γ-ray -induced Effects in Al:HfO_2-based Memristor Devices for Memory and Sensor Applications

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***Abstract*—We observe that γ-ray radiation affects the formation of the conducting bridge in Ag/Ti/Al:HfO_2/Pt devices. We suggest that the γ-ray breaks Hf-O bonds and affects the properties of metal/insulator interfaces. The radiation-induced interfacial layers promote the transition from write-once-read-many times (WORM) to reversible switching memories. The devices that undergo a higher radiation exposure exhibit a higher forming voltage that we could exploit to sense radiation; an electrical circuit to harness this phenomenon is also proposed. We also observe that the devices exhibit self-healing behavior, where the forming behavior restores once the radiation energy is released. The switching mechanism is explained and proposed to elucidate this phenomenon. This study not only provides insight into the development of memristor devices for space application but also their potential as multipurpose elements for reconfigurable circuits.**

***Index Terms*—Resistive memories, radiation sensors, total ionizing dose, ^{60}Co, γ-ray, hafnium oxide, memristor.**

I. Introduction

MEMRISTOR offers excellent promises for space applications due to its facile architecture, lightweight design, and low power consumption [1]; rad-hard memristors could realise future compute machines in space. Satellites lack computing capability since today's technology still relies on transistor-based compute machines, which are less tolerant towards radiation. Moreover, a high-energy radiation environment can also be found near us, from underground physics to nuclear medicine facilities to aerospace; this makes memristor technology have strong potential applications in various sectors.

Several groups suggested that HfO_2-based memristors are intrinsically rad-hard [2]–[6]. However, these reports focus on the reliability studies of the devices, while the potential beyond erasable memory applications exploiting radiation-induced effects has not yet been explored. Memristor is a metal/insulator/metal two-terminal sandwich device which operates based on the redox process in the cell to form and rupture a conduction channel across the insulator. The conduction channel controls the electron flow from the cathode to the anode and can consist of an oxygen vacancy filament [7], a metallic conducting bridge [8] or a combination of both [9]. In this work, we investigate the impact of ionizing γ-radiation on the formation of the conduction channel and exploit the phenomenon for potential applications in in-/erasable memories and radiation sensors.

II. Experimental Setup

The cross-point devices based on Ag/Ti/Al:HfO_2/Pt memristor stack having cell sizes of 1.5x1.5 µm and 55x55 µm were fabricated using a lithography technique. A 25-nm Pt bottom electrode (BE) with a 50 nm Ti adhesion layer was deposited on a SiO_2 substrate. Thereafter, 7-nm Al:HfO_2 with 6% Al film was deposited using an atomic layer deposition technique employing (Veeco Savannah S200) at 200 ºC using tetrakis (dimethylamino)hafnium (TDMAH, $Hf(N(CH_3)_2)_4$, Sigma-Aldrich),trimethylaluminum (TMA.$Al(CH_3)_3$ Sigma-Aldrich), and H_2O precursors. The Ag/Ti top electrode (TE) consists of a 30 nm Ag and 3.5-nm Ti stack. All metal depositions were conducted using an e-gun evaporator (Lab

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700, Leybold Optics GmbH). The devices were exposed to a γ-ray with a total ionizing dose of 0, 50 krad, and 5 Mrad (dose rate of 74,2 krad/hour, employing a ^{60}Co radioactive material at NTHU Radiation Center, Taiwan). Materials analysis was conducted using an X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM). The electrical characteristics were measured using a semiconductor analyzer (B1500 Keysight); the voltage sweep was applied on the TE while the BE was grounded, and a current compliance of 10 μA was used in the first sweep. Unless specified, the characterizations were conducted within 1 hour following the radiation exposure.

III. Results and Discussion

In pristine condition, the device exhibits write-once-read-many-times (WORM) behavior. The forming process switched the device from the pristine state to the low resistance state (LRS, On), and this process can be done either by positive or negative forming; however, the device is unable to be switched Off after the forming process, as shown in Figures 1(a) and (b). Neither subsequent negative nor positive sweeps up to 5 V can switch the device from LRS to a high resistance state (HRS, Off).

On the other hand, the device that receives a radiation dose of 5 Mrad is able to switch On and Off, as shown in Fig. 1(c). The first sweep process occurs at approximately +8 V; however, the subsequent negative sweep starts from an HRS and switches to an LRS, indicating a two-step forming process that involves both positive and negative sweeps. Hereafter, the device can be switched back to the HRS by employing a positive sweep to perform a reset process, and the switching process can be executed repeatedly, as depicted in Fig. 1(d), indicating its potential application for rewritable memories.

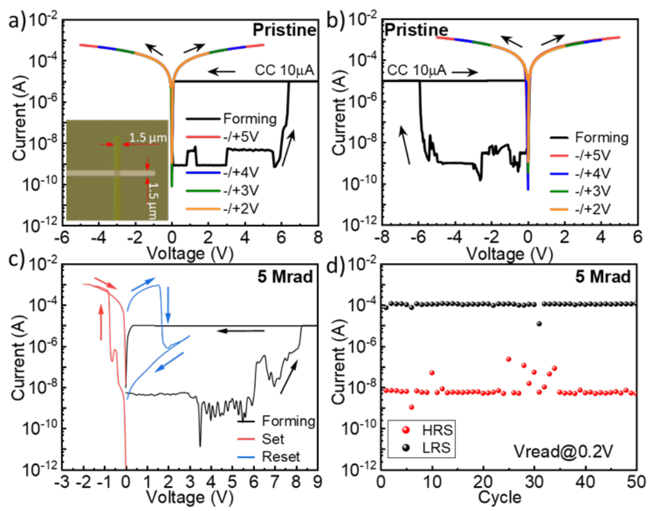

Fig. 1. Typical I-V curves of 1.5x1.5 μm devices (a) pristine device with positive and (b) negative forming, and (c) the device after 5 Mrad of γ-ray radiation. (d) Repeatable switching of the device (c). Inset in (a) shows the optical micrograph of a 1.5x1.5 μm cross-point architecture of the device.

We notice there is a significant increase in forming voltage (V_{form}) after radiation (Fig. 1(c)). We ran some tests to confirm whether there is a relationship between the radiation doses and the V_{form}, and the results are shown in Figure 2. We found that the devices tend to have a higher V_{form} as the dose increases, as depicted in Fig. 2(d). We also prepared control samples exposed to radiation and measured their electrical characteristics after 30 days; interestingly, regardless of the number of doses, all devices have V_{form} similar to the Pristine sample. This indicates that the devices are showing self-healing capability.

We hypothesized that the radiation might affect the quality of the Ti/Al:HfO_2 interface due to the radiation-induced defects in HfO_2 films [3], [6], [10]–[13]. To validate this hypothesis, we measured larger devices having an area of 3025 μm^2 (data not shown). We found that the V_{form} of the 3025 μm^2 pristine devices is similar to the V_{form} of the 2.25 μm^2 pristine devices (Fig. 2(a)); however, the V_{form} of the 3025 μm^2 irradiated devices increases significantly, ranging from 9 V to 20 V, with high fluctuation. This indicates that the interfacial effect rules the forming characteristics of the device [13], [14].

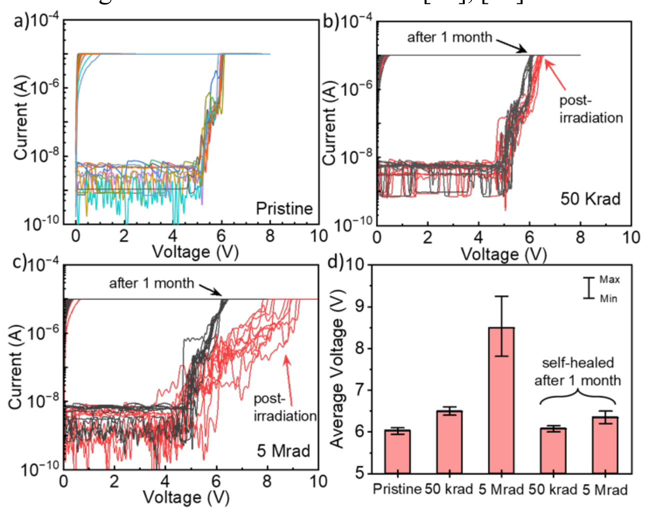

Fig. 2. Forming curves of 10 1.5x1.5 μm devices selected randomly (a) pristine, (b) 50 krad, and (c) 5 Mrad. (d) Average forming voltage of devices with different conditions.

It is reported that the concentration and distribution of oxygen play a significant role in the switching behaviour of memristor devices [9]; hence, we analysed the Hf4f peak XPS spectra to elucidate this phenomenon and the result is shown in Figure 3. We found that the irradiated sample has more of 3+ which is approximately 20%, while it is approximately 15% for the pristine sample. This indicates that the γ-ray radiation breaks Hf-O bonds and creates Vo defects in HfO_2 films [2]–[5], [15]–[17]. Note that no trace of Hf or Al metal states was detected, indicating both elements are in the oxidised state, and thus, the metal inclusion does not play a significant role in governing the switching characteristics in our devices [17]. Based on the above XPS analysis, we propose the switching schematic depicted in Figure 4 to explain the radiation-induced effects in our devices.

We suggest that the radiation not only breaks the Hf-O bonding in the lattice and generates the Vo defects but also drives oxygen ions to the top and bottom interfaces, forming TiOx and PtOx interfacial layers (Fig. 4(ii)). This will increase the effective thickness and electron barrier at the Ti/Al:HfO_2 interface. Thus, it limits the drift of Ag ions into the Al:HfO_2 layer during the forming process [8] (Fig. 4(iii)). Moreover, the PtOx layer also increases the electron barrier at the bottom interface Al:HfO_2/Pt[18]. Hence, the irradiated device requires a higher V_{form} to form a conducting bridge (Figs.1 and 2)[19]. However, these interstitial oxygens at the interfaces will diffuse back to the Al:HfO_2 once the radiation energy is released from the device due to the higher Gibbs free energy oxide formation of HfO_2 (ΔGf°= -1010 kJ/mol kJ/mole) than that of TiOy (ΔGf°= -513 – (-889) kJ/mole), and PtOx (ΔGf°= 1678 kJ/mol)[20], [21]; note that the ΔGf° is positive meaning the Pt-O bonds can be easily dissociated upon the release of radiation energy. Consequently, the devices exhibit a self-healing phenomenon (Figs. 2(b) and (c), Fig. 4(i)).

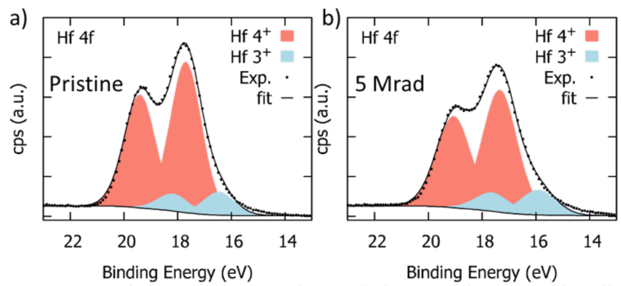

Figure 3. (a) Hf4f XPS spectra of (a) pristine and (b) 5Mrad irradiated Al:HfOx thin films.

We also suggest that the radiation-induced dissociation of Hf-O bonds helps to activate the reversible switching by reducing the excessive number of Ag ions drifting into the Al: HfO_2 layer. Without irradiation, the positive bias forming will ionize abundance Ag ions and drift to the Al:HfO_2 layer, making strong conducting bridges that cannot be ruptured during the reset process (Fig. 1(a), Fig 4(iv)) [22]. Similarly, the use of negative bias forming makes strong Vo filaments that induce high electron conduction between BE and TE, which makes it unable to ionize a sufficient amount of oxygen from the bottom interface to rupture the filament during the reset process [7]. As the TiOx barrier layer increases after irradiation, the positive bias forming can only trigger the drift of a number of Ag ions into the HfO_2 layer, making a weak conducting bridge. This weak bridge will instantaneously rupture when the electrical sweep is released, but it will serve as a seed for forming a complete conduction channel consisting of Vo-Ag ions defects upon the second step forming (negative bias)[23].

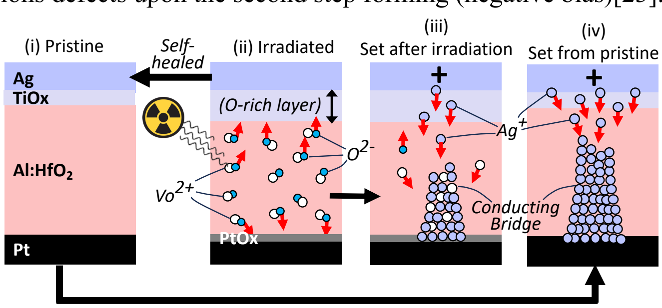

Figure 4. Schematic of the switching mechanism with and without irradiation.

This radiation-induced V_{form} changes phenomenon could be exploited for radiation sensor applications. As a proof of concept, we proposed a circuit to extract the V_{form} where the value can be calibrated to measure the corresponding doses the devices absorbed, as depicted in Figure 3. The voltage applied to the memristor is regulated by LM723, in which the output voltage range varies from 2 V to 28 V. The voltage increase is stepped by the digital potentiometer X9C103, which is controlled by the microcontroller. Once the voltage is biased to the memristor, the current flows to R4 and is detected by INA190. Therefore, the microcontroller calculates the average forming voltage and the compliance current. Fig. 5(b) shows the example measurement for the radiated device (5 Mrad). Our sensing method has several advantages compared to another proposed method[24]: (1) from a circuit-level perspective, our sensor is based on voltage changes, which is more straightforward in determining the dose, while another method relies on the switching speed that requires a clock component to read the signal; moreover, the switching speed in their method is up to 850 sec while ours is less than 1ms under DC operation which is more appealing for faster data acquisition. (2) from a device-level perspective, our device only requires a 7 nm switching layer rather than tens of μm thick to sense high radiation doses, showing potential for implementation in high-density embedded systems.

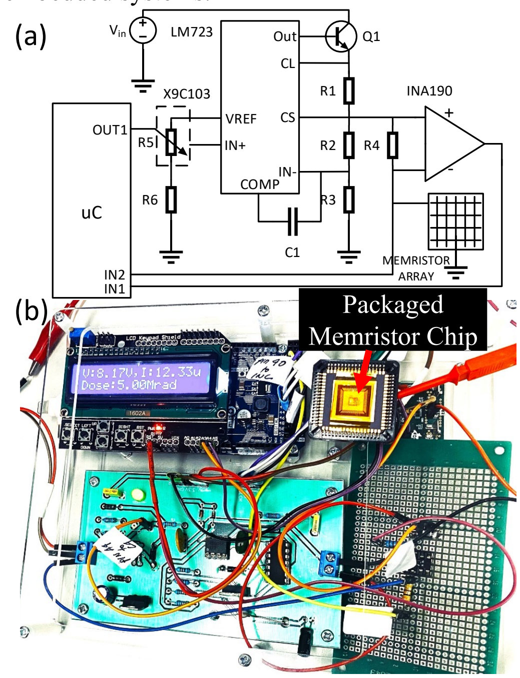

Figure 5. (a) Diagram of the Radiation Sensory System (RADSYS) circuit and (b) RADSYS prototype showing radiation dose received by the packaged chip.

IV. Conclusion

The devices prior to ionizing radiation can only be switched once; nevertheless, this behaviour could be useful for WORM memory applications. The radiation-induced defects in the Al:HfO_2 layer help to increase the effectiveness of the barrier layer, hindering an excessive number of Ag ions drifting into the switching layer during the forming process and leading to stable reversible switching, making it suitable for rewritable memory applications. The increase of the barrier layer after radiation leads to an increase in the forming voltage of the devices, and we exploited this phenomenon for radiation sensor applications that could be useful for measuring radiation doses in electronics; a circuit is developed as a proof concept. Further investigation into the relationship between the properties of radiation-induced interfacial layers via electron microscopy and the self-healing phenomenon is still underway.

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