Total Ionizing Dose Response of Hafnium-Oxide Based MOS Devices to Low-Dose-Rate Gamma Ray Radiation Observed by Pulse CV and On-site Measurements

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*Abstract*— This paper reports on the low-dose-rate radiation response of Al-HfO2/SiO2–Si MOS devices, where the gate dielectric was formed by atomic layer deposition with 4.7 nm equivalent oxide thickness. The degradation of the devices was characterized by a pulse capacitance-voltage (CV) and on-site radiation response techniques under continuous gamma (γ) ray exposure at a relatively low-dose-rate of 0.116 rad(HfO2)/s. A significant variation of the flat-band voltage shift of up to ± 1.1 V under positive and negative biased irradiation, with the total dose of up to 40 krad (HfO2) and the electric field of ~0.5 MV/cm, has been measured on the HfO2-based MOS devices using the proposed techniques, not apparent by conventional CV measurements. The large flat-band voltage shift is mainly attributed to the radiation-induced oxide trapped charges, which are not readily compensated by bias-induced charges produced over the measurement timescales of less than 5 ms. Analysis of the experimental results suggest that both hole and electron trapping can dominate the radiation response performance of the HfO2-based MOS devices depending on the applied bias. No distinct loop width variation has been found with irradiation in all cases.

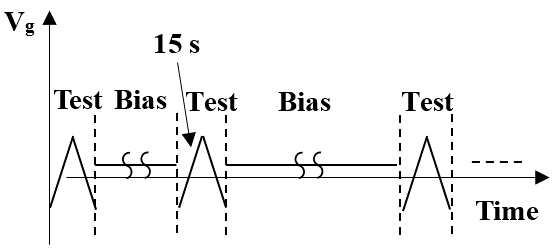
*Index Terms*—ALD, oxide trapped charges, hafnium oxide, low-dose-rate, gamma irradiation, pulse CV.

# INTRODUCTION

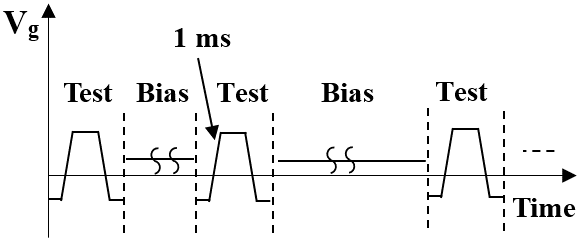
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S advanced Metal Oxide Semiconductor Field Effect Transistors (MOSFETs) technology continues to decrease the gate oxide thickness, the exponential increase in gate leakage current poses a major challenge for silicon dioxide (SiO2) based devices. In order to reduce the gate leakage current while maintaining the same gate capacitance, alternative gate insulator materials with higher dielectric constant (high-*k*) has become the preferred replacement of SiO2 gate dielectrics [1, 2]. By using high-*k* materials, the equivalent oxide thickness (EOT) of devices is less than 10 Å and significantly smaller leakage currents are observed compared to that of SiO2 [3-6]. Several high-*k* materials have been under consideration, such as hafnium oxide (HfO2), zirconium oxide (ZrO2), yttrium oxide (Y2O3), cerium oxide (CeO2), and their silicates [7-9]. Among these materials, the oxides of hafnium and zirconium dielectrics are most widely employed as they have relatively high dielectric constants of 15-25, relatively large band gap (5.8 eV) and high thermodynamic stability on silicon [10, 11]. In particular, HfO2 is more widely used than ZrO2 because it is more stable with silicide formation [12]. At present, advanced microelectronics devices and circuits are used in aerospace engineering, nuclear industry and radiotherapy equipment. These applications are unavoidably exposed to space-like radiation, which has a relatively low radiation dose rate at 10-2-10-6 rad(Si)/s [13, 14]. For this reason, it is necessary to understand the low-dose-rate radiation response of HfO2 based MOS devices. Currently, gamma (γ)-ray radiation sources can be employed in the laboratory to accurately evaluate and predict the radiation response of MOS devices in space-radiation environment [15, 16].

There has been a substantial body of research on the physical mechanisms of high-dose-rate total ionizing dose response of high-*k* materials in recent years [17-21]. The electrical characteristics of the materials such as flat-band voltage shift, electron trap density and interface trap density have been typically examined by carrying out off-site capacitance-voltage (CV) measurements [22, 23]. Arguably, the conventional and off-site radiation response measurements may underestimate the degradation of MOS devices. On the other hand, in MOSFETs technologies, there is a great interest in understanding the behavior of charge trapping in the oxide during and after pulse voltages [24]. For example, in flash memory technologies, program/erase pulse voltages are applied to the memory devices. It has been reported that the memory device performance is affected by defects in the bulk of oxide during the application of pulse voltages. These defects may lead to device charge trapping or charge leakage [25]. The pulse CV technique is suitable for observing the charge trapping behaviors in relatively short time, which is close to the actual conditions. Furthermore, it has also been found that the defects in HfO2 induce charging and neutralization behaviors during the applied pulse waveform. These behaviors affect the threshold voltage Vth instability of MOSFETs or even lead to device degradation [26]. Therefore, to gain a better understanding of these defects, the pulse CV technique is developed to measure the complete CV characteristic of MOS capacitors in a relatively short time. It reduces the impact of charge trapping on the measurement results, as opposed to the conventional CV technique. As a consequence, our group has recently developed a novel radiation response testing system, which is capable of estimating the radiation response of MOS devices whilst the devices are continuously irradiated by γ-rays. The related electrical characterization measurements can be completed in a few milliseconds. The principles and reliability of the system have been reported in our previous work [27]. Using this novel testing technique, the degradation of devices can be precisely detected as very few radiation-induced oxide trapped charges are compensated by bias-induced charges within the complete measurement cycle.



**Conventional CV**



**(a)**

**Pulse CV**

**(b)**

Despite the extent of ongoing research into the radiation response of high-*k* dielectrics, little work has been done on the fast charge trapping characteristics and long-term reliability of hafnium oxide under continuous low-dose-rate γ-ray exposure. In this work, we have studied the total ionizing dose radiation effect on HfO2 dielectric thin films prepared by atomic layer deposition (ALD). The radiation response of HfO2 gate dielectrics is evaluated by the pulse CV and on-site technique and compared to that extracted from conventional measurements using the flat-band voltage shift. To further verify the radiation response of HfO2 gate dielectrics obtained by the pulse technique, MOS capacitors with a silicon dioxide dielectric were also fabricated and tested. More radiation-induced oxide trapped charges were observed in both HfO2 and SiO2 dielectrics, via the proposed measurements. One possible explanation is that the fast characterization of pulse CV measurements induces less compensation of the trapped charges in HfO2. In addition, the radiation bias instability of the hafnium-based MOS capacitors is also discussed.

Fig. 1. Schematic of the gate voltage for CV measurements and bias voltage versus time characteristics of (a) conventional CV and (b) pulse CV measurements.

# Experimental Details

HfO2 thin films were deposited under identical conditions via ALD. The HfO2 and SiO2 MOS capacitors were formed on n-type silicon (1 0 0) wafers with a doping concentration of ~1015 cm-3. Prior to the gate stack fabrication, the wafers were subjected to standard RCA cleaning to remove organic and metallic contamination. The wafers were then washed in deionized water and finally etched in a solution (HF: H2O = 1:30) for 30 seconds to remove native oxides. The deposition of HfO2 thin films was carried out at 200 using tetrakis (dimethylamido) hafnium (IV) [(CH3)2N]4Hf as the precursor for HfO2 and deionized H2O as the oxidant. 160 cycles HfO2 were grown with the following sequence: precursor / purge / water / purge (150 ms / 25 s / 30 ms / 25 s). A SiO2 interfacial layer was formed between the HfO2 and the Si substrate. After deposition, the aluminum gate electrodes (500 nm thick and 0.3 mm2 gate area) were formed by electron beam evaporation through a shadow mask. The physical thicknesses of the HfO2 films and interfacial layer were 24 nm and 1.8 nm respectively, as measured by spectroscopic ellipsometry. Using this method of fabrication, the EOT of the HfO2 thin film was ~4.7 nm which was thicker than in devices of most commercial interest [28]. However, using devices with thicker dielectric has led to a significant radiation response being more relevant for investigation of the failure mechanism of hafnium oxide in space environment [22]. The reference SiO2 thin films were grown in dry O2 1000ºC to a thickness of 19 nm.

The fabricated samples were irradiated by a Cs137 γ-ray radiation source with energy of 662 keV in an on-site radiation response probe station system which was developed by our group [27]. Thermoluminescent dosimeters (TLDs) were employed to calibrate the absorbed dose rates of the irradiated high-*k* devices in the system. After taking into account the dose enhancement effect, the dose rate of the HfO2 and SiO2 thin films was 0.116 rad(HfO2)/s and 0.119 rad(SiO2)/s [21, 27, 29]. A total dose up to 45 krad (HfO2) was applied to all the irradiated HfO2 samples with a constant gate bias of +1 V or -1 V. During the biased irradiation, the pulse CV or conventional CV measurements were employed to investigate the charge trapping mechanism of HfO2 film at each total dose level. Fig. 1 shows a graph of the gate sweeping voltage and stress voltage (Vg) versus the sweeping/stress time in the conventional CV (a) and pulse CV (b) techniques. The stress voltage and the sweeping voltage are alternately applied to the MOS device during the biased irradiation tests. The irradiation exposure was uninterrupted during measurement. As shown in Fig. 1, the ramp-up and ramp-down of the pulse CV measurement completes within 1 ms, while the conventional technique finishes the measurements in a relatively long period. The conventional CV measurements were carried out using an Agilent 4284 LCR meter at a frequency of 1 MHz. The detailed working principles of the pulse CV measurements have already been reported in previous work [30]. The waveform of the applied gate pulse (CH1) and amplified output pulse (CH2) for pulse CV technique are shown in Fig. [2](#Fig1). The gate waveform voltage was ramped up from -2 V to +2 V with an edge time of *tr* and kept at +2 V for a time of *t*w-*tr*, then turned back to -2 V with the same edge time. The pulse width of *tw* was also indicated in Fig. 2. In the conventional CV measurements, the edge time is 10 s and the peak voltage duration (*t*w-*tr*) is 400 ms. Bias-induced degradation was also measured without irradiation at the same irradiation time and biases. All biased irradiation and electrical measurements were performed at room temperature.

Fig. 2. Voltage versus time characteristics of the pulse CV technique. An input pulse waveform (CH1) was applied to the gate of the HfO2 capacitor and an amplified output pulse waveform (CH2) was extracted. The input waveform was ramped up from -2 V to +2 V in an edge time of *tr* and kept for (*tw*-*tr*), then turned back to -2 V in the same edge time. The pulse width was indicated as *tw*.

# Results

Fig. 3. CV characteristics of the HfO2/SiO2-Si capacitor without irradiation exposure. The rising/falling edge time of gate pulse was 900 µs, and the pulse width was 1300 µs. The close similarity in the CV curves indicates that the same pre-irradiation flat-band voltage can be extracted from the two techniques and it provides a solid foundation for further investigation of radiation-induced oxide charge trapping. The corresponding loop width of the CV curves is shown in the inset.

Fig. 4. HfO2/SiO2-Si capacitor was irradiated with 662 keV γ-rays at a dose rate of 0.116 rad (HfO2)/s and biased at an electric field of 0.5 MV/cm during the irradiation. The radiation response of the device was dominated by the flat-band voltage shift (ΔVFB) as indicated, which was extracted from conventional CV measurement. The loop width versus the total dose of HfO2/SiO2 thin films is shown in the inset.

The accuracy and reliability of the proposed technique was verified by performing some pre-irradiation measurements on HfO2/SiO2-Si capacitors. [Fig. 3](#Fig2) shows the CV curves extracted from pulse CV measurements, when Vg was ramped up from -2 V to +2 V then turned back with an edge time of 900 µs with a pulse width of 1300 µs. The extracted CV curves overlap the results of high-frequency conventional CV data. The total dose radiation effects on a MOS device may cause a shift in the position of the flat-band voltage of the CV curve. The good agreement in the CV curves indicates that the two techniques measure the same pre-irradiation flat-band voltage, which provides a definite reference point for further investigation of radiation-induced oxide charge trapping. When Vg was ramped down followed by the rising edge in a short time, a small hysteresis between the two extracted CV curves was observed to form a “loop width” as shown in the inset of Fig. 3. The loop width between the “up” and “down” CV curves can be defined as ΔVFB (‘down’-‘up’). Zhao *et al*. [31, 32] have reported that the loop width originates from part of the charges in HfO2 dielectrics which can repeatedly be neutralized and recharged by charge injection from the substrate. It was also suggested that when the pulse width or stress time is longer than 1 s, the contribution of these cyclic charges to the ΔVFB is negligible. The sensitivity of the loop width to biased irradiation is investigated in the following part by performing long-term pulse CV measurements. There is a fall in the capacitance value of the pulse CV measurement within the range of 1.5 V to 2 V. The phenomenon is mainly due to the response time of the oscilloscope and the capacitance charging and discharging issues [30].

Fig. 6. Comparison of ΔVFB for the HfO2/SiO2-Si capacitors measured by pulse CV and conventional CV technique, in which the pulse CV measurements were carried out under irradiation up to 40.5 krad (HfO2) and without irradiation. In all cases, the electric field applied to the gate was 0.5 MV/cm. The rising/falling edge time of the gate pulse was 400 µs, and the pulse width was 800 µs. A large density of positive radiation-induced charges was extracted by pulse CV under biased irradiation.

To assess the radiation-induced charge trapping in HfO2 dielectrics, we use both the high-frequency conventional CV and pulse CV measurements. [Fig. 4](#Fig3) illustrates representative CV curves before and after radiation exposure of 1.1, 10.5, 15.2, and 45.5 krad (HfO2) respectively with the electric field of 0.5 MV/cm measured by the conventional CV technique. After a total dose of 45.5 krad (HfO2), we observed that the CV curves have a negative ΔVFB up to -0.15 V. Since the distribution of oxide trapped charges in the HfO2/SiO2 is not known, the trapped charges in the HfO2 and SiO2 layers can be considered as equivalent charges projected to the interface of HfO2/SiO2 and SiO2/Si with effective charge densities of *Qox* and *Qin*, respectively. As a result, the flat-band voltage shift due to the oxide trapped charges is calculated as:

Fig. 5. Pulse CV measurements from an irradiated HfO2/SiO2-Si capacitor with an electric field of 0.5 MV/cm applied to the gate. The rising/ falling edge time of gate pulse was 900 µs, and the pulse width was 1300 µs. A very large, −0.67 V, negative flat-band voltage shift was observed in the CV curves at total dose of 40.5 krad (HfO2), which indicated a large concentration of positive charges being generated in the oxide. The inset shows the loop width versus the total dose, suggesting no significant variations of loop width.

. (1)

where *A* is the area of the capacitor; *-q* is the electronic charge; *Cox* and *Cin* are the capacitances of HfO2 and SiO2 [33, 34]. Analysis of these data shows that the increase in the negative ΔVFB consists of the enhancement of net positive oxide trapping density in HfO2 and interfacial layers during irradiation. We tentatively attribute the hysteresis to the generation of net positive oxide trapped charges in HfO2 because it is clear that the thickness of interfacial layer is relatively small (1.8 nm) [35]. Nevertheless, it is conceivable that the positive oxide trapping density in SiO2 layer is high enough to affect the ΔVFB. However, the needed amount of trapping is in contrast with the typical radiation-induced oxide trap-charge density in SiO2 found previously [36].Effective interface trapping efficiencies were calculated using the method of Felix *et al* [37]. It is also suggested that in all cases, there is no discernible interface trap build-up at both HfO2/SiO2 and SiO2/Si interfaces with positive biased irradiation. The inset of Fig. 4 indicates the loop width versus the total dose of irradiated devices. It clearly shows that the loop width observed by conventional CV measurements is almost insensitive to the radiation exposure. As described earlier, the result in the inset of Fig. 4 supports the conclusion that the loop width originates from the cyclic charges in dielectrics and these cyclic charges can only be evaluated in a relatively short time.

To further determine the radiation response of HfO2 dielectrics, irradiation pulse CV measurements are performed on the HfO2/SiO2-Si capacitor with the same electric field compared with conventional evaluation as indicated in Fig. 5. The rising/ falling edge time of gate pulse was 900 µs and the pulse width was 1300 µs in all cases. A very large, -0.67 V, negative flat-band voltage shift is observed after a total dose of 40.5 krad (HfO2). The results shown in Fig. 5 indicate that a large concentration of net positive charges was generated in the HfO2/SiO2 oxide layer. As mentioned above, it is suggested that the build-up of the positive oxide trapped charges is primarily generated in HfO2 dielectric layer, since no significant oxide trapping is expected in the ultrathin SiO2[35]. The inset of Fig. 5 shows the loop width versus the total dose of the irradiated devices as observed by pulse CV measurements. The small increase in loop width is likely due to the fact that more bias-induced electrons are injected into HfO2 to neutralize the positive cyclic charges which are located in shallow traps in the HfO2 [31]. It is also suggested that the generation of these positive cyclic charges is consistent with some radiation-induced holes which are generated and trapped in HfO2 during the positive biased irradiation.

Fig. 6 summarizes the flat-band voltage shifts of the stacked HfO2/SiO2-Si capacitors, which are extracted from pulse and conventional CV measurements at each total dose level with 1 V gate bias. In order to separate the bias-instability and radiation-caused shifts, the ΔVFB of the devices under positive bias without radiation exposure was also observed by using the pulse technique. The rising and falling edge times of the gate pulse were 400 µs and the pulse width was 800 µs. The time scale of the top axis is matched to the bias time when performing pulse CV measurements without irradiation. Positive electric field on the device for more than 105 hours without irradiation results in a maximum value of ΔVFB of 66 mV as represented by the dark squares in Fig. 6. The small hysteresis is attributed to the bias-induced electrons which are tunneling from the silicon substrate and are trapped into HfO2 with the energy level below the bottom edge of the Si conduction band [32, 38, 39]. The result indicates that only very few bias-induced electrons which exist in the deeper energy level can be extracted from the pulse technique. The devices exposed to gamma radiation show a negative ΔVFB of up to -793 mV and -80 mV, respectively from pulse and conventional CV measurements. The differences between the ΔVFB with and without irradiation clarify the effects of gamma radiation on HfO2 film. Therefore, this negative ΔVFB in Fig. 6 could be due to radiation-induced positive charge trapping and compensation of bias-induced electrons in HfO2 layers. Analysis of these data shows that a large concentration of radiation-induced positive oxide trapped charges is generated in the oxide. However, the conventional measurement exhibits very few net positive charges. One possible explanation is that the recovery of ΔVFB using the conventional method may be due to the trapping process of the biased-induced tunneling electrons in the oxide during the long duration of the measurement with positive gate bias. Conversely, a large density of the negative oxide trapped charges would be de-trapped with less trapping occurring before the completion of pulse CV measurement. This also explains the relatively small hysteresis observed in pulse CV measurements without irradiation. In this case, a large concentration of the bias-induced negative oxide trapped charges were de-trapped and only the charges trapped in deep energy levels were extracted [32, 40, 41].

Fig. 7 is a plot of representative CV curves of a HfO2/SiO2-Si capacitor obtained from pulse CV measurements. The capacitor was irradiated at total doses of 0.11, 10.5, 15.2, and 45.5 krad (HfO2) with a gate bias of -1 V. The rising/ falling edge time of gate pulse was identical with the same conditions as in the positive biased irradiation experiment in Fig. 5. The results in Fig. 7 indicate that a large concentration of net negative charges has been generated in the HfO2 layer under negative biased irradiation. A positive ΔVFB of 0.99 V is comparable to the negative ΔVFB observed in Fig. 5 in terms of the magnitude for the same total dose. This confirms the existence of a large density of electron traps in HfO2 as suggested in the explanation for the recovery of ΔVFB in conventional positive biased irradiation experiment. The bidirectional flat-band voltage shifts observed under opposite-biased irradiation indicate that both positive and negative trapped charges dominate the radiation response of the HfO2/SiO2 capacitors [42].

Fig. 7. CV plot of the HfO2/SiO2-Si capacitor irradiated at different doses with an electric field of -0.5 MV/cm applied to the gate. The measurements were carried out by pulse CV technique. The rising/ falling edge time of gate pulse was 900 µs, and the pulse width was 1300 µs. Positive flat-band voltage shifts up to 0.89 V were observed after irradiation to 40.5 krad (HfO2).

To further verify that the bias-induced charge trapping and de-trapping in HfO2 are responsible for the recovery of radiation-induced ΔVFB by using conventional evaluation, we examine the radiation response for the HfO2/SiO2 capacitors by using both the pulse and conventional CV measurements at -1 V gate bias as shown in Fig. 8. Similar to positive biased radiation, the pulse CV measurements were carried out with and without irradiation exposure. The applied gate pulse was identical with the conditions in the positive biased irradiation experiment as presented in Fig. 6. The dark crosses in Fig. 8 represent the ΔVFB of the capacitors under negative bias without radiation exposure. ΔVFB up to -80 mV was observed in the negative biased device without irradiation. This small negative hysteresis is likely due to the fact that the bias-induced positive charges are tunneling from the silicon substrate and are trapped into HfO2 with the energy level above the top edge of the Si valence band [31, 43]. After a total dose exposure up to 40.5 krad (HfO2), we observed positive ΔVFB of 986 mV and 67 mV respectively obtained using the pulse and conventional techniques. The result has a good agreement with the ΔVFB extracted from positive biased irradiation. As mentioned earlier, this ΔVFB is mainly due to the radiation-induced charge trapping and the compensation of bias-induced charges in HfO2 layers. Similarly, we attribute the recovery of ΔVFB measured by the conventional measurement to the trapping of the bias-induced substrate hole injection (SHI) in HfO2 oxide during the measurement.

Fig. 8. Comparison of ΔVFB for the HfO2/SiO2-Si capacitors measured by the pulse CV and conventional CV techniques, in which the pulse CV measurements were carried out under irradiation up to 40.5 krad (HfO2) and without irradiation. In all cases, the electric field applied to the gate was -0.5 MV/cm. The rising/falling edge time of the gate pulse was 400 µs, and the pulse width was 800 µs. The time scale on the top axis is matched to the bias time when performing the pulse CV measurements without irradiation.

**(b)**

**(a)**

Fig. 9. Energy band diagrams of a HfO2/SiO2-Si capacitor during biased irradiation and CV measurements: (a) +1 V biased irradiation. Radiation-induced positive charges transported to HfO2/SiO2 interface and trapped in the HfO2 to induce negative ΔVFB. Meanwhile, electrons were injected from Si and trapped in HfO2 to compensate holes trapping. (b) CV measurements ramped up from -2 V. Initially, the negative oxide trapped charges were de-trapped and a relatively large negative ΔVFB can be extracted at E = -0.5 MV/cm. Conventional measurements completed the process of ramp up from -2 V to +2 V in a relatively long time, in which de-trapped electrons were tunneling to HfO2 again inducing strong recovery of ΔVFB. (c) CV measurements ramped down from +2 V, the de-trapped electrons were tunneling to HfO2 again. (d) +1 V biased irradiation.

Ev

EF (s)

Ec

**Al**

**HfO2**

**SiO2**

**N-Si**

**(a)**

EF (m)

Ev

EF (s)

Ec

**(b)**

**CV measurement ramp up from -2 V**

**Electrons de-trapping**

**CV measurement ramp down from +2 V**

**Biased irradiation at Vg = 1 V**

**Biased irradiation at Vg = 1 V**

Ev

EF (s)

Ec

**Effective hole trapping capture**

EF (m)

EF (m)

EF (m)

**(c)**

**(d)**

**Bias-induced charge trapping**

**Electrons trapping**

**Al**

**HfO2**

**SiO2**

**N-Si**

Ev

EF (s)

Ec

# Discussion

To better understand the mechanisms of radiation-induced charge trapping and the compensation of bias-induced charges in HfO2, Fig. 9 shows the energy band diagrams of the stacked HfO2/SiO2-Si capacitor during positive biased irradiation and CV measurements. Under the +1 V biased irradiation as shown in Fig. 9 (a), radiation-induced positive charges will transport toward HfO2/SiO2 interface via defects and then trapped in the bulk of HfO2 to form positive oxide trapped charges, while most of the radiation-induced electrons are swept out of oxide to the gate electrode [18]. As the SiO2 layer is very thin, the accumulation of radiation-induced charges at the interface due to the barrier of HfO2/SiO2 is negligible [44]. Meanwhile, the bias-induced electrons tunnel from the Si substrate and are trapped in the HfO2 as indicated in Fig. 9 (a). These bias-induced electrons significantly compensate the radiation-induced hole trapping in either shallow and/or deep energy levels generated during positive biased irradiation (see Fig 9(a)) [32, 38, 39]. As a result, the concentration of net positive charges in HfO2 is determined by the generation of radiation-induced positive charges and the compensation of bias-induced electrons.

Fig. 10. ΔVFB as a function of the total dose obtained from pulse CV measurements with different edge time of the gate pulse. The electric fields applied to the gate were (a) -0.5 MV/cm and (b) 0.5 MV/cm. The inset in each figure was a plot of ΔVFB versus the edge time for the HfO2/SiO2-Si capacitor at different dose levels. The magnitude of ΔVFB was observed to increase with the decrease of the edge time under both positive and negative bias at all total dose levels.

During the ramp-up process of CV measurements, the gate sweeping voltage is ramped up from -2 V to +2 V. Initially at electric field of -2 V, a large concentration of bias-induced electrons, which are generated during positive biased irradiation, are de-trapped and forced out of HfO2 as illustrated in Fig. 9 (b). This suggests that a relatively large density of net positive charges can be extracted at this stage. Only very few bias-induced anti-neutralization electrons at deep energy level would affect the density of net positive charges. In other words, a large value of ΔVFB would be also observed at –2 V during the ramp-up process. A similar mechanism was also indicated by Zhou *et al.* [45]. It was reported that the significant densities of dipolar defects were created during irradiation in the gate stacks. During positive bias, electrons compensated the trapped positive charges, while for negative bias, electrons were forced out of oxide. These defects may impact MOS device radiation response significantly.

When the gate sweeping voltage is ramped to +2 V, the de-trapped electrons are tunneling back to HfO2 again to compensate the positive oxide trapped charges as shown in Fig. 9 (c). This compensation would induce strong recovery of the initial ΔVFB which is observed at Vg = -2 V. Since the ramp-up of the pulse CV measurement completes within 1 ms, the fast characterization will complete the whole measurement process before most of the de-trapped electrons tunnel back to HfO2 [31]. In general, the pulse CV technique completes the evaluation with very little recovery of ΔVFB. However, the conventional technique completes the process of ramp-up in a relatively long period. Thus, the radiation-induced positive charges will be compensated by the bias-induced electrons during the measurements and these processes will induce the recovery of ΔVFB. As a result, the ΔVFB with strong recovery would be extracted by conventional technique. Similarly, the recovery of radiation-induced ΔVFB obtained by the conventional measurement under negative biased irradiation is likely to be due to the compensation of bias-induced positive charges as a result of the relatively long test time.

Fig. 11. Comparison of ΔVFB for the SiO2 and HfO2 based capacitors measured by the pulse CV and conventional CV techniques, respectively under the irradiation of up to 32.8 krad (SiO2) and 40.5 krad (HfO2). In all cases, the electric field applied to the gate was 0.5 MV/cm. The rising/falling edge time of the gate pulse was 400 µs, and the pulse width was 800 µs.

The above analysis indicates that increasing the test time leads to less net oxide trapped charges in the oxide. Furthermore, the test time during pulse CV measurements is mainly affected by the edge time (*tr* and *tf*). In order to observe the significant effect of the test time on the radiation response of the devices, ΔVFB as a function of the total dose measured by pulse CV measurements with various edge time of the gate pulse are illustrated in Fig. 10. The electric field applied to the gate was -0.5 MV/cm and 0.5 MV/cm as shown in Fig. 10 (a) and Fig 10 (b) respectively. The results of Fig. 10 (a) indicate that the density of net negative charges decreases with the increase of the edge time in a range of 300 µs ~ 900 µs. From the trend of ᐃVFB summarized in the inset, we tentatively suggest that the radiation response extracted from pulse CV measurements would be identical to that of the conventional CV measurements if the edge time is large enough. Similarly, the results of Fig. 10 (b) indicate that the density of net positive charges decreases with the increase of the edge time. It can be concluded that both the positive and negative time-dependent fast charge trapping/de-trapping dominate the radiation response of HfO2 dielectrics.

In addition to edge time, the peak voltage time (*tw-tr*) of the input pulse waveform also affects the test time of CV measurements. The effects of the peak voltage time on the loop width without irradiation have been discussed in our previous work [46]. It was observed that with a longer peak voltage time, the loop width remained at a lower level. The result suggested that the longer peak voltage time leads to more electron charge trapping in oxide. Similarly, in this study, the increase of the peak voltage duration may induce more neutralization of positive cyclic charges. In general, a larger loop width may be extracted with longer peak voltage duration. On the other hand, increasing the pulse width time would also generate more radiation-induced positive charges. However, the time of biased irradiation in the experiment is much longer than the pulse width time. We hence tentatively suggest that the effect of the peak voltage time (*tw-tr*) on the concentration of net positive oxide trapped charges is negligible.

The impact of pulse magnitude on the loop width and flat-band voltage shift is also considered. It has been reported that the pulse magnitude will affect the loop width of CV curves without irradiation as indicated in the previous research [30]. The results showed that the loop width of LaAlO3 was increased with an increase of pulse magnitude. This has been attributed to the positive cyclic charges with deeper energy levels that may exist in the bulk of high-*k* oxide, which can only be neutralized with larger electric field. In this study, it has been indicated that more positive cyclic charges, which are located in shallow traps of HfO2, are generated during the biased irradiation. These results suggest that increasing the pulse magnitude may lead to more neutralization and recharging of positive cyclic charges with deeper energy levels. As a result, a higher pulse magnitude would cause a larger loop width during biased irradiation pulse CV measurements. Similar to the loop width, when the pulse magnitude is increased, it is suggested that the bias-induced negative oxide trapped charges with deeper energy levels may be de-trapped during the pulse CV measurements. The stronger de-trapping process denotes the decrease in compensation of the radiation-induced positive charges. Hence, a larger concentration of net positive oxide trapped charges would be extracted, resulting in an increase of the flat-band voltage shift.

There is one more benefit to perform the pulse CV technique for evaluating the biased irradiation response of high-*k* dielectrics. The radiation response obtained from pulse CV measurements is closer to the way devices would behave in actual operating conditions. As indicated in Fig. 1, the biased irradiation measurements can be divided into two parts: testing and biasing. During both of these two processes, the irradiation exposure is uninterruptedly applied to the devices. The values of the gate voltages remain constant during the biasing processes. While during the testing processes, the gate voltages are swept between the positive and negative polarity. As a consequence, the reversed gate voltages with irradiation would lead to the decrease of net oxide trapped charges in HfO2. For example, positive charges are trapped in the oxide during the +1 V biased irradiation. During the sense process, the gate voltages are swept from -2 V to +2 V. Negative radiation-induced charges are trapped in the oxide during -2V to 0 V, which induces a recovery of ΔVFB. Therefore, a longer test process (i.e. a longer interruption of bias) would cause a stronger recovery of ΔVFB. A conventional CV test normally takes several seconds or even longer. However, a pulse CV test completes the whole measurement process in relatively short time (just 1 millisecond) which allows data extraction of ΔVFB with less recovery. Moreover, in actual operating conditions, an operating MOS circuit will not be interrupted by any test processes. Therefore, the test process is desired to be as short as possible.

To probe further the radiation response of HfO2 gate dielectrics evaluated by the pulse technique, MOS capacitors with a silicon dioxide (SiO2) dielectric were employed. Previous results in the literature demonstrated that the radiation response of SiO2 was dominated by the positive charge trapping[36]. Hence, only the positive biased irradiation effect on SiO2 was measured. Fig. 11 shows the flat-band voltage shifts of the SiO2-based capacitors, which are extracted from pulse and conventional CV measurements at each total dose level with positive bias. The dose scale of the top axis is matched to the total dose of SiO2 when performing positive biased irradiation. A total dose of up to 32.8 krad (SiO2) was applied to the irradiated SiO2 samples. The devices exposed to gamma radiation show a negative ΔVFB of up to -224 mV and -31 mV from pulse and conventional CV measurements, respectively. Similar to HfO2, the negative ΔVFB could be due to radiation-induced positive charge trapping and compensation of bias-induced electrons in SiO2 layers. The results indicate that the pulse CV technique extracts a lager flat-band voltage shift as compared to the conventional CV technique. As explained above, the recovery of ΔVFB measured by the conventional method may take place due to a large density of biased-induced electrons trapped in the oxide. Conversely, most of these negative oxide-trapped charges would be de-trapped and less trapping occurred before the completion of the pulse CV measurement. As indicated in Fig. 11, the two dielectrics have similar difference of ΔVFB obtained from the pulse and conventional CV measurements. The results extracted from SiO2 identify the reliability of the proposed measurement system. At all total dose levels, the value of ΔVFB of HfO2 remains at a higher level for both the pulse and conventional technique. This is because the positive oxide-trapped charge density in HfO2 is much larger than that in SiO2 [20, 28].

The annealing effects do exist in real cases, especially in low-dose-rate irradiation exposure. There are two kinds of annealing effects: annealing during irradiation and post-irradiation annealing. During irradiation, the main cause of annealing is the sense process, as discussed above. As for the post-irradiation annealing, the bias-induced charges would tunnel to the oxide and be trapped in both deep and shallow energy levels of the oxide to compensate the radiation-induced charges. With regard to conventional CV measurements, the accumulation of these bias-induced oxide trapped charges would cause significant recovery of ΔVFB as indicated by Dixit *et al* [28]. However, this study has been focused only on the on-site radiation-induced charge trapping behaviors in HfO2. We have not done the post-irradiation annealing study of HfO2. We recognize it as a crucial issue to be extensively discussed in our future work.

# Conclusions

In this paper, the low-dose-rate radiation responses of HfO2/SiO2–Si capacitors have been characterized by pulse and conventional CV measurements under continuous γ-ray exposure. We have found that a very large concentration of radiation-induced oxide trapped charges is generated in the oxide. However, the conventional measurement extracts very small values of ΔVFB. This has been attributed to the compensation of radiation-induced oxide trapped charges by bias-induced charges for measurements completed in a relatively long time (more than 7 seconds). It has also been demonstrated that both the positive and negative trapping/de-trapping dominate the radiation response of HfO2 dielectrics.

Consequently, a framework and measurement methodology has been proposed for better understanding the mechanisms of radiation-induced charge trapping and compensation of bias-induced charges in HfO2 stacks. During the measurements, the bias-induced oxide trapped charges tunnel into HfO2 again to cause recovery of radiation-induced ΔVFB. Fast characterization using pulse CV can measure these effects and avoid the compensation of the bias-induced charges. Moreover, the density of effective trapped charges decreases with the increase of the edge time. According to the results in this work and our previous study, we tentatively suggest that the effect of the peak voltage time on the concentration of net oxide trapped charges is negligible. A higher pulse magnitude would cause larger ΔVFB during the biased irradiation pulse CV measurements. Similar to HfO2, the SiO2-based capacitors exposed to gamma radiation show a negative ΔVFB of up to -224 mV and -31 mV, respectively from pulse and conventional CV measurements. These results further support that the radiation response of HfO2 was correctly estimated by using the proposed measurement system. The significant ΔVFB suggests that it is quite challenging for HfO2 to replace SiO2 in combined radiation and bias environment. However, the large bidirectional radiation-induced ΔVFB of HfO2-based capacitors was only extracted from pulse CV and on-site measurements. There are results reported in the literature illustrating that positive oxide trapped charges, electron traps, and protons play significant role in the ionizing radiation response of MOS devices with HfO2 gate dielectrics [42]. On the other hand, the discussions in this study were focused only on the radiation response of ~ 24 nm HfO2 dielectrics instead of considering real devices, with thinner dielectrics of most commercial interest. Such a thickness is relevant for investigation of the failure mechanisms of hafnium oxide. Since the HfO2-based devices are less sensitive to irradiation or bias with thinner dielectrics [28], the present study is, as yet, unable to precisely estimate the irradiation effect for real applications devices having thinner gate dielectrics. Therefore, more future work will be needed to identify with certainty the radiation-induced charge trapping behavior in HfO2 gate dielectrics and its dependence on the dielectric thickness.

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References

[1] E. P. Gusev, E. Cartier, D. A. Buchanan, M. Gribelyuk, M. Copel, H. Okorn-Schmidt, and C. D'Emic, “Ultrathin high-*k* metal oxides on silicon: Processing, characterization and integration issues,” *Microel. Eng.,* vol. 59, no. 1-4, pp. 341-349, Nov. 2001.

[2] G. D. Wilk, R. M. Wallace, and J. M. Anthony, “High-*k* gate dielectrics: Current status and materials properties considerations,” *J. Appl. Phys.,* vol. 89, no. 10, pp. 5243-5275, May. 2001.

[3] T. Z. Ma, S. A. Campbell, R. Smith, N. Hoilien, B. Y. He, W. L. Gladfelter, C. Hobbs, D. Buchanan, C. Taylor, M. Gribelyuk, M. Tiner, M. Coppel, and J. J. Lee, “Group IVB metal oxides high permittivity gate insulators deposited from anhydrous metal nitrates,” *IEEE Trans. Electron Dev.,* vol. 48, no. 10, pp. 2348-2356, Oct. 2001.

[4] A. Kawamoto, J. Jameson, P. Griffin, K. J. Cho, and R. Dutton, “Atomic scale effects of zirconium and hafnium incorporation at a model silicon/silicate interface by first principles calculations,” *IEEE Electron Device Lett.,* vol. 22, no. 1, pp. 14-16, Jan. 2001.

[5] E. Nadimi, G. Roll, S. Kupke, R. Ottking, P. Planitz, C. Radehaus, M. Schreiber, R. Agaiby, M. Trentzsch, S. Knebel, S. Slesazeck, and T. Mikolajick, “The Degradation Process of High-*k* SiO2/HfO2 Gate-Stacks: A Combined Experimental and First Principles Investigation,” *IEEE Trans. Electron Dev.,* vol. 61, no. 5, pp. 1278-1283, May. 2014.

[6] M. Houssa, L. Pantisano, L. A. Ragnarsson, R. Degraeve, T. Schram, G. Pourtois, S. De Gendt, G. Groeseneken, and M. M. Heyns, “Electrical properties of high-*k* gate dielectrics: Challenges, current issues, and possible solutions,” *Mater. Sci. Eng., R.,* vol. 51, no. 4-6, pp. 37-85, Apr. 2006.

[7] G. D. Wilk, R. M. Wallace, and J. M. Anthony, “Hafnium and zirconium silicates for advanced gate dielectrics,” *J. Appl. Phys.,* vol. 87, no. 1, pp. 484-492, Jan. 2000.

[8] Z. K. Yang, W. C. Lee, Y. J. Lee, P. Chang, M. L. Huang, M. Hong, C. H. Hsu, and J. Kwo, “Cubic HfO2 doped with Y2O3 epitaxial films on GaAs(001) of enhanced dielectric constant,” *Appl. Phys. Lett.,* vol. 90, no. 15, pp. 3, Apr. 2007.

[9] H. C. Aspinall, J. Bacsa, A. C. Jones, J. S. Wrench, K. Black, P. R. Chalker, P. J. King, P. Marshall, M. Werner, H. O. Davies, and R. Odedra, “Ce(IV) Complexes with Donor-Functionalized Alkoxide Ligands: Improved Precursors for Chemical Vapor Deposition of CeO2,” *Inorg. Chem.,* vol. 50, no. 22, pp. 11644-11652, Nov. 2011.

[10] G. D. Wilk, and R. M. Wallace, “Electrical properties of hafnium silicate gate dielectrics deposited directly on silicon,” *Appl. Phys. Lett.,* vol. 74, no. 19, pp. 2854-2856, May. 1999.

[11] M. Gutowski, J. E. Jaffe, C. L. Liu, M. Stoker, R. I. Hegde, R. S. Rai, and P. J. Tobin, “Thermodynamic stability of high-*k* dielectric metal oxides ZrO2 and HfO2 in contact with Si and SiO2,” *Appl. Phys. Lett.,* vol. 80, no. 11, pp. 1897-1899, Mar. 2002.

[12] S. Stemmer, “Thermodynamic considerations in the stability of binary oxides for alternative gate dielectrics in complementary metal-oxide-semiconductors,” *J. Vac. Sci. Technol., B.,* vol. 22, no. 2, pp. 791-800, Mar-Apr. 2004.

[13] K. F. Galloway, and R. D. Schrimpf, “MOS device degradation due to total dose ionizing radiation in the natural space environment: A review,” *Microel. J.,* vol. 21, no. 2, pp. 67-81, Jan. 1990.

[14] P. C. Adell, and L. Z. Scheick, “Radiation Effects in Power Systems: A Review,” *IEEE Trans. Nucl. Sci.,* vol. 60, no. 3, pp. 1929-1952, Jun. 2013.

[15] L. Ratti, M. Manghisoni, E. Oberti, V. Re, V. Speziali, G. Traversi, G. Fallica, and R. Modica, “Response of SOI bipolar transistors exposed to γ-rays under different dose rate and bias conditions,” *IEEE Trans. Nucl. Sci.,* vol. 52, no. 4, pp. 1040-1047, Aug. 2005.

[16] D. M. Fleetwood, “Total Ionizing Dose Effects in MOS and Low-Dose-Rate-Sensitive Linear-Bipolar Devices,” *IEEE Trans. Nucl. Sci.,* vol. 60, no. 3, pp. 1706-1730, Jun. 2013.

[17] A. Rao, J. D'sa, S. Goyal, and B. R. Singh, “Radiation Induced Charge Trapping in Sputtered ZrO2:N Dielectric Thin Films on Silicon,” *IEEE Trans. Nucl. Sci.,* vol. 61, no. 4, pp. 2397-2401, Aug. 2014.

[18] D. Cao, X. H. Cheng, T. T. Jia, L. Zheng, D. W. Xu, Z. J. Wang, C. Xia, Y. H. Yu, and D. S. Shen, “Total-Dose Radiation Response of HfLaO Films Prepared by Plasma Enhanced Atomic Layer Deposition,” *IEEE Trans. Nucl. Sci.,* vol. 60, no. 2, pp. 1373-1378, Apr. 2013.

[19] M. Ding, Y. H. Cheng, X. Liu, and X. L. Li, “Total Dose Response of Hafnium Oxide based Metal-Oxide-Semiconductor Structure under Gamma-ray Irradiation,” *IEEE Trans. Dielectr. Electr. Insul,* vol. 21, no. 4, pp. 1792-1800, Aug. 2014.

[20] J. A. Felix, J. R. Schwank, D. M. Fleetwood, M. R. Shaneyfelt, and E. P. Gusev, “Effects of radiation and charge trapping on the reliability of high-*k* gate dielectrics,” *Microel. Reliab.,* vol. 44, no. 4, pp. 563-575, Apr. 2004.

[21] A. Dasgupta, D. M. Fleetwood, R. A. Reed, R. A. Weller, M. H. Mendenhall, and B. D. Sierawski, “Dose Enhancement and Reduction in SiO2 and High-*k* MOS Insulators,” *IEEE Trans. Nucl. Sci.,* vol. 57, no. 6, pp. 3463-3469, Dec. 2010.

[22] F. B. Ergin, R. Turan, S. T. Shishiyanu, and E. Yilmaz, “Effect of γ-radiation on HfO2 based MOS capacitor,” *Nucl. Instr. Meth. Phys. Res. B,* vol. 268, no. 9, pp. 1482-1485, May. 2010.

[23] V. Singh, N. Shashank, D. Kumar, and R. K. Nahar, “Effects of heavy-ion irradiation on the electrical properties of rf-sputtered HfO2 thin films for advanced CMOS devices,” *Radiat. Eff. Defects Solids,* vol. 167, no. 3, pp. 204-211, Mar. 2012.

[24] W. D. Zhang, B. Govoreanu, X. F. Zheng, D. R. Aguado, A. Rosmeulen, P. Blomme, J. F. Zhang, and J. Van Houdt, “Two-pulse C-V: A new method for characterizing electron traps in the bulk of SiO2/high-*k* dielectric stacks,” *IEEE Electron Device Lett.,* vol. 29, no. 9, pp. 1043-1046, Sep. 2008.

[25] M. Rosmeulen, E. Sleeckx, and K. D. Meyer, "Electrical Characterisation of Silicon-Rich-Oxide Based Memory Cells Using Pulsed Current-Voltage Techniques." in *Proc.* *Solid-State Device Research Conference,* Firenze, Italy,Sept 2002, pp. 471-474.

[26] C. Z. Zhao, M. B. Zahid, J. F. Zhang, G. Groeseneken, R. Degraeve, and S. De Gendt, “Threshold voltage instability of p-channel metal-oxide-semiconductor field effect transistors with hafnium based dielectrics,” *Appl. Phys. Lett.,* vol. 90, no. 14, pp. 3, Apr. 2007.

[27] Y. Mu, C. Z. Zhao, Y. Qi, S. Lam, C. Zhao, Q. Lu, Y. Cai, I. Z. Mitrovic, S. Taylor, and P. R. Chalker, “Real-time and on-site γ-ray radiation response testing system for semiconductor devices and its applications,” *Nucl. Instr. Meth. Phys. Res. B,* vol. 372, pp. 14-28, Apr. 2016.

[28] S. K. Dixit, X. J. Zhou, R. D. Schrimpf, D. M. Fleetwood, S. T. Pantelides, R. Choi, G. Bersuker, and L. C. Feldman, “Radiation Induced Charge Trapping in Ultrathin HfO2-Based MOSFETs,” *IEEE Trans. Nucl. Sci.,* vol. 54, no. 6, pp. 1883-1890, Dec. 2007.

[29] D. M. Fleetwood, P. S. Winokur, and J. R. Schwank, “Using laboratory X-ray and cobalt-60 irradiations to predict CMOS device response in strategic and space environments,” *IEEE Trans. Nucl. Sci.,* vol. 35, no. 6, pp. 1497-1505, Dec. 1988.

[30] C. Zhao, C. Z. Zhao, Q. F. Lu, X. Y. Yan, S. Taylor, and P. R. Chalker, “Hysteresis in Lanthanide Aluminum Oxides Observed by Fast Pulse CV Measurement,” *Materials,* vol. 7, no. 10, pp. 6965-6981, Oct. 2014.

[31] C. Z. Zhao, J. F. Zhang, M. H. Chang, A. R. Peaker, S. Hall, G. Groeseneken, L. Pantisano, S. De Gendt, and M. Heyns, “Stress-induced positive charge in Hf-based gate dielectrics: Impact on device performance and a framework for the defect,” *IEEE Trans. Electron Dev.,* vol. 55, no. 7, pp. 1647-1656, Jul. 2008.

[32] C. Z. Zhao, J. F. Zhang, M. B. Zahid, B. Govoreanu, G. Groeseneken, and S. De Gendt, “Determination of capture cross sections for as-grown electron traps in HfO2/HfSiO stacks,” *J. Appl. Phys.,* vol. 100, no. 9, pp. 10, Nov. 2006.

[33] V. A. K. Raparla, S. C. Lee, R. D. Schrimpf, D. M. Fleetwood, and K. F. Galloway, “A model of radiation effects in nitride-oxide films for power MOSFET applications,” *Solid-State Electron.,* vol. 47, no. 5, pp. 775-783, May. 2003.

[34] C. X. Li, X. Zou, P. T. Lai, J. P. Xu, and C. L. Chan, “Effects of Ti content and wet-N2 anneal on Ge MOS capacitors with HfTiO gate dielectric,” *Microel. Reliab.,* vol. 48, no. 4, pp. 526-530, Apr. 2008.

[35] G. X. Duan, C. X. Zhang, E. X. Zhang, J. Hachtel, D. M. Fleetwood, R. D. Schrimpf, R. A. Reed, M. L. Alles, S. T. Pantelides, G. Bersuker, and C. D. Young, “Bias Dependence of Total Ionizing Dose Effects in SiGe-SiO2/HfO2 pMOS FinFETs,” *IEEE Trans. Nucl. Sci.,* vol. 61, no. 6, pp. 2834-2838, Dec. 2014.

[36] J. R. Schwank, M. R. Shaneyfelt, D. M. Fleetwood, J. A. Felix, P. E. Dodd, P. Paillet, and V. Ferlet-Cavrois, “Radiation Effects in MOS Oxides,” *IEEE Trans. Nucl. Sci.,* vol. 55, no. 4, pp. 1833-1853, Aug. 2008.

[37] J. A. Felix, D. M. Fleetwood, R. D. Schrimpf, J. G. Hong, G. Lucovsky, J. R. Schwank, and M. R. Shaneyfelt, “Total-dose radiation response of hafnium-silicate capacitors,” *IEEE Trans. Nucl. Sci.,* vol. 49, no. 6, pp. 3191-3196, Dec. 2002.

[38] K. Xiong, J. Robertson, M. C. Gibson, and S. J. Clark, “Defect energy levels in HfO2 high-dielectric-constant gate oxide,” *Appl. Phys. Lett.,* vol. 87, no. 18, pp. 3, Oct. 2005.

[39] S. Zafar, A. Callegari, E. Gusev, and M. V. Fischetti, “Charge trapping related threshold voltage instabilities in high permittivity gate dielectric stacks,” *J. Appl. Phys.,* vol. 93, no. 11, pp. 9298-9303, Jun. 2003.

[40] G. Puzzilli, B. Govoreanu, F. Irrera, M. Rosmeulen, and J. Van Houdt, “Characterization of charge trapping in SiO2/Al2O3 dielectric stacks by pulsed C-V technique,” *Microel. Reliab.,* vol. 47, no. 4-5, pp. 508-512, Apr-May. 2007.

[41] W. D. Zhang, J. F. Zhang, M. Lalor, D. Burton, G. Groeseneken, and R. Degraeve, “On the mechanism of electron trap generation in gate oxides,” *Microel. Eng.,* vol. 59, no. 1-4, pp. 89-94, Nov. 2001.

[42] X. J. Zhou, D. M. Fleetwood, L. Tsetseris, R. D. Schrimpf, and S. T. Pantelides, “Effects of Switched-bias Annealing on Charge Trapping in HfO2 Gate Dielectrics,” *IEEE Trans. Nucl. Sci.,* vol. 53, no. 6, pp. 3636-3643, Dec. 2006.

[43] V. V. Afanas'ev, and A. Stesmans, “Stable trapping of electrons and holes in deposited insulating oxides: Al2O3, ZrO2, and HfO2,” *J. Appl. Phys.,* vol. 95, no. 5, pp. 2518-2526, Mar. 2004.

[44] A. Y. Kang, P. M. Lenahan, and J. F. Conley, “The radiation response of the high dielectric-constant hafnium oxide/silicon system,” *IEEE Trans. Nucl. Sci.,* vol. 49, no. 6, pp. 2636-2642, Dec. 2002.

[45] X. J. Zhou, D. M. Fleetwood, J. A. Felix, E. P. Gusev, and C. D. Emic, “Bias-temperature instabilities and radiation effects in MOS devices,” *IEEE Trans. Nucl. Sci.,* vol. 52, no. 6, pp. 2231-2238, Dec 2005.

[46] Q. F. Lu, C. Zhao, Y. F. Mu, C. Z. Zhao, S. Taylor, and P. R. Chalker, “Hysteresis in Lanthanide Zirconium Oxides Observed Using a Pulse CV Technique and including the Effect of High Temperature Annealing,” *Materials,* vol. 8, no. 8, pp. 4829-4842, Aug 2015.

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