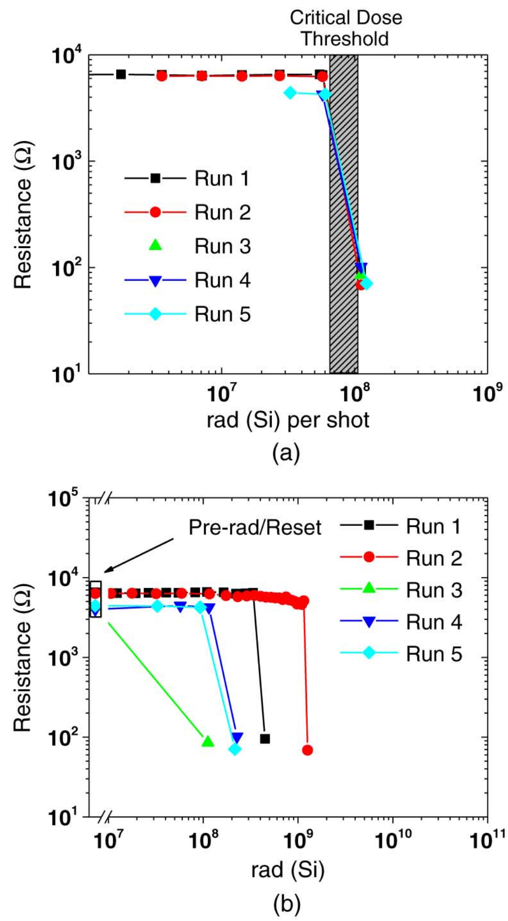

Fig. 3. (a). Resistance vs. rad(Si) per shot for a TaO_x memristor irradiated with 28 MeV Si ions. The part was reset between runs. Duplicate shots are omitted for a given run. The dose per shot threshold appears to be in the range of 60-120 Mrad(Si). (b). Resistance vs. rad(Si) for a TaO_x memristor irradiated with 28 MeV Si ions. The part was reset between runs. The dose is cumulative for a given run. There is not a clear total dose threshold.

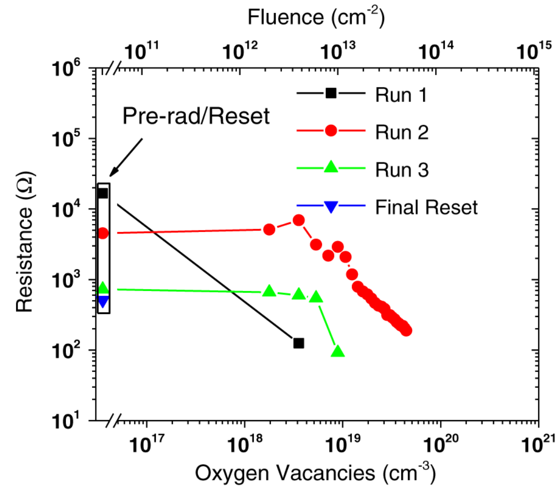

Fig. 4. Resistance versus calculated average oxygen vacancy concentration (bottom x-axis) and fluence (top x-axis) for a TaO_x memristor irradiated with 28 MeV Si ions. The part was reset between each run.

the fluence on the top x-axis for another TaO_x device irradiated with 28 MeV Si. In this experiment, the first and third runs end with an abrupt change likely due to ionization, whereas the second run shows gradual resistance degradation. The shots in run one and three that change the resistance of the device deliver doses of 1.1 Grad(Si), whereas each shot in run two delivers 550 Mrad(Si), indicating that the critical dose per shot may range from 550 Mrad(Si) to 1.1 Grad(Si). This switching behavior is consistent with the critical ionizing dose threshold per shot seen for the previous part (Fig. 3(a)), but the threshold for switching due to ionization is roughly an order of magnitude higher for this part. This may be due to device to device variation, as these are research quality parts. For the second run, the dose per shot remains below the threshold for switching due to ionization and shows gradual resistance degradation similar to the parts irradiated with 800 keV Ta. Resistance degradation due to displacement damage does not occur until a concentration of $\sim 5.5 \times 10^{18}$ cm^{-3} oxygen vacancies are created, which corresponds to a Si ion fluence of 6×10^{12} cm^{-2}. The oxygen vacancy concentration threshold is consistent between devices irradiated using 800 keV Ta ($\sim 10^{19}$ cm^{-3}) and 28 MeV Si ($\sim 5.5 \times 10^{18}$ cm^{-3}). Thus, the gradual resistance degradation seen in these experiments are likely due to oxygen vacancies created by displacement damage. The similar threshold also suggests that ionization effects may not have a significant impact on the resistance degradation caused by displacement damage.

C. 800 keV Ta Ion Irradiation–TiO_2

TiO_2 memristors irradiated with 800 keV Ta show different behavior compared to TaO_x memristors. Fig. 5 plots R_{OFF} for a TiO_2 memristor versus the calculated average concentration of oxygen vacancies created on the bottom x-axis and fluence on the top x-axis. For the first three runs the resistance increases slightly, beginning around a fluence of 10^{11} cm^{-2}, then decreases. The fourth run shows a significant drop in resistance at similar fluence levels. After run two the device was cycled repeatedly, being set and then reset. The off-state resistance was initially reset to 15 kΩ, a typical value for the first two runs as seen in Fig. 5. At this point, the device was set and reset five times to see if the off-state resistance was consistent. During the process of being set and reset between run two and run three, the resistance degraded from 15kΩ to 750Ω over the course of five cycles. A larger reset current of -4 mA (increased from -3 mA) was applied, resulting in a higher R_{OFF} of 30 kΩ, which can be seen for run three in Fig. 5. R_{OFF} did not show the same degradation after the remaining runs, but the variation increased with the resistance varying between 10 kΩ and 200 kΩ over five cycles after the final run.

The radiation response of another TiO_2 memristor is plotted in Fig. 6. Similar to the degradation of the previous device, after the final run, the resistance dropped from 7.5 kΩ to 1.5 kΩ after being set and reset twice. The resistance begins to change around a fluence of 10^{11} cm^{-2}. Unlike TaO_x memristors, the resistance of the TiO_2 memristors tends to increase gradually then decrease abruptly, instead of just degrading gradually. However, while the devices show abrupt decreases in resistance, the resistance does not decrease to the levels seen in TaO_x devices, which would degrade to resistances in the hundreds of ohms,

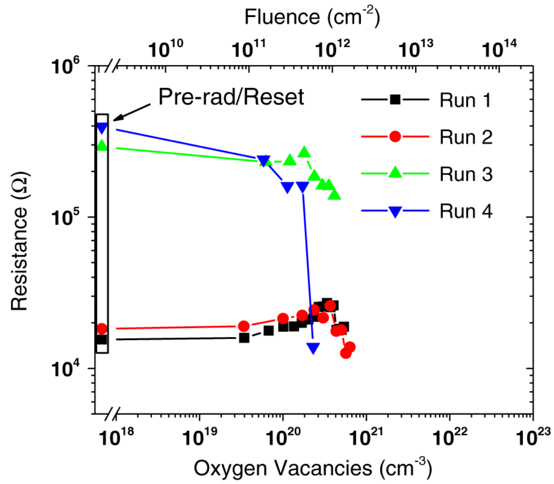

Fig. 5. Resistance versus calculated average oxygen vacancy concentration (bottom x-axis) and fluence (top x-axis) for a TiO_2 memristor irradiated with 800 keV Ta ions. The part was reset between each run. Between run two and three the part was reset five times and the off-state resistance gradually degraded. The reset current was increased from -3 mA to -4 mA for runs three and four.

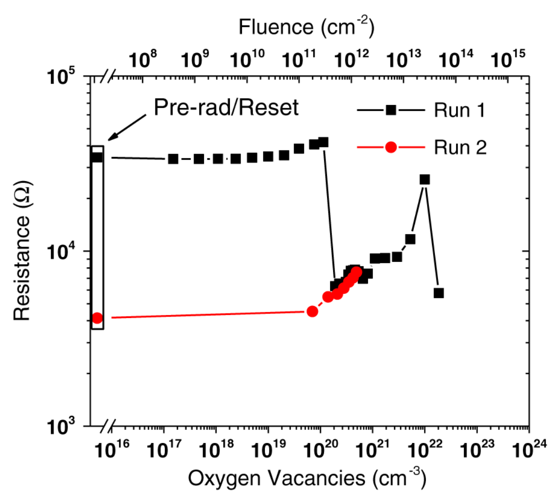

Fig. 6. Resistance versus calculated average oxygen vacancy concentration (bottom x-axis) and fluence (top x-axis) for a TiO_2 memristor irradiated with 800 keV Ta ions. The part was reset normally between run one and two.

a common on-state resistance for the set currents used for both types of devices.

D. 28 MeV Si Ion Irradiation–TiO_2

A TiO_2 memristor irradiated with 28 MeV Si ions showed evidence of ionization effects similar to TaO_x devices, which display a high critical threshold for ionizing dose per shot between reads, below which no effect is observed. Fig. 7(a) plots the off-state resistance versus calculated dose per shot. The device switches to a lower resistance when the dose delivered per shot between reads reaches 300 Mrad(Si). Fig. 7(b) plots off-state resistance versus calculated total dose per run. The values at which the device changes resistance range from 100 Mrad(Si) to 1 Grad(Si), indicating that the resistance changes in these devices are also not likely due to total dose. Unlike the TaO_x device, there is variability in both the fluence required to switch the resistance of a single device from run to run and the resistance value to which the device switched. The TiO_2 device switches to resistance values ranging from 100 Ω to 3 kΩ. Also, one of the five shots that caused the changes in resistance was 150 Mrad(Si), half the value of all the other values of 300 Mrad(Si).

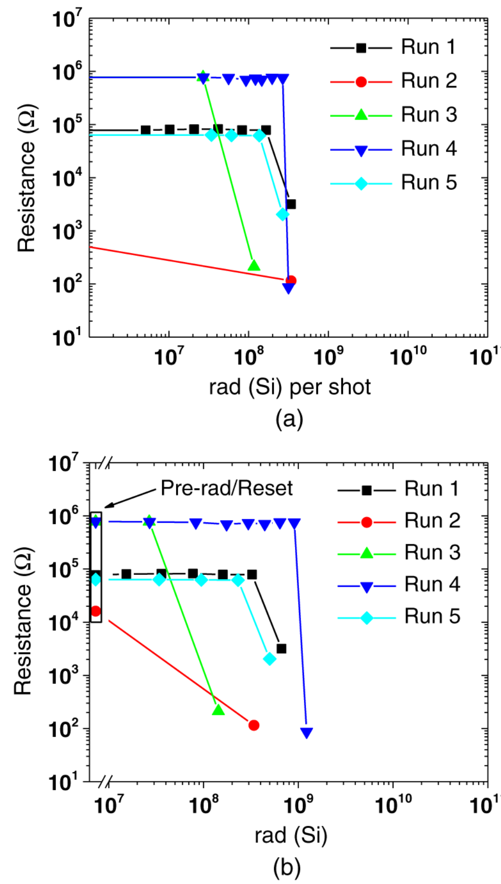

Fig. 7. (a). Resistance vs. rad(Si) per shot for a TiO_2 memristor irradiated with 28 MeV Si ions. The part was reset between runs. Duplicate shots are omitted for a given run. The dose per shot threshold appears to be roughly 300 Mrad(Si), although one resistance change occurred at 150 Mrad(Si). (b). Resistance vs. rad(Si) for a TiO_2 memristor irradiated with 28 MeV Si ions. The part was reset between runs. The dose is cumulative for a given run. There is not a clear total dose threshold.

E. 10 keV X-Ray Irradiation –TaO_x *and* TiO_2

TaO_x and TiO_2 memristors showed a high tolerance for ionizing dose when being irradiated with 28 MeV Si ions. However, the total dose required to change resistance may be different for X-ray irradiation due to potential differences such as charge yield. 10 keV X-rays only cause ionization, unlike 28 MeV Si ions which cause displacement damage as well. Previously, 10 keV X-ray experiments showed TaO_x memristors changing resistance states at doses as low as 10 krad(Si), although Co^{60} irradiation up to a dose of 500 krad(Si) did not significantly affect them [11]. TaO_x memristors and a TiO_2 memristor exposed to 10 keV X-ray irradiation in this study showed little change in resistance. Devices one and four are from the same TaO_x wafer as the devices irradiated with heavy ions, while devices two and three are from a different TaO_x wafer. Device five is from the same TiO_2 wafer as the devices irradiated with heavy ions. Devices were irradiated after being switched into either the

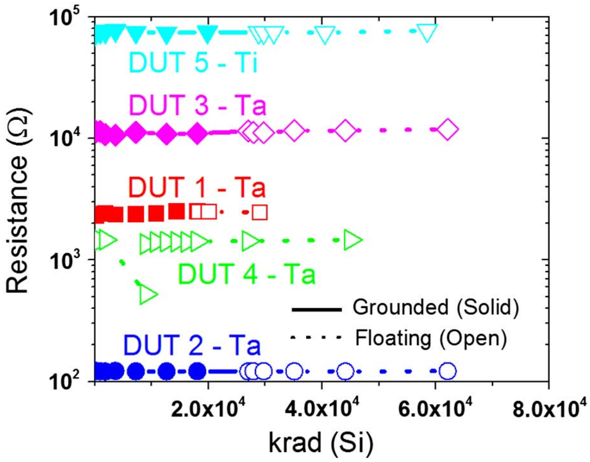

Fig. 8. Resistance versus krad(Si) for four TaO_x parts and one TiO_2 part. DUT 4 was set to the on-state prior to irradiation. All other parts were set to the off-state. Solid lines indicate pins were grounded, dotted lines indicate pins were floating. Read measurements were taken at every point. The highest dose per step was 9 Mrad(Si) for DUT 1 and 18 Mrad(Si) for DUTs 2-4.

off-state or the on-state and a read sweep was applied after each irradiation to determine the resistance. During some irradiations, all pins were grounded together. For other irradiations, the parts were left floating. While these parts may not necessarily be floating in applications, these tests were performed to see whether either setup is more vulnerable to charge buildup. The dose rate was 6000 rad(Si)/s. Fig. 8 plots the resistance versus dose for several TaO_x memristors and a TiO_2 memristor. Each was irradiated under both grounded and floating conditions (except DUT 4, which was only irradiated in the floating condition). Based on ionization data from 28 MeV Si irradiations, applying a read sweep mitigates the effects of ionization, so an increasingly higher dose per step was used. Three of the TaO_x devices shown are in the off-state, while DUT 2 is in the on-state. DUT 5, the TiO_2 device, is in the off-state. DUT 4, one of the TaO_x devices, is the only device that showed any change in resistance during irradiation. The dose of the step that caused this resistance change is 7.2 Mrad(Si). The part did not fully switch to the on-state and reset back to its original resistance without incident. Further irradiations up to a dose of 18 Mrad(Si) at a time did not cause any further changes. Two additional TaO_x devices (not shown) were also irradiated with single step doses of up to 18 Mrad(Si) and showed no changes in resistance.

Aside from one partial switch that was not repeatable, there was no effect from 10 keV X-ray irradiation up to doses of 18 Mrad(Si) per step and total doses of up to 63 Mrad(Si). Although the relationship between the calculated dose for the 28 MeV Si results and the dose for the 10 keV X-ray results is unknown, given the extremely high dose calculations from the 28 MeV Si data, the lack of response to 10 keV X-rays is not surprising. Further work is needed to more fully explore the potential differences between floating and grounded irradiations.

The X-ray results in this work do not show the sensitivity seen in [11]. Most devices show little change at doses beyond the 10 krad(Si) that upset many devices previously. There were some differences between these experiments. While the device structure and packaging were the same, the devices irradiated in [11] were from an older manufacturing batch and device quality may have been improved. Cable connections were shielded to reduce potential noise in this work. An Agilent 4145B was used for X-ray data collection in [11] and a 4156C was used in this work.

IV. Discussion

The percolation model for oxide breakdown [19], [20] has been used as a framework for modeling resistive switching [21]. TaO_x devices fall into the valence change mechanism class of memristors, and switching can be understood in terms of oxygen vacancies either forming a conductive pathway or dispersing to rupture a conductive pathway. Displacement damage is believed to affect memristor resistance through the creation of oxygen vacancies, which modulate the conductivity of the oxide layer [7], [11], [22]. Resistance likely begins to change when enough oxygen vacancies have been created near enough to each other to form a pathway that completes the conduction channel.

Resetting a memristor with degraded resistance after irradiation restores much of its original off-state resistance, as seen in Figs. 2 and 4, and the devices tested so far remain functional after irradiation. However, there appears to be some cumulative damage from the irradiation. The off-state resistance tends to decrease after each irradiation, which can be seen in Figs. 2 and 4. Subsequent irradiations in Fig. 2 show resistance degrading at earlier fluences and in larger increments. If not all of the oxygen vacancies that are created are removed through oxidation or diffusion then it may be easier to create a percolation path of defects during subsequent irradiations.

Resetting a device multiple times may gradually return the conduction channel region closer to its original state. Fig. 9 plots resistance versus calculated average oxygen vacancy concentration on the bottom x-axis and fluence on the top x-axis for a TaO_x memristor irradiated with 800 keV Ta ions. The first four runs show similar trends of resistance degradation at lower fluences as the number of runs increases. After run four, the device was reset ten times. Subsequently, the fluence required for the onset of degradation is seven times higher than the previous run. After run five, the device was reset twenty times. The initial resistance of the device then doubled from the previous run. There was an initial drop in resistance at lower fluences, but all of the remaining degradation occurred at the same fluence as run five, seven times higher than the runs before them.

TiO_2 memristors also belong to the valence change mechanism class of memristors and are often considered similar to TaO_x memristors, but their response to displacement damage is significantly different. Instead of a gradual degradation of resistance with increasing fluence, resistance gradually increases and occasionally drops. The fluence required to cause a drop in resistance varied from part to part and even on different runs on the same part. Some devices show decreasing resistance during repeated cycling after irradiation. The only change observed in post-rad behavior for TaO_x devices is a gradual recovery of resistance discussed in the preceding paragraph. The reason for the difference in radiation responses between TaO_x and TiO_2 memristors is unclear at this point. It may be due to differences in the chemical bonding in the materials or differences in the size and shape of the channel region and the ensuing changes

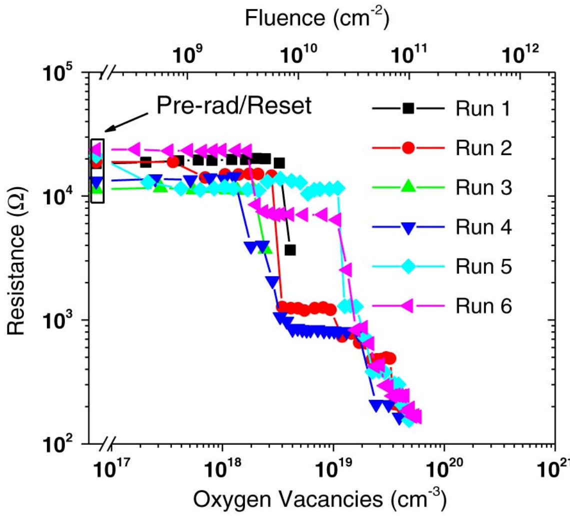

Fig. 9. Resistance versus calculated average oxygen vacancy concentration (bottom x-axis) and fluence (top x-axis) for a TaO_x memristor irradiated with 800 keV Ta ions. The part was reset between each run. The device was reset ten times after run four and twenty times after run five.

that radiation causes. TiO_2 devices appear to be more resistant to large resistance changes caused by displacement damage initially, but are more prone to having degraded reliability in post-radiation behavior. Radiation may simply be exacerbating a difference between the material system as tantalum based devices have shown some of the highest endurance [8], or it may be due to a difference in switching mechanisms, or a combination of factors.

10 keV X-ray exposures suggest that charge buildup (ionization) effects are minimal in both TaO_x and TiO_2 memristors, but the ion beam results indicate that there is an effect if enough charge is deposited. Previously, TaO_x based memristors with an oxide thickness of 50 nm showed changes in resistance after doses of 180 krad(Si) from Co^{60} gamma rays [23]. Devices with a thickness of 25 nm showed fewer changes in resistance. TaO_x memristors tested last year by Sandia showed little change after 500 krad(Si) [11] and devices presented here, which have an oxide thickness of 10 nm, were unaffected by doses of 18 Mrad(Si) from 10 keV X-rays and doses in the range of 60 Mrad(Si) to 1 Grad(Si) from 28 MeV Si ions. Decreasing the thickness of the oxide may reduce the vulnerability of these devices to ionization damage.

V. Conclusion

Our results indicate that there are differences in the radiation response of TaO_x and TiO_2 memristors. However, both types appear to be tolerant to very high levels of radiation before device characteristics are affected, in excess of those required for most rad-hard non-volatile memory space applications. It appears that both materials have a critical ionizing dose threshold between read operations below which they are insensitive to radiation and beyond which resistance changes significantly. Applying small read before this threshold is reached appears to prevent these changes, possibly by draining accumulated charge. This realization may be useful for rad-hard implementation as read voltages can be applied periodically, potentially making the devices practically insensitive to total ionizing dose effects. Devices do not show changes in resistance due to displacement damage from fluences of 10^{10} cm^{-2} or below for 800 keV Ta ions or fluences of 10^{11} cm^{-2} or below for 28 MeV Si ions. Ionizing doses of up to 18 Mrad(Si) per step from 10 keV X-rays did not consistently change resistances. Ionizing doses in the range of 60 Mrad(Si) to 1 Grad(Si) were required to change the resistance of devices exposed to 28 MeV Si ions and applying small voltages and current may mitigate vulnerability to ionization damage.

The behavior of the TaO_x devices irradiated with 800 keV Ta ions appears more consistent and stable after irradiation compared to the post-irradiation off-state resistance degradation seen in the TiO_2 devices irradiated with 800 keV Ta ions in this work, though further investigation on a larger number of devices would be useful. Additionally, TaO_x devices show the potential to recover degraded resistance due to displacement damage with repeated cycles. Further investigation is required to identify and understand the different mechanisms responsible for the degradation in these materials. Regardless, device characteristics appear unchanged for both materials at high total doses and fluences and show great promise for use in radiation-hardened non-volatile memory applications.

Acknowledgment

The authors would like to thank K. Myers (Sandia) for packaging and bonding the devices used in this study and D. Buller for running the accelerator at Sandia's Ion Beam Laboratory. They would also like to thank R. Schrimpf (Vanderbilt), B. Doyle (Sandia), J. Stanley (Sandia), S. Swanson (Sandia), M. Van Heukelom (Sandia), and S. Decker (UNM/Sandia) for useful discussions.

References

[1] J. Hutchby and M. Garner, in *Assessment of the Potential & Maturity of Selected Emerging Research Memory Technologies Workshop & ERD/ERM Working Group Meeting*, Jul. 2010.

[2] M. J. Marinella, "The future of memory," presented at the Aerospace Conf., Big Sky, MT, Mar. 2013.

[3] P. R. Mickel, A. J. Lohn, B. J. Choi, J. J. Yang, M.-N. Zhang, M. J. Marinella, C. D. James, and R. S. Williams, "A physical model of switching dynamics in tantalum oxide memristive devices," *Appl. Phys. Lett.*, vol. 102, p. 223502, 2013.

[4] F. Miao, J. P. Strachan, J. J. Yang, M.-X. Zhang, I. Goldfarb, A. C. Torrezan, P. Eschbach, R. D. Kelley, G. Medeiros-Ribeiro, and R. S. Williams, "Anatomy of a nanoscale conduction channel reveals the mechanism of a high-performance memristor," *Adv. Mater.*, vol. 23, pp. 5633–5640, 2011.

[5] J. J. Yang, D. B. Strukov, and D. R. Stewart, "Memristive devices for computing," *Nature Nanotechnol.*, vol. 8, pp. 13–24, 2013.

[6] W. M. Tong, J. J. Yang, P. J. Kuekes, D. R. Stewart, R. S. Williams, E. DeIonno, E. E. King, S. C. Witczak, M. D. Looper, and J. V. Osborn, "Radiation hardness of TiO_2 memristive junctions," *IEEE Trans. Nucl. Sci.*, vol. 57, pp. 1640–1643, Jun. 2010.

[7] H. J. Barnaby, S. Malley, M. Land, S. Charnicki, A. Kathuria, B. Wilkens, E. DeIonno, and W. M. Tong, "Impact of alpha particles on the electrical characteristics of TiO_2 memristors," *IEEE Trans. Nucl. Sci.*, vol. 58, pp. 2838–2844, Dec. 2011.

[8] M. J. Lee, C. B. Lee, D. Lee, S. R. Lee, M. C. Ji, H. Hur, Y.-B. Kim, C.-J. Kim, D. H. Seo, S. Seo, U.-I. Chung, I.-K. Yoo, and K. Kim, "A fast, high-endurance and scalable non-volatile memory device made from asymmetric $Ta_2O_5 - x/TaO_{2-x}$ bilayer structures," *Nat. Mater.*, vol. 10, pp. 625–630, Jul. 2011.

[9] A. C. Torrezan, S. John Paul, M. R. Gilberto, and R. S. Williams, "Sub-nanosecond switching of a tantalum oxide memristor," *Nanotechnology*, vol. 22, pp. 485203-1–485203-8, Dec. 2011.

[10] Z. Wei, Y. Kanzawa, K. Arita, Y. Katoh, K. Kawai, S. Muraoka, S. Mitani, S. Fujii, K. Katayama, M. Iijima, T. Mikawa, T. Ninomiya, R. Miyanaga, Y. Kawashima, K. Tsuji, A. Himeno, T. Okada, R. Azuma, K. Shimakawa, H. Sugaya, T. Takagi, R. Yasuhara, K. Horiba, H. Kumigashira, and M. Oshima, "Highly reliable $\mathrm{TaO_x}$ ReRAM and direct evidence of redox reaction mechanism," *IEDM Tech. Dig*, pp. 1–4, 2008.

[11] M. J. Marinella, S. M. Dalton, P. R. Mickel, P. E. Dodd, M. R. Shaneyfelt, E. Bielejec, G. Vizkelethy, and P. G. Kotula, "Initial assessment of the effects of radiation on the electrical characteristics of $\mathrm{TaO_x}$ memristive memories," *IEEE Trans. Nucl. Sci.*, vol. 59, pp. 2987–2994, Dec. 2012.

[12] Y. Wang, H. Lv, W. Wang, Q. Liu, S. Long, Q. Wang, Z. Huo, S. Zhang, Y. Li, Q. Zuo, W. Lian, J. Yang, and M. Liu, "Highly stable radiation-hardened resistive-switching memory," *Elec. Dev. Lett.*, vol. 31, no. 12, pp. 1470–1472, Dec. 2010.

[13] X. He, W. Wang, B. Butcher, S. Tanachutiwat, and R. E. Geer, "Superior TID hardness in $\mathrm{TiN/HfO_2/TiN}$ ReRAMs after proton radiation," *IEEE Trans. Nucl. Sci.*, vol. 59, no. 5, pp. 2550–2555, Oct. 2012.

[14] J. J. Yang, M. X. Zhang, J. P. Strachan, F. Miao1, M. D. Pickett, R. D. Kelley, G. Medeiros-Ribeiro, and R. S. Williams, "High switching endurance in $\mathrm{TaO_x}$ memristive devices," *Appl. Phys. Lett.*, vol. 97, p. 232102, 2010.

[15] J. F. Ziegler [Online]. Available: www.srim.org, SRIM-2012

[16] M. R. Shaneyfelt, P. S. Winokur, T. L. Meisenheimer, F. W. Sexton, S. B. Roeske, and M. G. Knoll, "Hardness variability in commercial technologies," *IEEE Trans. Nucl. Sci.*, vol. 41, no. 6, pp. 2536–2543, Dec. 1994.

[17] P. S. Winokur, G. K. Lum, M. R. Shaneyfelt, F. W. Sexton, G. L. Hash, and L. Scott, "Use of COTS microelectronics in radiation environments," *IEEE Trans. Nucl. Sci.*, vol. 46, no. 6, pp. 1494–1503, Dec. 1999.

[18] G. L. Hash, M. R. Shaneyfelt, F. W. Sexton, and P. S. Winokur, "Radiation hardness assurance categories for COTS technologies," *Radiation Effects Data Workshop*, pp. 35–40, Jul. 1997.

[19] R. Degraeve, G. Groeseneken, R. Bellens, J. L. Ogier, M. Depas, P. J. Roussel, and H. E. Maes, "A consistent model for the thickness dependence of intrinsic breakdown in ultra-thin oxides," *Tech. Dig. Int. Electron Devices Meet.*, pp. 863–866, 1995.

[20] J. H. Stathis, "Percolation models for gate oxide breakdown," *J. Appl. Phys.*, vol. 86, pp. 5757–5766, 1999.

[21] S. Long, C. Cagli, D. Ielmini, M. Liu, and J. Sune, "Analysis and modeling of resistive switching statistics," *J. Appl. Phys.*, vol. 111, p. 074508, 2012.

[22] E. DeIonno, M. D. Looper, J. V. Osborn, and J. W. Palko, "Displacement damage in $\mathrm{TiO_2}$ memristor devices," *IEEE Trans. Nucl. Sci.*, vol. 60, no. 2, pp. 1379–1383, Apr. 2013.

[23] L. Zhang, R. Huang, D. Gao, P. Yue, P. Tang, F. Tan, Y. Cai, and Y. Wang, "Total ionizing dose (TID) effects on $\mathrm{TaO_x}$-based resistance change memory," *IEEE Trans. Elect. Dev.*, vol. 58, no. 8, pp. 2800–2804, Aug. 2011.