Ionizing Radiation Effects on Nonvolatile Memory Properties of Programmable Metallization Cells

J. L. Taggart, Student Member, IEEE, Y. Gonzalez-Velo, Member, IEEE, D. Mahalanabis, Student Member, IEEE, A. Mahmud, Student Member, IEEE, H. J. Barnaby, Senior Member, IEEE, M. N. Kozicki, Member, IEEE, K. E. Holbert, Senior Member, IEEE, M. Mitkova, Senior Member, IEEE, K. Wolf, Student Member, IEEE, E. Deionno, and A. L. White

Abstract—The impact of ionizing radiation on the retention and endurance of programmable metallization cells (PMC) ReRAM cells is investigated and presented for the first time, with additional work on resistance switching. This study shows that $^{60}$Co gamma-ray exposure has a minimal effect on the retention of PMC devices, up to a total ionizing dose (TID) of 2.8 Mrad ($^{60}$Co, $^{60}$Co), the maximum TID level tested. The retention of both high resistance states (HRS) and low resistance states (LRS) during exposure was tested. Endurance appears to be slightly reduced with gamma-ray exposure. The endurance was tested to maximum TID of 4.62 Mrad ($^{60}$Co, $^{60}$Co). DC response characterizations were also performed on PMC devices after cumulative dose exposures with 50 MeV protons and 100 keV electrons. The data show that PMCs are most sensitive to proton irradiation incident from the backside of the device. For the electron exposures, it is shown that the LRS is mostly unaffected, but the HRS drifts to lower resistance values with an increase in radiation exposure.

Index Terms—CBRAM, chalcogenide, conductive bridging RAM, endurance, ionizing radiation, memory, nano-ionic memory, non-volatile, PMC, programmable metallization cell, ReRAM, retention, total ionizing dose.

I. INTRODUCTION

PROGRAMMABLE metallization cells (PMCs) [1] are a novel type of nano-ionic resistive random access memory (ReRAM) [2], [3]. They are recognized as one of the most promising alternatives to Flash technology for nonvolatile memory applications [4]. PMC devices also exhibit properties that suggest their suitability for neuromorphic computation [5], [6]. It has been shown that the basic functionality of most ReRAM technologies (i.e., both cation based and anion based) is largely unaffected by exposure to ionizing radiation, even at high total dose levels [7]–[10]. In the case of PMCs, previous works have demonstrated that dc resistance switching is maintained after $^{60}$Co gamma-ray exposure to total ionizing dose (TID) levels as high as 10 Mrad(Ge$_{30}$Se$_{70}$) [9], [10]. A recent study also presented the effects of ionizing radiation on data retention in a 128 kbit conductive bridge random access memory (CBRAM), a commercial variant of PMCs [11], [12], but only to a TID up to 5 Mrad(Si) [13], [14]. In this work we report for the first time the impact of high levels of ionizing radiation ($^{60}$Co gamma-rays) on PMC data retention and cycling endurance. Investigations of the dc resistance switching response of PMCs are also expanded to a broader class of ionizing particles (i.e., electrons and protons).

In the results and discussion section, we present data showing the impact of $^{60}$Co gamma-rays exposure on memory retention in the PMC’s low resistance state (LRS) and high resistance state (HRS). The results of endurance testing on gamma-irradiated PMCs are also reported. Finally, the resistance switching response of PMCs exposed to 100 keV electrons and 50 MeV protons are presented. The experimental results reveal that none of the critical specifications of PMCs are drastically modified by ionizing radiation exposure, which further demonstrates the high level of radiation tolerance in this technology. Some of the radiation-induced effects observed in the endurance testing are examined in more detail in order to understand the broader impact of irradiation on actual memory arrays.

II. DEVICE STRUCTURE AND OPERATION

A. Technology Overview

PMC devices are a simple stacked structure. The device consists of a thin film of nickel as the bottom inert electrode (cathode), interfaced to a solid-electrolyte layer of chalcogenide glass (amorphous Ge$_{30}$Se$_{70}$) photo-doped with silver and a thin layer of silver for the top active electrode (anode). The silver contact is partially covered with aluminum to ensure good contact when probing or packaging the devices. A micrograph and cutaway diagram of the layers is shown in Fig. 1. This technology relies on oxidation and reduction reactions to form a conductive silver filament through the electrolyte layer [1]–[3]. When a positive bias is applied to the top active electrode, the silver is oxidized (loses electrons), creating silver cations that migrate through the Ge$_{30}$Se$_{70}$, and reduce (gains electron) on the inert nickel (grounded) contact. In a short amount of time (~ 61 ns), a conductive filament composed of metallic bonded silver will form to complete a low resistance connection to the
silver top layer [Fig. 2(c)] [15]. The resistance of the filament can be further decreased by applying a bias until a specified compliance current is reached. The larger the compliance current, the thicker the filament [16], [17]. To dissolve the silver filament, a negative bias is applied to the top active contact with respect to the inert contact. Under this condition, the silver is oxidized, and migrates back to the active silver contact, resulting in a high resistance across the device. The process of filament creation and dissolution is illustrated in Figs. 2(a)–2(f). When considering memory applications, the programmed low resistance state (LRS) can represent one bit value while the high resistance state (HRS) represents another.

PMC devices can be programmed by sweeping the active contact voltage to a positive value and erased by sweeping to a negative value. The programmed LRS is controlled by limiting the current. The higher the compliance current (I_{prog}), the thicker the filament, resulting in a resistance lower than that of a filament formed at a lower current compliance. A typical current-voltage (I-V) curve is shown in Fig. 3. The resistance state of the device can be measured by applying a small voltage (less than the programming threshold) and measuring the current.

B. Device Fabrication

The results presented in this paper are obtained on three different batches of PMCs, all manufactured in the NanoFab facility at Arizona State University. The fabrication process starts by depositing 100 nm insulating layer of SiO₂ on a silicon wafer using a TorrVac VC-320 electron-beam evaporator. A 100 nm thin-film of nickel is evaporated without braking vacuum in the TorrVac. For the devices used during retention testing, the wafer is removed from the TorrVac and the nickel layer is etched to form dog bone style cathode contact bars. The batches used during endurance testing and resistance switching testing have
a continuous, unaltered, thin-film layer of nickel as the cathode contact. After nickel deposition and etching, the wafer is placed back into the TorrVac and 100 nm of SiO₂ is deposited and thenetched to form vias to the cathode contact. The wafer is then placed in a Cressington 308 thermal evaporator where 60 nm of Ge₃₅Se₇₀, followed by 30 nm of silver film is deposited. The wafer is removed from the Cressington and placed under a UV (λ = 324 nm, 300 mJ/cm²) lamp for 1 hour to photo-dope the chalcogenide layer with the 30 nm of silver. After doping, the wafer is placed back into the Cressington where an additional 35 nm of silver is deposited to create the device anode. In the final steps, a total of 800 nm of aluminum is deposited using the TorrVac to create the contact pads for the anode and cathode. For the crossbar style devices used during retention testing, 400 nm of aluminum is first deposited and lifted off to create the top dog bone contact with an additional 400 nm of aluminum deposited on the contact pads at the ends of the nickel and aluminum dog bones.

The results presented on the resistance switching capabilities were obtained on the same batch of devices used in [9]. The cycling results were obtained on devices from a different, more recent batch with a postprocessing annealing performed at 80 °C for 1 hour. The crossbar devices were annealed in air at 120 °C for 20 minutes.

III. EXPERIMENT SETUP

A. Memory Retention After γ-Ray Exposures

During a retention test, the value of the programmed resistance state is measured periodically to investigate the nonvolatility of the memory cell. The devices were packaged open top, with no lid. Retention testing after TID exposure was conducted on three PMCs programmed in the LRS and five PMCs erased into the HRS. The four devices were programmed into a LRS by sweeping the voltage at the anode of the PMC from 0 V to 0.5 V and limiting the maximum current to a 1 μA compliance, as shown in the “Set” curve in Fig. 3. The five devices in HRS were erased by sweeping the voltage across the anode to cathode from 0 V to −0.5 V as shown in the “Erase” curve in Fig. 3. Two control devices were programmed to a LRS limited with a 1 μA compliance and were not exposed to gamma radiation. Another two devices were used as the control for the HRS and were also not exposed to gamma-ray radiation. All tested devices were 5 μm in diameter.

The devices were exposed with all pins left floating in a Gammacell 220 at a dose rate of 478.5 rad [Ge₃₅Se₇₀]/min. The retention measurements were conducted after each dose step, using an Agilent 4156C semiconductor parameter analyzer connected, via low noise triaxial cables, to an Agilent 16442B test fixture with a 28 pin DIP socket fixture. The resistance state was measured by sampling the current when 10 mV was applied continuously from anode to cathode.

B. Cycling Endurance After γ-Ray Exposures

In a cycling or endurance test, the ability of a memory cell to be set to the LRS and reset to the HRS repeatedly is investigated. This cycling test is performed by applying a train of voltage pulses to set and reset the PMC cell. The setup used to conduct the test is described in Fig. 4. A positive voltage pulse applied on the anode of the device sets it to the LRS, whereas a negative voltage pulse resets it to the HRS (Fig. 5). In this method, the device resistance is manipulated by applying a bias for a fixed amount of time. The longer the bias is applied, the lower the resistance will become as the filament broadens. For the 10 ms pulsewidth used in this experiment, the LRS is approximately 10Ω (shown in Fig. 7), which corresponds to a compliance current of 1 mA when using a compliance current method for programming [17].

After the write and erase pulses, a small amplitude pulse is applied to sense the resistance value of the PMC. An arbitrary waveform generator (Tektronix AWG 520) was used to generate the pulse train of write/read/erase/read signals. An oscilloscope (Agilent 54832D MSO) was used to retrieve the signals to observe if the cells were set or reset, and to compute the resistance values after a given number of cycles. This is the first time that this type of characterization has been performed on irradiated PMCs.

Several tiles of bare devices were initially placed in the Gam-macell 220 with contacts left floating. At periodic TID, a tile of devices was removed, leaving the remaining devices to be exposed to higher TID. The removed devices were cycled as described above, until the HRS began to decrease. The devices exposed to gamma-ray radiation were compared to the behavior of control devices not exposed to radiation.
Fig. 6. Retention of PMC devices initially programmed to a LRS with $I_{\text{prog}} = 1 \mu$A, and devices erased into a HRS then exposed to an accumulative TID of 2.8 Mrad (Ge$_{30}$S$_{70}$). The control (Ctrl) devices were not exposed to radiation.

C. DC Resistance Switching After Electron and Proton Exposures

Exposure to 100 keV electrons was conducted on PMCs devices at The Aerospace Corporation. Devices were step stressed to increasing fluence (i.e., increasing dose) then swept from 0.5 V to 0.5 V and back to 0.5 V at the end of each exposure step to retrieve the resistance switching characteristics and obtain the typical $R_{\text{on}}$ and $R_{\text{off}}$ values [9]. The samples’ pins were left floating during exposure. A total of 24 devices with a diameter of 5 $\mu$m were characterized. Those devices were divided in three sets of samples switched/programmed with different programming currents ($I_{\text{prog}} = 10 \mu$A, 50 $\mu$A, 100 $\mu$A). For each $I_{\text{prog}}$, six PMCs have been exposed to electrons and characterized and two PMCs have been characterized as control parts. 50 MeV proton exposures were conducted at the UCB-LBNL cyclotron, with PMCs exposed from the front side and from the backside. Only one fluence of 90 $\mu$m was used during the proton exposures. Similar to the electron tests, different sets of PMCs have been characterized before and after exposure with $I_{\text{prog}} = 10 \mu$A, 50 $\mu$A and 100 $\mu$A.

IV. RESULTS AND DISCUSSION

A. Memory Retention After $\gamma$-Ray Exposures

Results obtained on exposed (as a function of time and TID) and control devices (as a function of time) are presented in Fig. 6. Control measurements were performed on four devices, two in the LRS and two in the HRS. For the exposed devices, five devices were erased into the HRS and four devices were programmed to a LRS using $I_{\text{prog}} = 1 \mu$A. It is shown that devices in both the LRS and HRS maintained state for TID up to 2.8 Mrad(Ge$_{30}$S$_{70}$) (the maximum TID tested on the presented parts).

The hashed area in Fig. 6 defines the HRS. The HRS of individual device varied between 1.3 M$\Omega$ to 200 M$\Omega$. The threshold of 4.5 M$\Omega$ is the median HRS of the 13 devices tested before exposure to radiation. The trends shown in Fig. 6 are the mean state of the devices tested for each condition. The whiskers show the minimum and maximum range of values. As shown in Fig. 6, no abrupt state change (LRS to HRS or HRS to LRS) occurred due to radiation exposure. The LRS of the exposed devices increased within the first 24 hours of the test but this behavior was also seen in the control devices. Exposure to $^{90}\text{Sr}$ does not appear to have a significant effect on the retention behavior of the LRS. The HRS of the exposed devices remained stable during the entire test. Over time, the HRS control devices drifted to higher resistances.

One control device programed to the HRS and one programmed to the LRS, suddenly went low, shown by the long whiskers around 4000 minutes in Fig. 6. This behavior has been seen several times during the testing of these devices. Each time a control measurement was taken, the packaged tile was placed in the test fixture for the duration of the measurement, then promptly removed and placed in a light-tight box. The act of placing the package in and removing the package from the test fixture, may have resulted in a static discharge that caused two of the control devices to program to a lower resistance state. The reason for this test procedure was to mimic the testing procedure of the irradiated devices. After each dose step, the irradiated packages were removed from the Gammacell and placed in the test fixture to obtain measurements. The package was then removed from the test fixture and placed back in the Gammacell for the next dose.

B. Cycling Endurance After $\gamma$-Ray Exposures

Representative endurance plots (where the HRS and LRS resistance values are plotted as a function of the cycle number) for devices exposed to incremental TID are presented in Fig. 7. The trend lines for each total dose and control in Fig. 7 is the mean of three devices for a total of 12 devices tested.

For the control devices tested in this work, the maximum number of cycles achieved was generally between $1.5 \times 10^4$ to $2 \times 10^4$ cycles. As shown in Fig. 7, the control begins to exhibit a decrease in the HRS resistance after $10^4$ cycles. After $1.5 \times 10^4$ cycles, the ratio between the HRS and LRS of the control reduced below 100, constituting a failure for this scenario. Irradiated devices were cycled up until $1 \times 10^4$ cycles, the value at which the control devices began to deteriorate.
C. DC Resistance Switching After Electron and Proton Exposures

Fig. 8 shows the cumulative distributions of $R_{on}$ and $R_{off}$ switched with an $I_{prog} = 10 \ \mu A$ for 100 keV electron exposure. Similar results were observed for devices programmed with $I_{prog} = 50 \ \mu A$ and 100 $\mu A$. It is shown that $R_{on}$ does not vary with TID [Fig. 8(a)], whereas $R_{off}$ is observed to decrease with exposure for TID higher than 100 krad ($\text{Ge}_{35}\text{Se}_{70}$) [Fig. 8(b)]. This decrease in $R_{off}$ is also observed on devices characterized with all three programming current compliance levels. The five LRS data points that overlap into the HRS are due to a device that switched to a high resistance during its programming sweep. This behavior may be due to a weak point in the formed filament. It is clear from Fig. 8(c) that the majority distribution of HRS resistance $R_{off}$ (red symbols) and LRS resistance $R_{on}$ (black symbols) do not overlap even after exposure to electrons up to 12 Mrad ($\text{Ge}_{35}\text{Se}_{70}$), further demonstrating the radiation hardness in the switching characteristics of PMCs.

In Fig. 9 and Fig. 10, cumulative distributions obtained on devices exposed to 50 MeV protons incident to the front side and back side of the devices are presented. The devices were switched using a dc sweep with an $I_{prog}$ of 50 $\mu A$ [Fig. 9, Fig. 10(a)] and $I_{prog}$ of 100 $\mu A$ [Fig. 10(b)]. For the proton exposures, a decrease in $R_{off}$ was observed for both back and front side exposed devices. A slight decrease of the $R_{on}$ is also observed for the samples exposed from the back and switched with the higher programming currents (100 $\mu A$). The shift in $R_{off}$ is seen to be more significant due to back side irradiation than from front side. When exposed from the back side, protons travel through 500 $\mu m$ of Si, 100 nm of SiO$_2$, and 100 nm of Ni before entering the active $\text{Ge}_{35}\text{Se}_{70}$ region. Nuclear interactions in the silicon substrate layer may induce cascades of recoiled nuclei that result in displacement damage and ionization in the device layers [18]. During front side irradiation, the proton is directly incident on the active layers of the PMC device which consists of 35 nm of Ag, and 60 nm of $\text{Ge}_{35}\text{Se}_{70}$. The 50 MeV protons pass through the active layers with little interaction during front side irradiation.

V. CONCLUSION

The impact of total ionizing dose on the retention and endurance of PMC memory cells is investigated for the first time in this work. PMCs are used as memory cells in novel commercial NVM circuits (e.g., CBRAM technology), and the effects studied on PMCs could enable a better understanding of the impact of radiation on such memory circuits and any other applications based on PMC or CBRAM technology. It has previously been shown that for metal-oxide based ReRAM cells exposed to gamma-rays and x-rays, the most sensitive state is the HRS [8]. In this work, it is shown that $^{60}$Co gamma ray exposure levels up to 2.8 Mrad ($\text{Ge}_{35}\text{Se}_{70}$) have little impact on the LRS and HRS retention of these devices. Similar to what has been observed on metal-oxide based ReRAM, the LRS is maintained after several
Fig. 10. Cumulative distribution of $R_{on}$ and $R_{off}$ after 50 MeV proton back side (Ni cathode end) exposure. $R_{on}$ and $R_{off}$ values are obtained at 50 mV on the dc resistance switching characteristic. (a) Programming current of 50 $\mu$A. (b) Programming current of 100 $\mu$A.

Mrad of total dose. This is a result that expands upon recent studies [13], [14] of retention conducted directly on a commercial GeS$_2$ based CBRAM memory circuit (128 kbit EEPROM type circuit), where it was found that for TIDs up to 5 Mrad no errors appeared on the data stored in the memory array. The endurance of PMCs was shown here to be impacted by TID with a decrease in the total number of set/reset cycles that can be performed on the cells after exposure. Nevertheless, no decrease in dynamic range was observed on the exposed cells (the HRS and LRS maintain the same resistance levels and the same $R_{off}/R_{on}$ ratio) for cycles below $10^4$. The resistance switching of PMCs during 100 keV electron exposures and 50 MeV proton exposures for high levels of TID is also presented in this work and expands upon previous studies conducted with $^{60}$Co gamma–rays [9]. It has been shown that 100 keV electron irradiation reduces the HRS with increasing dose. When exposed to 50 MeV protons, no effect is seen during front side irradiation but the HRS decreases after back side exposure. This shift is most likely due to recoiled particles from the substrate layers that induces ionization in the active device layers. The results obtained during these studies confirms the ability to maintain functionality, the ability to program the PMC devices to a HRS or LRS state, after exposure to various radiation environments.

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**REFERENCES**


