Electrical characterization of defects created by γ-radiation in HfO_2-based MIS structures for RRAM applications

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Abstract

The γ-radiation effects on the electrical characteristics of MIS capacitors based on HfO_2, and on the resistive switching characteristics of the structures have been studied. The HfO_2 was grown directly on silicon substrates by atomic layer deposition. Some of the capacitors were submitted to a γ ray irradiation using three different doses (16, 96 and 386 kGy). We studied the electrical characteristics in the pristine state of the capacitors. The radiation increased the interfacial state densities at the insulator/semiconductor interface, and the slow traps inside the insulator near the interface. However, the leakage current is not increased by the irradiation, and the conduction mechanism is Poole-Frenkel for all the samples. The switching characteristics were also studied, and no significant differences were obtained in the performance of the devices after having been irradiated, indicating that the fabricated capacitors present good radiation hardness for its use as a RS element.

INTRODUCTION

Advanced microelectronic devices are used in a variety of applications, and some of them are to work in harsh environments, such as space navigation, radiology equipment, instrumentation for nuclear energy plants and detectors for high-energy physics experiments. Metal-insulator-semiconductor (MIS) transistors are often exposed to a flux of particles or photons, and the ionizing radiation effects can give rise to defects inside the insulator, which may degrade device performance and reduce the lifetime. [1,2] However, in some cases the measured defect density remains almost constant due to the approximately equal electron an hole trapping inside the insulator. [3] In addition, a generalized response of high-k based MIS capacitors to irradiation cannot be assumed, because it depends on precursors and processing treatments. [4] For example, S. Maurya [5] observed a decrease in the interfacial state density (D_{it}) when γ-irradiating MIS capacitors using HfO_2 as gate dielectric, whereas other authors observed the opposite behavior in a similar device. [6]

On the other hand, Resistive Random Access memories (RRAMs) are one of the most promising alternatives to substitute flash nonvolatile memories. [7,8] The operation of these devices consists in a change in the electrical resistance of a material, a metal oxide layer usually. A filament formed inside the oxide, between two metal electrodes, is responsible for the resistive switching (RS) phenomenon: [9] a set bias closes the filament obtaining a low resistance state (LRS), whereas a reset bias breaks the filament giving place to a high resistance state (HRS). This behavior has been observed both in MIS and in metal-insulator-metal (MIM) capacitors. In traditional floating gate memories, it is well stablished that γ rays produce electron-hole pairs that can be trapped in the floating gate oxide, degrading the device performance. [10] However, the radiation effects on filamentary based memories are still not fully understood. K. Agashe *et al.* observed a decrease in the resistance value during HRS operation in TiO_2-based MIS capacitors due to the traps created inside the insulator by the radiation. For doses higher than 25 kGy the switching characteristic disappeared.[11] W. Duan *et al.* also founded a decrease in the resistance value during both HRS and LRS operation for WO_x film-based RRAMs. [12] However, in the case of HfO_2, the impact of radiation in the electrical characteristics has been found to be lower: S-H. Lin et al. founded no significant differences in the HRS and LRS values when the samples were γ-irradiated up to doses of 5 Mrads. However, the forming and set voltages decreased when increasing the irradiation dose. [13] R. Fang *et al.* also found no functionality changes in switching devices using hafnium oxide up to doses of 5.2 Mrad (HfO_2). However, they found that the filament weakened after irradiation due to the oxygen vacancies created by the radiation, which could surround the filament. [14]

In this work, we study the effect of γ-radiation on the electrical properties of hafnium oxide (HfO_2)-based MIS capacitors. In order to study the radiation effects, the electrical measurements were carried out before and after being exposed to three different irradiation doses (16.1 kGy, 96.6 kGy, and 386.4 kGy), using capacitance-voltage (C-V), deep level transient spectroscopy (DLTS), flat-band voltage transients (V_{FB}-t), and current-voltage (I-V) measurements. These capacitors are to be used as resistive switching devices, so we have also studied the effect of the radiation on the HRS and LRS resistance values and on the set and reset voltages.

EXPERIMENTAL SET-UP

The HfO_2 dielectric layers were atomic layer deposited (ALD) at 225 ºC on <100> n-type silicon wafers with resistivity in the range 7 – 13 mΩ cm. Tetrakis(dimethylamino)hafnium was used as the hafnium precursor, and water was used as the oxygen precursor. Nitrogen was used as carrier and purge gas. The thickness of the HfO_2 layers was 20 nm. After the oxide deposition, 200-nm-thick Ni metal electrodes were deposited by magnetron sputtering.

Some of the capacitors were subjected to a γ-ray (^{60}Co) irradiation, using an irradiation rate of 15 kGy/h. Three different doses were applied to the samples: 16.1 kGy (1 h irradiation), 96.6 kGy (6 h irradiation) and 386.4 kGy (24 h irradiation). No bias was applied to the samples during the irradiation.

The electrical measurements in the pristine state were carried out putting the sample in a light-tight electrically shielded Oxford DM1710 cryostat. The electrical parameters were measured at several temperatures ranging from the liquid nitrogen temperature (≈ 77 K) to room temperature. The temperature was monitored and kept constant using an Oxford ITC 502 temperature controller. C-V measurements were carried out using an Agilent 4294A Impedance Analyzer. Deep level transient spectroscopy technique was used to measure the interfacial state density (D_{it}). The measurement was carried out using a Boonton 72B capacitance meter, an HP 54501A digital oscilloscope to record the capacitance transients, and an HP 8112A pulse generator to apply the bias pulses. I-V curves were measured using an HP 4155B Semiconductor Parameter Analyzer. Finally, an Agilent N6700B bias source, a Keithley 6517A electrometer, and the Boonton capacitance meter were used for recording the V_{FB} transients. The resistive switching characteristics were obtained at room temperature, using the HP 4155B Semiconductor Parameter Analyzer.

EXPERIMENTAL RESULTS

The metal-insulator-semiconductor structures were first studied at a pristine state (not electroformed), so the filament had not been formed yet. Figure 1 shows the normalized capacitance-voltage characteristics measured at 100 kHz and room temperature. The stretch-out of the C-V curves is larger when the capacitors are irradiated. This means the irradiation has damaged the insulator/semiconductor interface, increasing the interfacial state density (D_{it}). The interfacial state density has been measured using the deep level transient spectroscopy technique. DLTS measurements revealed the interfacial state density increased from a value of about 8×10^{11} cm^{-2} eV^{-1} at midgap for non-irradiated samples to values ranging from $(3\text{-}5)\times10^{12}$ cm^{-2} eV^{-1} at midgap regardless of the dose applied. In the case on SiO_2 on silicon, the interfacial state density usually increases, [15] but this does not always happen for HfO_2 on silicon: sometimes the irradiation can improve the interface quality, [16] and even it can get an improvement for low doses but again worsen for high doses. [17] This has sometimes been attributed to a decrease in the oxygen deficiencies. [18]

Figure 1 also shows an increase in the hysteresis amplitude for the irradiated samples. The hysteresis phenomenon in MIS capacitance-voltage curves is related to slow traps inside the insulator, near the interface with the silicon substrate. These traps are also known as disorder-induced gap states (DIGS) due to the model proposed by Hasegawa et al. These defects can trap and detrap charge coming from the semiconductor in a slower way than the interfacial states, as the process in tunneling assisted. [19] The slow traps inside the insulator can be qualitative detected by measuring flat-band voltage transients. To obtain the flat-band voltage transients we use a feedback system that varies the applied gate voltage accordingly to keep the capacitance at its flat-band voltage value. The origin of experimentally observed transients departs from the equation:

$$V_{FB}(t) = \Phi_{MS} - \frac{Q_i}{C_{ox}} - \frac{1}{\varepsilon_{ox}}\int_0^{t_{ox}} \rho_{ox}(x,t)\cdot x\cdot dx \qquad (1)$$

As the oxide charge density, $\rho_{ox}(x,t)$, varies with time and distance due to the trapped charge, variations on the flat-band voltage will appear. Figure 2 shows flat-band voltage transients for non-irradiated and for irradiated samples. The transient amplitude increases for irradiated samples, which implies an increase in the slow traps inside the insulator. We have observed this behavior in MIS capacitors based on Al_2O_3 and HfO_2, and irradiated with electrons, [20] and in Al_2O_3 and Gd_2O_3-based capacitors subjected to a γ-ray irradiation. [21] This behavior does not seem to depend neither on the insulator nor on the type of radiation.

Figure 3 shows the current-voltage (I-V) characteristics. The measurements were carried out in the accumulation regime, i.e., with positive voltage applied to the metal electrode with the silicon substrate grounded. The current density remains below 1 μA/cm^2 up to biases of about +4V regardless the irradiation dose applied to the samples. There are almost no differences in the leakage current before the breakdown. The conduction mechanisms were studied by measuring the leakage current at different temperatures ranging from liquid nitrogen temperature to room temperature. Figure 4 shows, as an example, the I-V curves corresponding to the sample irradiated with a dose of 386.4 kGy. The I-V characteristics in the high electric field range fit the Poole-Frenkel mechanism, as shown in Figure 4. This mechanism is bulk limited, associated with the field enhanced thermal excitation of charge carriers form traps. In the Poole-Frenkel regime, the current follows the equation:

$$I = I_0 exp\left(\frac{\beta_{PF}E^{1/2}}{KT}\right) E \quad (2)$$

The value of the field lowering coefficient, β_{PF}, is very similar for all the samples (2.49×10^{-5} eV m$^{1/2}$ V$^{-1/2}$ for the non-irradiated sample and 2.56×10^{-5} eV m$^{1/2}$ V$^{-1/2}$ for the sample irradiated with the highest dose). The theoretical value is around 4×10^{-5} eV m$^{1/2}$ V$^{-1/2}$ taking into account the HfO_2 refractive index is about 1.8. The discrepancy is small, and could be due to other conduction mechanisms contributing to the total leakage current.

It is known that the radiation breaks Hf-O bonds inside the bulk dielectric, which creates oxygen vacancies and oxygen interstitials. [13] These defects would enhance the leakage current, but in the present case the density of defects seems not to bet high enough to increase leakage current.

After the electrical characterization in the pristine states, we studied the resistive switching behavior. A complete study of the RS behavior of the non-irradiated sample was previously performed. [22] Unipolar switching behavior was observed, as shown in Figure 5, applying negative voltage sweeps to the Ni top electrode with the silicon substrate grounded. The forming step consisted in applying a voltage sweep with a current compliance of 100 μm, which was stopped when the dielectric breakdown occurred and the compliance current was reached. The switching mechanism is the formation and rupture of a metallic conductive filament (CF) between the top electrode and the Si substrate, created during the forming step. This mechanism has been observed not only for Ni electrode, but also for Ta, Pt or Cu. [23] The RS characteristics were obtained for the irradiated samples. Figure 6 shows the cumulative distribution functions of set (V_{SET}) and reset (V_{RESET}) voltages corresponding to 1000 RS cycles. No significant differences were observed for the irradiated samples, since the obtained differences are of the same order of magnitude as the sample-to sample variability. Figure 7 shows the current values measured in the HRS and LRS states, measured at a bias of -0.5 V, after 100 RS cycles. In the high resistance state, the cycle-to-cycle variability is higher than the effect that radiation may have caused. In the low resistance state, the current even seems to decrease for the irradiated samples, although the differences are of the same order of the sample-to-sample variability. Neither the endurance has been affected by the radiation , as after 1000 RS cycles, the window between HRS and LRS states remains about four orders of magnitude. We can conclude that these samples show a good hardness to γ-radiation in the range of the doses applied in this work, for their use as resistive switching devices.

CONCLUSIONS

In this work, we have studied the effect of photon irradiation on the electrical properties of HfO_2-based MIS capacitors using three different irradiation doses. The capacitors are to be used as switching elements for RRAM applications. The dielectric layers were grown using the atomic layer deposition technique. An electrical characterization study was carried out in the pristine state, before the samples were electroformed. C-V characteristics showed a stretch-out when for irradiated samples, indicating an increase in the interfacial state densities between the oxide and the semiconductor. This was confirmed using the deep level transient spectroscopy technique. The C-V characteristics also showed an increase in the hysteresis amplitude, meaning higher defect concentration inside the bulk insulator. The flat-band voltage transients appear due to the charge trapping and detrapping by these slow defects. The flat-band voltage amplitude increased for the irradiated samples. These defects also can increase the leakage current through the insulator. However, we obtained almost the same leakage current regardless of the irradiation dose, so probably, the density of the defects inside the insulator created by the irradiation is not high enough to enhance the leakage current. The conduction mechanisms in the insulator in the pristine state was studied, and we observed a Poole-Frenkel mechanism, as usual in high-k dielectrics. The β_{PF} value was similar in all the samples (about 2.5×10^{-5} eV $m^{1/2}$ $V^{-1/2}$), and very close to the theoretical value.

Then, the samples were electroformed to study the RS characteristics. The samples showed an unipolar switching behavior. The bias at which the forming is performed, the set and rest biases and the resistance in the high and low resistance states remains almost constant for all the irradiation doses. Most of the obtained differences are of the same order of magnitude as the sample-to sample and cicle-to-cycle variabilities. The endurance is also good after 1000 sweeping cycles.

The defects created by the γ-radiation seems not to affect the RS characteristics. The defects created in the oxide/semiconductor interface do not affect the characteristics because in our devices, the metallic conductive filament responsible for the switching mechanism is formed with metal ions coming from the top electrode (Ni in our samples), so the influence of the silicon bottom electrode is of minor importance. On the other hand, the density of the defects created inside the bulk insulator is not high enough to influence the device performance. Although the irradiation can affect the behavior of the MIS capacitor for its use as a transistor (mainly because the interfacial state density will worsens the channel mobility), we can conclude that the structure shows good radiation hardness for its use as a RS element.

ACKNOWLEDGMENTS

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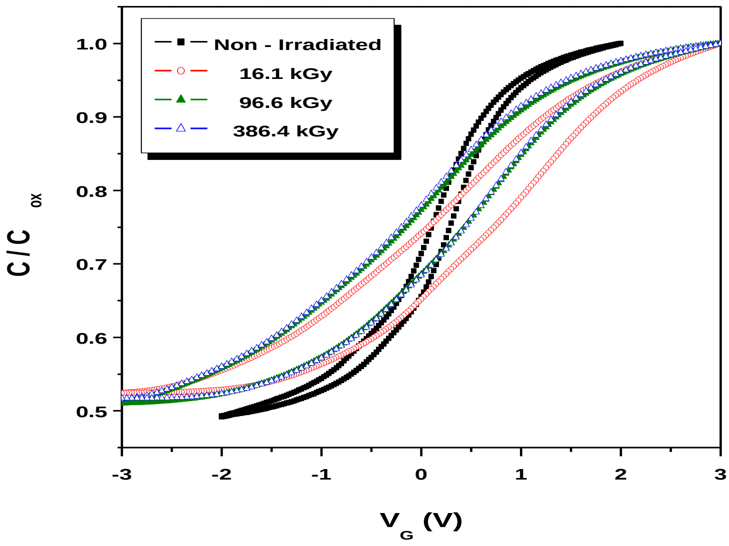

Figure 1. Normalized capacitance-voltage (C-V) characteristics measured at 100 kHz and at room temperature.

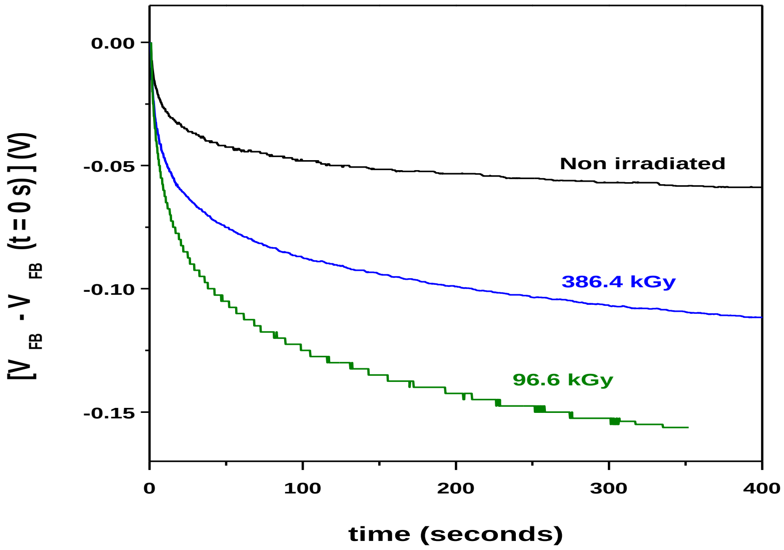

Figure 2.Flat-band voltage transients for non-irradiated and irradiated samples measured at room temperature.

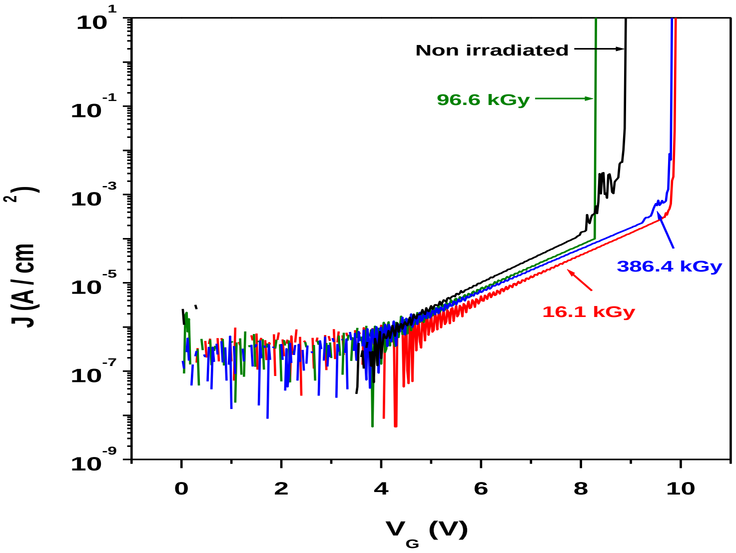

Figure 3. Current-voltage characteristics measured at room temperature for the non-irradiated and irradiated samples.

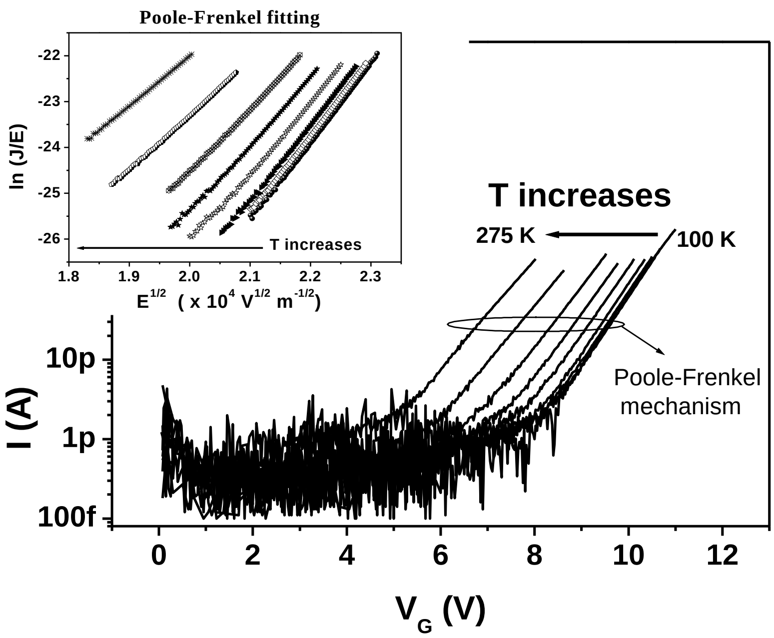

Figure 4. Current–Voltage characteristics measured at several temperatures and Poole-Frenkel fitting corresponding to a sample irradiated with a dose of 386.4 kGy.

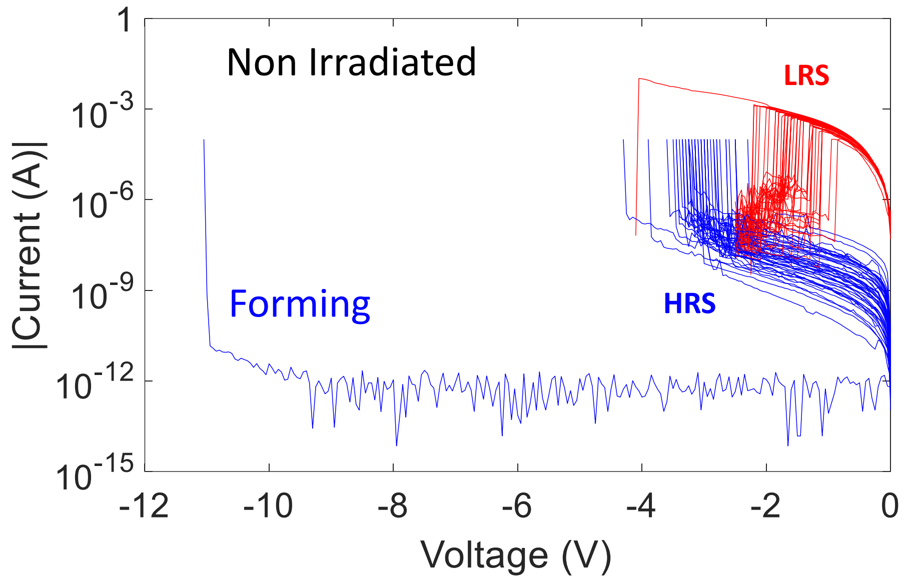

Figure 5. I-V curves of the first 50 RS cycles, showing the LRS and HRS states, corresponding to the non-irradiated sample. The figure also shows the forming step.

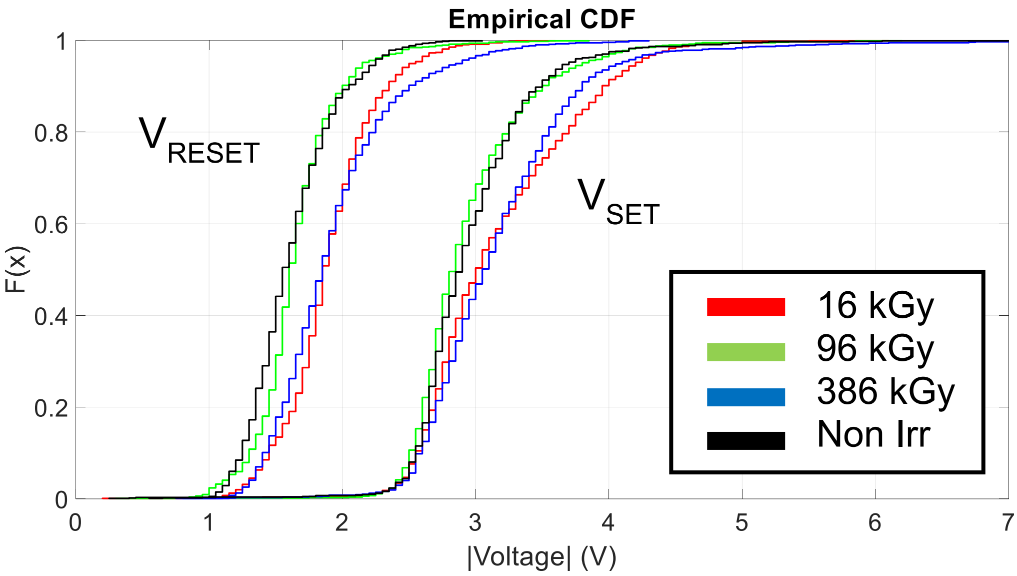

Figure 6. Cumulative distribution functions of set (V_{SET}) and reset (V_{RESET}) voltages corresponding to 1000 RS cycles.

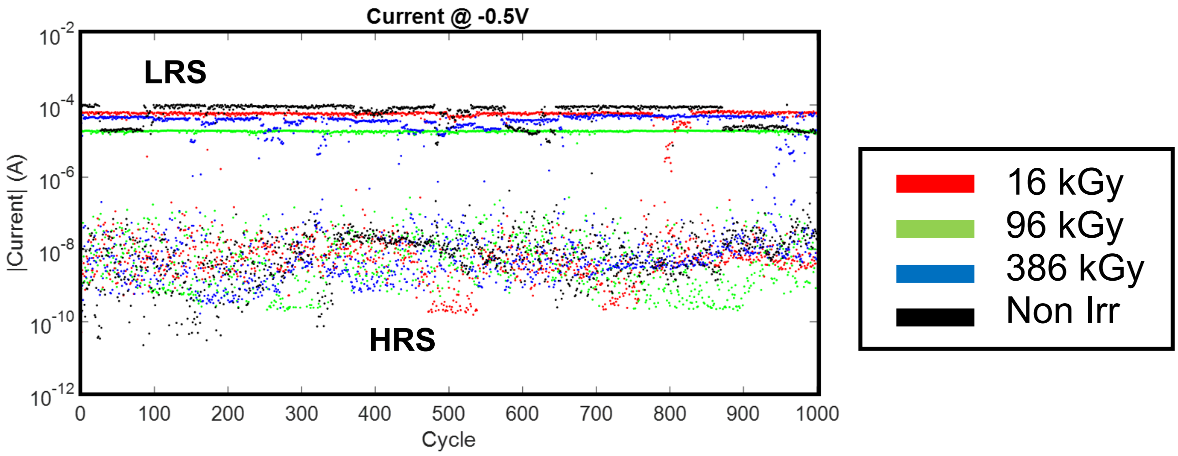

Figure 7. Current measured at -0.5 V in the LRS and HRS states during a process of 1000 RS cycles.