Comparative Analysis of MIS Capacitance Structures With High-k Dielectrics Under Gamma, ^{16}O and p Radiation

C. P. Quinteros, L. Sambuco Salomone, E. Redin, J. M. Rafí, M. Zabala, A. Faigón, F. Palumbo, and F. Campabadal

***Abstract*—MIS capacitance structures, with Hafnium Oxide, Alumina and nanolaminate as dielectrics were studied under gamma photons ^{60}Co, 25 MeV oxygen ions and 10 MeV protons radiation using capacitance-voltage (C-V) characterization.**

The main trend of the results shows that the nanolaminates stack presents the highest levels of hysteresis and stretch-out of the C-V curves, suggesting that interface layers between dielectrics could play a relevant role in the study of the radiation response.

***Index Terms*—High-k gate dielectrics, MOS devices, radiation effects.**

I. Introduction

SINCE many candidates have been proposed to replace SiO_2, such as Hafnium Oxide (HfO_2), Alumina (Al_2O_3), the combination of them in a nanolaminate multilayer gate oxide stack seems to be an appropriate choice as alternative gate dielectrics because they combine the best characteristics of them: large band gap (in the case of Al_2O_3) and high dielectric constant (in the case of HfO_2).

The radiation response of high-k (mono- and multi-layer) based MOS devices is thus a topic of significant importance to the radiation effects community; but the present understanding of the radiation response of those stacks is limited.

A recent paper suggests that electron trapping could dominate the radiation induced trapped charge build up [1], [2], while another study the post-BD I-V characteristics, and the shift of the capacitance-voltage (C-V) curves after ion irradiation [3]. However, further studies are needed to conclude about the radiation response of high-k nanolaminates.

Since trapping seems to dominate the radiation response, it is relevant to understand the role of interfaces of a high-k nanolaminate stack under different radiation sources. To date, a study about it has not been performed in this kind of advanced stacks.

In this paper it is studied the radiation effects on different sources (gamma photons ^{60}Co, 25 MeV oxygen ions and 10 MeV protons) on MIS capacitance structures with HfO_2, Al_2O_3 and Al_2O_3/HfO_2-based multilayer nanolaminate stacks as dielectrics.

In this study, it has begun to develop an understanding of the role of the interfaces between dielectrics in nanolaminates regarding the radiation response of the structure. Based on the variation of hysteresis, stretch-out and shift of the C-V curves, it has been possible evaluate the charge trapping effect and the generation of interface states, deducing that the interfaces between dielectrics in the gate stack have a relevant role in the radiation response.

II. Experimental Details

A. Samples Details

MIS capacitors with HfO_2, Al_2O_3 and nanolaminate ($Al_2O_3/HfO_2/Al_2O_3/HfO_2/Al_2O_3$) as oxide layer were grown through atomic layer deposition (ALD) at the Instituto de Microelectrónica de Barcelona (IMB-CNM, CSIC) [4].

The samples were fabricated on n-type silicon wafers with a resistivity of 1–12 Ωcm (doping concentration of $4\times10^{14}-5\times10^{15}$ at/cm^3) and on p-type silicon wafers with a resistivity of 4–40 Ωcm (doping concentration of $3\times10^{14}-3\times10^{15}$ at/cm^3).

A field oxide of 400 nm was grown by thermal oxidation at 1100°C. Windows were opened for the HfO_2/Al_2O_3 ALD by photolithography and wet etching. After deposition, the samples were first cleaned for 10 minutes with H_2O_2/H_2SO_4 and later for 10 seconds with HF. The ALD process was performed in 100 cycles at a constant temperature of 225°C, resulting in an oxide thickness of approximately 10 nm. After removal of oxide from the back side, both wafer sides were metalized with Al -0.5% Cu and the front side patterned to get capacitors in the active areas and bonding pads on the field oxide. Further details about the structures under investigation can be found in [4]. The samples were characterized by Transmission Electron Microscopy

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C. P. Quinteros and F. Palumbo are with the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and CNEA, San Martín 1650, Argentina (e-mail: cquinter@tandar.cnea.gov.ar; palumbo@cnea.gov.ar).

L. S. Salomone and E. Redin are with the Device Physics Laboratory–Microelectronics, Physics Department, School of Engineering, University of Buenos Aires, Buenos Aires, Argentina (e-mail: lsambuco@fi.uba.ar).

A. Faigón is with the Device Physics Laboratory–Microelectronics, Physics Department, School of Engineering, University of Buenos Aires, Buenos Aires, Argentina, and also with the CONICET, San Martín 1650, Argentina.

J. M. Rafí, M. Zabala, and F. Campabadal are with the Instituto de Microelectrónica de Barcelona, Centro Nacional de Microelectrónica, Consejo Superior de Investigaciones Científicas (CSIC), Barcelona, Spain.

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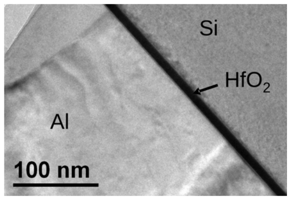
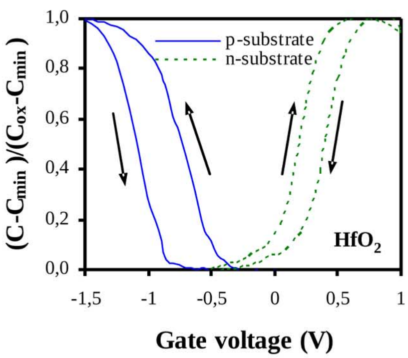
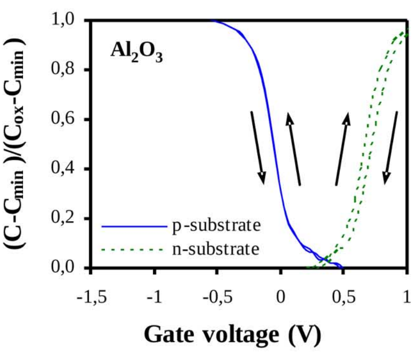


Fig. 1. A TEM image of $Al/HfO_2/Si$ stack. The oxide thickness is 10 nm.



(a)



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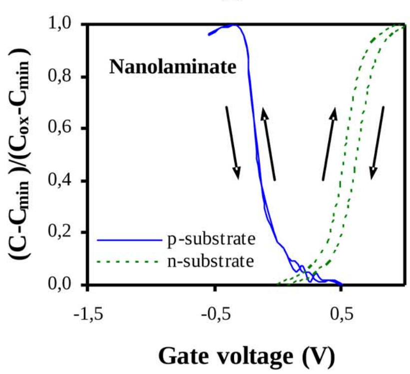

(c)

Fig. 2. C-V curves measured before irradiation for the three types of insulating layer: (a) Hafnium Oxide (HfO_2), (b) Alumina (Al_2O_3), and (c) nanolaminate. The area of all the capacitors was 3.24×10^{-4} cm^2. For n-substrate, the HfO_2-based samples had the higher hysteresis $V_H \sim 200$ mV, while Al_2O_3-based samples had only a hysteresis value four times lower. In the case of nanolaminate, the hysteresis value was of ~ 100 mV. For p-substrate, the HfO_2 capacitors again showed the higher hysteresis value $V_H \sim 400$ mV, while Al_2O_3 and nanolaminate showed a less than 50 mV hysteresis value.

(TEM); a TEM image of the HfO_2-based capacitors is shown in Fig. 1.

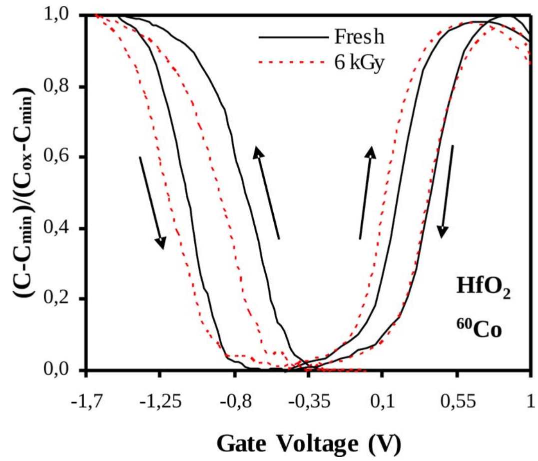

Fig. 3. A comparison between the C-V characteristics before and after 6 kGy γ-ray irradiation (^{60}Co) in HfO_2-based capacitors. For both type of substrates, a displacement of the C-V cycles towards negative voltages and a increment in the hysteresis value were observed.

B. Measurements and Irradiations

Fig. 2 shows C-V characterization, using the HP 4277A LCZ meter at 1 MHz, for all samples before irradiation.

It is observed for the HfO_2 samples a large hysteresis, ~ 400 mV for p-substrate and ~ 200 mV for n-substrate. Less than 50 mV of hysteresis was observed in the case of p-substrate for Al_2O_3 and nanolaminate, and a hysteresis of $\sim$ 50 mV and 100 mV was observed for n-substrate in Al_2O_3 and nanolaminate, respectively. This effect is consistent with previous results [5]–[10].

To test the response under radiation, different sets of samples have been exposed to protons of 10 MeV and oxygen ions of 25 MeV using the TANDAR accelerator (it is a tandem, Van de Graaf accelerator of 20 MV with a sputtering ion source) and to gamma rays (^{60}Co) both at CNEA (National Commission of Atomic Energy). Irradiation was interrupted periodically to perform high frequency, 1 MHz, C-V measurements. During irradiation the gate and substrate terminals were kept floating.

In order to compare the effects of the different radiation sources, the ion fluence was converted to ionizing dose (measured in Gy (SiO_2)) according to [11].

III. Radiation Effects

A. Gamma Rays

In two consecutive sessions, different sets of MIS capacitors were irradiated using a ^{60}Co source up to an accumulated dose of 6 kGy and 30 kGy. Fig. 3 shows the C-V curves for both kinds of substrates with HfO_2 as insulating layer before and after irradiation under a total dose of 6 kGy. It is observed a shift towards the left of the C-V curves was observed in both cases, $\sim$ 140 mV for p-substrate and $\sim$ 70 mV for n-substrate. The same behavior (not shown) was observed for Al_2O_3 and nanolaminate.

Fig. 4 shows ΔV_C, which is the voltage shift at constant capacitance, as a function of the accumulate dose for all devices.

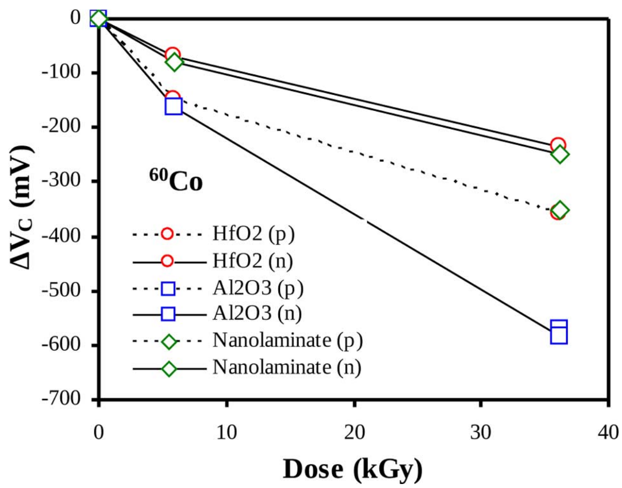

Fig. 4. Constant capacitance voltage-shift ΔV_C versus dose for all the devices irradiated with γ-ray irradiation (^{60}Co). It was observed that the C-V cycles shifted towards negative voltages in all the cases, which is consistent with the capture of positive charge inside the insulator.

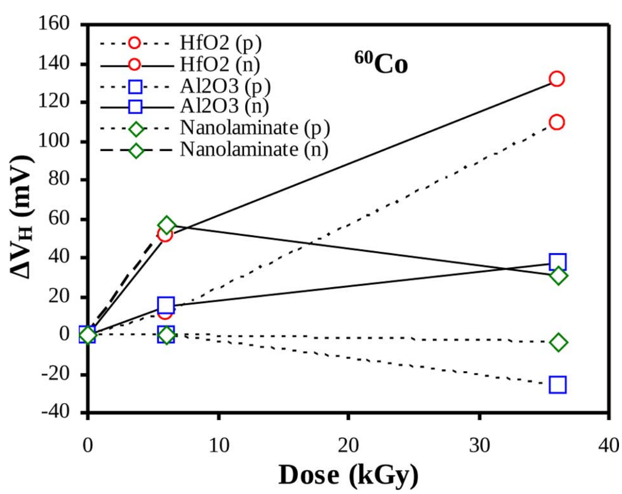

Fig. 5. Variation in the hysteresis value ΔV_H versus dose for all the devices irradiated with gamma rays. It was observed a $\sim$ 120 mV increase in the case of HfO_2-based capacitors for both types of substrate. Otherwise, a little change was observed in Al_2O_3 and nanolaminate.

A negative shift in C-V curves is observed, indicating an accumulation of trapped positive charge in the dielectric layer in agreement with other results [12]–[14].

The dynamic of the C-V hysteresis after radiation was also studied. Fig. 5 shows ΔV_H, which is the hysteresis value, as function of the accumulated dose. Since the hysteresis phenomenon is strongly dependent on the electric field [7], [10], the change in ΔV_H could be due to the change in the applied voltage referred to flat-band voltage, $V_{\rm FB}$, as a consequence of the radiation-induced $V_{\rm FB}$-shift. In other words, the same voltage applied before and after irradiation may result in different electric fields, and, thus, in different hysteresis amplitudes.

In order to test this effect, it was studied the dynamic of the applied voltage across the MIS stack (V_C) to keep constant the capacitance value. This feedback measurement methodology was used on MIS stacks with n-type substrate and Al_2O_3 oxide layer. Fig. 6 shows the results of ΔV_C as function of the time

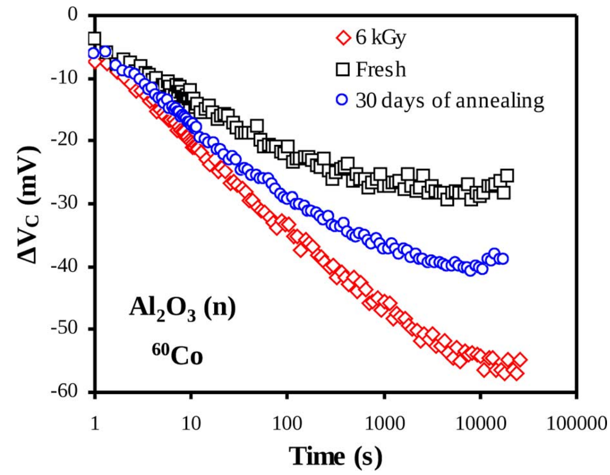

Fig. 6. Applied bias V_C across the MIS stack keeping constant the capacitance value as function of the time. It is observed ΔV_C, before ^{60}Co irradiation, after a total absorbed dose of 36 kGy, and after 30 days of RT annealing. The displacement of V_C is measured after applying an initial voltage $V_G = 1$. A increase of the slope was observed as due to the irradiation, while the 30 days of RT annealing partially restored the original slope.

for the following conditions: before the irradiation, after a total accumulated dose of 36 kGy, and 30 days after irradiation.

It is observed in all cases that the $\Delta V_C(t)$ a $\log(t)$ behavior, which is consistent with the tunneling front theory [15]–[17]. After the irradiation, the slope of the curve increase, while after 30 days of RT annealing, it was found a decrease of the slope towards the initial value.

It could be caused by recombination of a fraction of the radiation induced trapped charge, shifting the C-V curve towards positive values, and generating that the slope of $\Delta V_C(t)$ tends to the pre-irradiation value. This effect could be a support to the hypothesis that the increase in the hysteresis during irradiation could not be caused by generation of new traps (for ^{60}Co source), but to an increase in the density of available traps due to the change in the electric field, which is also a consequence of the radiation-induced $V_{\rm FB}$-shift.

B. *Oxygen Ions*

Fig. 7 shows the C-V characteristics for Al_2O_3 [Fig. 7(a)] and nanolaminate [Fig. 7(b)] capacitors before and after oxygen-ions irradiation for an accumulated fluence of 1×10^{11} ions/cm^2 which correspond to an accumulated dose of 1 kGy according to [11].

In the case of Al_2O_3, it was observed a slightly shift of the C-V curves towards negative bias (on the order of 10 mV) with an hysteresis increment of about 50 mV, while for nanolaminate capacitor the hysteresis increment is in the order of 800 mV.

In this case the negative shift observed in C-V curves indicates an accumulation of trapped positive charge in the dielectric layer, which is smaller than those produced by gamma rays (Fig. 4).

On the other hand, the hysteresis effect is bigger than in gamma radiation. This could be attributed to the creation of trapped charge at the oxide–silicon interface [18]. In fact, the hysteresis effect is more relevant in nanolaminate stack than in Al_2O_3-based capacitors, which present various interfaces (not only oxide with semiconductor), one for each sublayer.

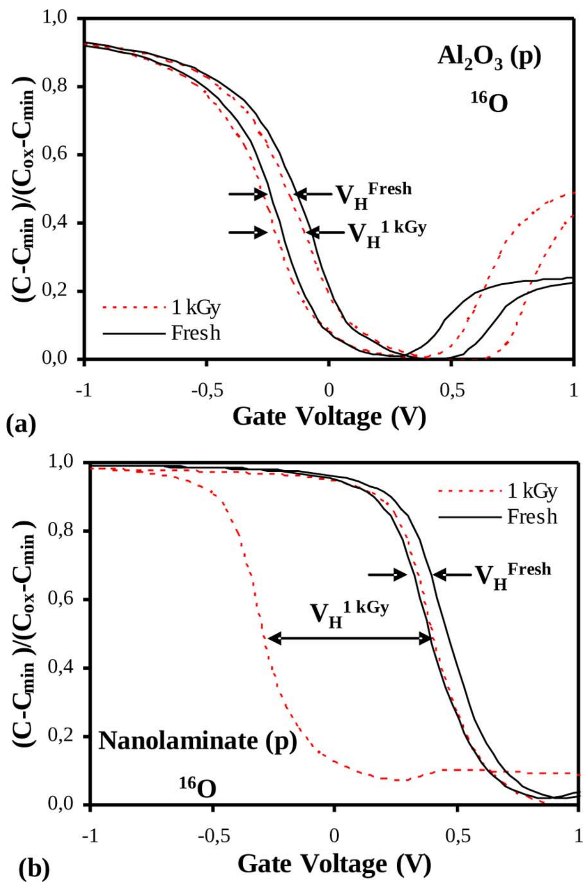

Fig. 7. (a) C-V characteristics before and after oxygen-ion irradiation (total dose: 1 kGy, total fluence: 1×10^{11} ions/cm^2) for: (a) a p-type Al_2O_3-based capacitors; and (b) a p-type nanolaminate-based capacitor. Both materials present a slightly negative V_C-shift of about 30–50 mV. With respect to the hysteresis, the Al_2O_3-based capacitors showed a increment of about 50 mV, while a much larger increment of 800 mV was observed in the case of the nanolaminate.

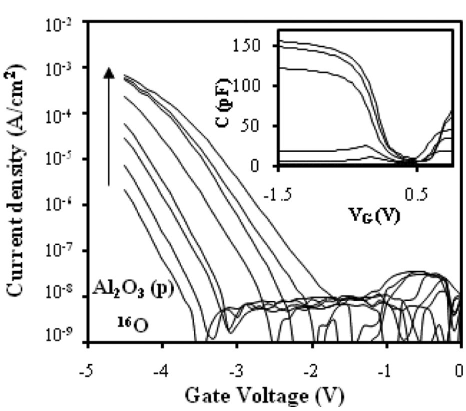

Fig. 8. I-V characteristics of p-type Al_2O_3-based capacitors during oxygen-ion irradiation sessions (total dose: 1 kGy, total fluence: 1×10^{11} ions/cm^2). The inset shows the decrease of accumulation capacitance while the irradiations were performed. This could be due to an increase in the series resistance and leakage current and/or to a gradual reduction of the dielectric constant.

In both cases it is observed a decrease of accumulation capacitance for higher doses. Fig. 8 shows a typical case of it for p-type Al_2O_3 capacitors. The inset of Fig. 8 shows the reduction on accumulation capacitance for larger accumulation dose, which is accompanied by an increase of the leakage current at low bias.

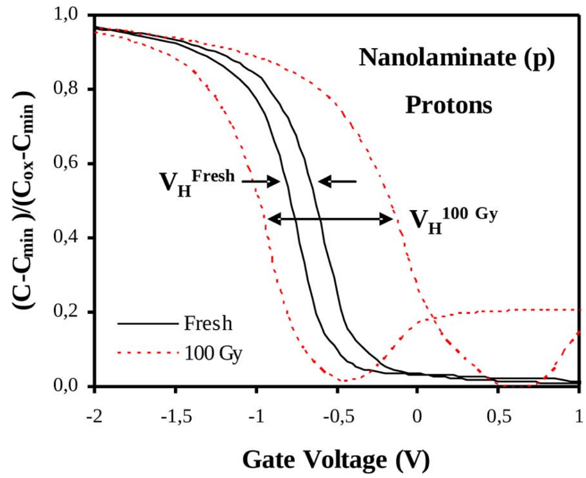

Fig. 9. C-V characteristics of p-type nanolaminate -based capacitors before and after proton irradiation (total dose: 100 Gy). A positive displacement of the invertion-to-accumulation curve was observed, which is consistent with the presence of negative charge inside the dielectric. Also, a increment of the hysteresis value was observed, similarly as in the case of oxygen irradiation.

The reason of this effect could be attributed to the increase of the leakage current and series resistant and/or to a gradual reduction of the dielectric constant. In the former case, it has been reported an increase of the series resistant after irradiation [19]–[21] that affects the substrate layer by means of displacement damage [19] and the back contact of the structure [20]. The effect of the series resistance in conjunction with a large leakage current (Fig. 8) could introduce a significant reduction in the accumulation capacitance as reported in [22].

On the other hand, anomalous change of the dielectric constant has been reported in high-k nanolaminates after electron-beam irradiation [23] and after annealing in oxygen atmosphere [24]. In this latter case, the diffusion of oxygen atoms out of the high-k materials could generate an interfacial layer with lower dielectric constant which affects the overall capacitance value. For our experimental conditions, it is possible to assume that the generation of dangling bonds contributes to this effect [25].

C. Protons

Different set of samples have been irradiates with 10 MeV protons. Fig. 9 shows hysteresis characteristics of the C-V curves before and after irradiation for nanolaminate MIS stack. Contrary to the previous case, the accumulation capacitance remains constant during the irradiations up to an accumulated dose of 100 Gy.

It is observed a hysteresis increment of about 700 mV (Fig. 9)

Another relevant characteristic of the irradiation with protons is the occurrence of a "stretch-out" of the C-V curves. Fig. 10 shows a typical evolution of the C-V curves as function of accumulated dose. It is observed an initial shift towards positive bias (curve 2) and a turn around effect for higher dose accompanied with the "stretch-out" of the curve (curve 3) indicating generation of interface traps and charge trapping.

The MIS stacks with Al_2O_3 gate oxide shows similar characteristics under the same irradiation conditions (results not shown), but the magnitude of the hysteresis and "stretch-out" effects are not as relevant as in the case of nanolaminates.

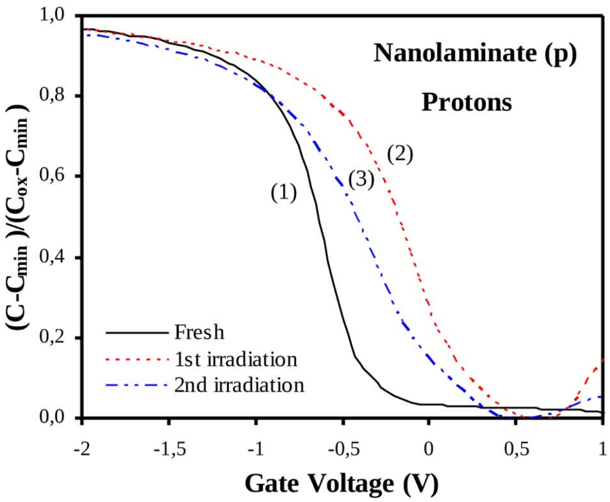

Fig. 10. C-V characteristics of p-type nanolaminate-based capacitors during proton irradiation sessions (total dose: 400 Gy). The figure shows that after an initial positive V_C-shift, when the dose was increasing a turn-around effect appeared accompanied with a "stretch-out" of the characteristics, which indicate both the generation of interface states and charge trapping.

TABLE I
SUMMARY OF EFFECTS OBSERVED IN SAMPLES WITH DIFFERENT DIELECTRICS IRRADIATED WITH GAMMA RAYS, OXYGEN IONS AND PROTONS. TC: TRAPPED CHARGE; IT: INTERFACE TRAPS

Dielectric **Radiation**	*Al_2O_3*	*Nanolaminate*	*HfO_2*
Gamma-rays ^{60}Co	$\Delta V_C < 0$ → TC $\Delta V_H \approx 0$	$\Delta V_C < 0$ → TC $\Delta V_H \approx 0$	$\Delta V_C < 0$ → TC $\Delta V_H > 0$ → IT
Oxygen ions 25 MeV	$\Delta V_C \approx 0$ $\Delta V_H > 0$ → IT	$\Delta V_C \approx 0$ $\Delta V_H > 0$ → IT	Without information
Protons 10MeV	Turn-around effect $\Delta V_H > 0$ → IT	Turn-around effect $\Delta V_H > 0$ → IT	Without information

IV. SUMMARY

In this work, radiation damage of high-k MIS stacks was studied using electrical characterization. Our observations, under different sources of radiation are summarized in Table I in terms of the voltage shift at constant capacitance ΔV_C (trapped charge), and hysteresis of the C-V curves ΔV_H (interface traps) for all kind of high-k dielectrics under study.

It has been found out, in all cases, that gamma photons are efficient to generate positive trapped charge ($\Delta V_C < 0$, Fig. 4) but not to damage the interface ($\Delta V_H = 0$, Fig. 5).

On the other hand, 10 MeV proton and 25 MeV oxygen irradiation shows a different behaviour. It has been observed that the increasing of the hysteresis and stretch-out (this only for protons) of the C-V curves are more significant that the voltage shift at constant capacitance, indicating a relevant generation of interface traps.

It is important to note that the nanolaminate stack shows the highest levels of hysteresis and stretch-out of the C-V curves, in both radiation conditions. This result suggests that the interface between dielectric layers plays a relevant role in the study of the radiation response.

The interactions involved in the MIS stack under those radiation sources are quite different, making a physical-based correlation between them difficult, particularly if different high-k dielectrics layers are taken into consideration. However, the main trend of the results reported in this work gives some signs to understand the radiation hardness of nanolaminate gate oxides.

Although the differences between radiation sources (protons, oxygen ions and gamma photons) appears to be originated in the relative much lower recoil energies produced by the secondary electrons through Compton effect in a ^{60}Co source [26], the number of interfaces between dielectrics and the material thickness in the gate stack seems to affect the radiation response.

The oxide thickness of our samples are similar, thus it is not observed large differences of the accumulation of trapped charge. In fact, Fig. 4 does not show relevant variations of V_C.

On the other hand, as in previous studies for the case of HfO_2/SiO_2 [1], [2], the increase of the hysteresis and stretch-out of the C-V curves suggests that electron trapping may be an important problem and could dominate radiation induced trapped charge build up under some processing conditions.

Although our results are probably too limited to draw a definitive conclusion, we may reasonably conjecture that the radiation response of Al_2O_3/HfO_2 nanolaminates based devices is fundamentally different than that of conventional Si/SiO and dominated by the trapping effects on the interfaces.

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