Total Dose Radiation Response of Nitrided and Non-nitrided SiO_2/4H-SiC MOS Capacitors

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***Abstract*—The total dose radiation response of nitrided and non-nitrided n-type 4H-SiC is reported for metal oxide semiconductor capacitors exposed to 10-keV X-rays under positive bias. The radiation response is affected strongly by differences in the SiC band gap and interface/near interface SiO_2 trap density from typical Si MOS devices. Significantly higher net trapped positive charge densities were observed in nitrided n-SiC MOS capacitors compared to the non-nitrided samples. The mechanisms contributing to the differences in the charge trapping in these devices are discussed. Differences in the interfacial layer between SiO_2/Si and SiO_2/SiC are responsible for the observed dissimilarities in charge trapping behavior.**

***Index Terms*—Capacitors, metal-oxide-semiconductor (MOS), nitrided, radiation damage, silicon carbide (SiC), total dose, X-ray.**

I. Introduction

SILICON has been the most widely used semiconductor material and has remained largely unchallenged in the microelectronics industry for the past several decades. However, silicon is not ideal for some high power applications where a larger energy gap and higher thermal conductivity are desirable. Silicon carbide (SiC) possesses unique physical properties that are extremely favorable for high temperature and high-power electronics. These properties (values mentioned for 4H-SiC polytype) include a wide band gap ($\sim$ 3.3 eV), high thermal conductivity (4.5 W cm^{-1} s^{-1}), high electron saturation velocity (2.0×10^7 cm s^{-1}) and a high breakdown field (2.0 MV cm^{-1}) [1], [2]. The ability to grow thermal oxides (SiO_2) using conventional thermal oxidation (like Si) is a major advantage for the development of SiC metal oxide semiconductor field effect transistors (MOSFETs) [3], [4]. Recent developments in SiC device technology have opened up the aerospace and aircraft domains for SiC based power electronics, where these devices could be utilized for substantial weight savings and enhanced jet engine performance. Among the numerous SiC polytypes (that is, having the same chemical composition, but with different crystal structures from different stacking orders), 4H- and 6H-SiC are commercially available in a quality considered appropriate for device applications. Currently, the 4H-SiC polytype has gained more importance as compared to the others due to its significantly higher and more isotropic bulk carrier mobility [5]. This work focuses on the effects of ionizing radiation on the charge trapping behavior of MOS capacitors fabricated on 4H-SiC substrates.

Historically, 4H-SiC MOSFETs suffered from low inversion channel mobilities due to extremely high pre-irradiation interface trap densities (D_{it}) close to the 4H-SiC conduction band-edge ($D_{it} > 10^{13}$ cm^{-2} eV^{-1}). Annealing in hydrogen, which is a key in improving the quality of the interface in SiO_2/Si is not effective in the case of SiC [6]. Alternatively, nitridation of the SiO_2/SiC interface has emerged as the most effective solution to reduce the pre-irradiation interface trap densities. Nitridation via post-oxidation annealing in NO results in significant reduction of D_{it} ($D_{it} \sim 10^{12}$ cm^{-2} eV^{-1} at $E_c - E \sim 0.1$ eV) and subsequently improves channel mobility [7]–[10]. For applications in radiation environments, it is important to study the radiation tolerance of 4H-SiC MOS devices. In this paper, we report the x-ray radiation response of positively biased ($E_{ox} =\sim +1.5$ MV/cm) nitrided and non-nitrided 4H-SiC MOS capacitors grown on the (0001) Si face. We compare the results of these irradiations to previously published data for grounded irradiations and find significant differences, mainly due to enhanced hole trapping [11]–[14]. These results provide new insights into the nature of charge trapping at the SiO_2/SiC interface.

II. Experiments

Commercially available 4H-SiC (n-type, (0001) Si-face) substrates with nitrogen doping of 5×10^{15} cm^{-3}, were used to fabricate the MOS capacitors. A 10 μm thick epitaxial layer was grown on these n+ substrates. Before the oxidation step, samples were cleaned using an industry standard RCA cleaning procedure. Approximately 34 nm thick oxides were grown by performing dry oxidation at 1150°C for 4 h. The samples were annealed in flowing Ar for 30 min at the same temperature after oxidation. Some of the samples were subsequently nitrided at 1175°C in flowing NO for 2h. The gas was changed back to Ar and the temperature ramped down to 900°C before removing

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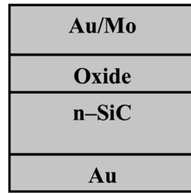

Fig. 1. Schematic diagram of the capacitor stack with Au/Mo gate metal contact, $\sim$ 34 nm thermal oxide, 4H-SiC substrate, and Au back contact.

the samples from the furnace. Two layers of gate metal, namely 100 nm of Mo followed by 100 nm of Au, were deposited by DC sputtering. Circular MOS capacitor contacts with diameters of 350 μm and 700 μm were patterned and defined using standard photolithography and lift-off techniques. A schematic of the capacitor stack is as shown in Fig. 1.

The capacitors were characterized using capacitance voltage (CV) measurements to measure the effective oxide charge and interface trap density (D_{it}—calculated by comparing the high frequency and quasistatic measurements) before irradiation [15]. Pre-irradiation CV measurements on the nitrided and non-nitrided capacitors verified the effect of nitrogen incorporation in reducing the interface trap density (D_{it}) from $\sim 7 \times 10^{12}$ cm^{-2} eV^{-1} to 1×10^{12} cm^{-2} eV^{-1} at $E_c - E = 0.2$ eV after nitridation.

Nitrided and non-nitrided SiC MOS capacitors were irradiated in an ARACOR 10-keV X-ray source at a dose rate of 31.5 krad (SiO_2)/min. Post-irradiation characterization was performed by similar CV measurements. The irradiations were performed as a function of bias and dose for the two different samples. The samples were exposed at room temperature to doses of 30 to 10 000 krad(SiO_2) at a positive bias ($E_{ox} =\sim 1.5$ MV/cm) during irradiation. The CV curves were measured at 100 kHz at room temperature with a ramp rate of 0.5 V/s for the dc voltage sweeps. The shifts in these curves were compared with the pre-irradiation high-frequency curves for calculating radiation-induced charge buildup. The Winokur and McWhorter charge separation technique was used for further analysis [16].

For Si MOS devices, the midgap voltage shift, ΔV_{mg} is frequently assumed to be proportional to the increase in oxide-trap charge density. The stretchout in the CV curves between midgap and flatband along the voltage axis, commonly referred to as ΔV_{it}, was used to estimate the increase in the interface trap density following the irradiations [16]–[18]. It should be noted that midgap voltage shifts for a wide band-gap material such as SiC include significant contributions from deep interface traps (which appear as fixed charge) in addition to the oxide trapped charge, as we discuss further below. Hence, effects that usually would be observed in the threshold or flatband voltage for Si MOS devices can be observed in midgap voltage for SiC MOS devices. In addition, in SiC, the major fraction of ΔV_{it} arises from interface traps with energy levels between flatband and $\sim$ 0.6 eV from the conduction band edge [19]. This contrasts with Si where the energy levels of the interface traps measured from CV analysis are located between flatband and inversion. In order to further investigate the radiation-induced charge, isochronal annealing studies were performed by annealing at a positive bias of 5 V at temperatures from 25°C to 175°C [20]. The sample was heated in 25°C steps and held at the respective temperatures for 10 min before cooling back down to room temperature for CV measurements. The contributions from the positive and the negative charges were extracted from these measurements.

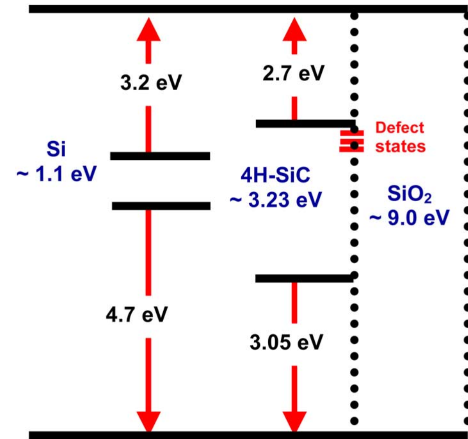

Fig. 2. Schematic of the band diagram of Si, 4H-SiC and SiO_2 shows that the wider band gap in the case of 4H-SiC results in the interface buildup being observed which otherwise would have figured outside the Si band gap.

III. Results and Discussion

A. Fundamental Band Gap and Interlayer Differences in SiO_2/Si and SiO_2/SiC

It is important to understand the basic differences between the SiO_2/Si and the SiO_2/SiC MOS systems before addressing the radiation damage behavior. As the bulk of the oxide grown on SiC is stoichiometrically similar to oxides grown on Si, bulk hole trapping is expected to be similar to the trapping in SiO_2/Si capacitors when exposed to radiation. On the other hand, the SiO_2/SiC interface is markedly different than Si. In addition, there exists a considerable difference in the band gap and band offsets of Si and SiC with respect to SiO_2. A detailed schematic diagram of the band gap of SiC and Si with respect to SiO_2 is shown in Fig. 2. Note that certain intrinsic defects common to both the SiO_2/Si and SiO_2/SiC system may fall within the band gap of SiC, but not in Si. Furthermore, in SiC, the response times of the interface traps during the CV sweep increase exponentially with energy from the band edge. As a consequence, interface traps deeper in the SiC band gap ($E_c - E \sim 0.6$ eV to $E_c - E \sim$ midgap for n-SiC), appear as fixed charge, as they do not respond to changes in the applied bias during the time scale of the CV measurements [19].

B. Radiation Results (Nitrided & Non-Nitrided)

Figs. 3 and 4 show the radiation response of nitrided and non-nitrided SiO_2/4H-SiC samples under positive bias. For the non-nitrided devices, initially the CV curves shift to the left due to a predominance of trapped positive oxide-trap charge, but then shift to the right with higher doses owing to the buildup of negative charge. Contrary to the non-nitrided case, the nitrided samples continued to show a monotonic increase in the net positive charge for all irradiation doses up to 10 Mrad(SiO_2), as evident from Fig. 4. ΔV_{mg} and ΔV_{it} are plotted as functions of dose for both sample types in Figs. 5 and 6, respectively. At

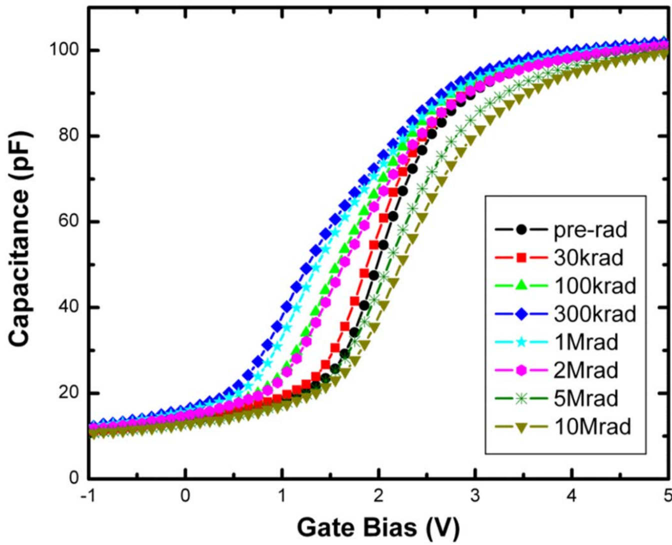

Fig. 3. 100 kHz CV curves showing first positive charge trapping, and then a turnaround from positive to negative charge trapping for non-nitrided capacitors biased at 1.5 MV/cm.

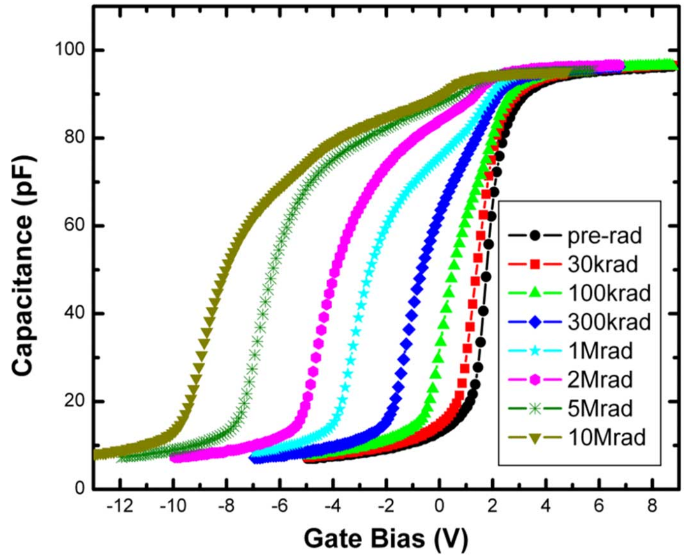

Fig. 4. 100 kHz CV curves showing the increased positive charge trapping for positively biased ($E_{ox} = \sim +1.5$ MV/cm) nitrided capacitors.

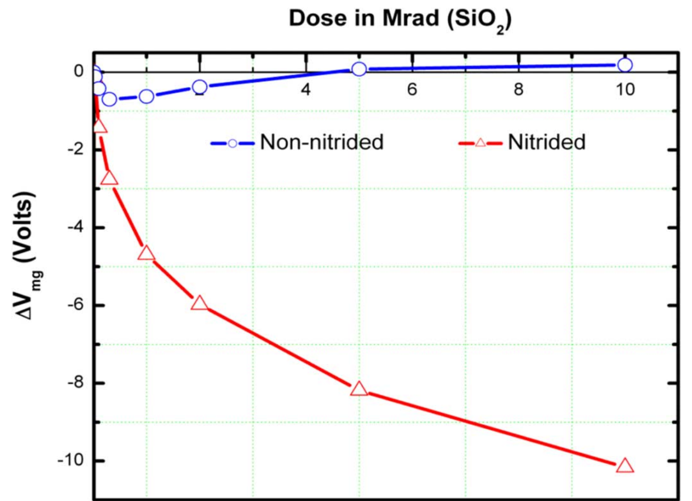

Fig. 5. Voltage shifts (ΔV_{mg}) as a function of dose in Mrad(SiO_2) for nitrided and non-nitrided samples positively biased at 1.5 MV/cm.

doses higher than 300 krad(SiO_2), the turnaround in Δ V_{mg} is seen clearly for the non-nitrided devices in Fig. 5; these show much lower net trapped positive oxide-trap charge than the nitrided devices. For higher doses, negative charge trapping dominates for the non-nitrided devices. Hence a charge compensation effect is observed for the non-nitrided samples similar to earlier work using electron injection [21]. The turnaround from net positive to negative charge trapping in midgap voltage for the non-nitrided samples can be attributed to deep interface trap buildup ($E_c - E \sim 0.6$ eV to midgap) and/or negative charge buildup due to near-interfacial electron traps [12], [13], [22]. The precursors to these electron traps may not be charged during pre-irradiation characterization when the Fermi level sweeps through the band gap, but become charged due to ionizing radiation. Earlier studies have reported interface trap buildup at non-nitrided SiO_2/SiC interfaces resulting from electron injection via photo and Fowler-Nordheim methods [21]–[24]. A significant density of acceptor states was observed at the SiO_2/SiC interface after electron injection as compared to SiO_2/Si [21], [23]. This was tentatively ascribed to the presence of excess carbon in the form of carbon clusters with sp^2 bonding at the SiO_2/SiC interface. Thus, the turnaround observed in the midgap voltage plotted in Fig. 5 may be due to the result of compensation of positive charge from both negatively charged deep interface traps and near-interface electron traps.

In the nitrided case, the midgap voltage shifts due to the increase in the oxide trap charge with increasing dose do not show a turnaround effect and net positive charge trapping continues to the highest dose studied. Hence, the nitridation process and/or the nitrided interlayer, on the order of ≤ 1 nm from the SiO_2/SiC interface, must contribute in an essential way to the observed differences in trapping between the nitrided and the non-nitrided samples [25]. The Δ V_{mg} was observed to be about -10 V at 10 Mrad(SiO_2) for the nitrided capacitors. This does not appear to reach saturation, indicating the possibility of more hole trapping for doses above 10 Mrad(SiO_2).

The values of Δ V_{it} estimated from the differences in the flatband and midgap voltage shifts indicate a small increase in interface-trap density in both cases (nitrided and non-nitrided), plotted as a function of dose in Fig. 6, however once again we caution that this measures only relatively shallow interface traps in SiC MOS devices, with deeper traps contributing to midgap voltage shifts, in contrast to Si MOS devices, where the full interface-trap distribution contributes to ΔV_{it}.

C. Mechanisms for Enhanced Positive Charge Trapping in Nitrided Capacitors

We first note that much larger shifts in the nitrided SiC MOS devices studied here are observed than in previous studies of devices irradiated without bias [11]–[14], owing to the increased charge yield for biased irradiation, as opposed to unbiased irradiation [26]. One obvious reason for the extremely large positive oxide-trap charge densities in these devices is the large

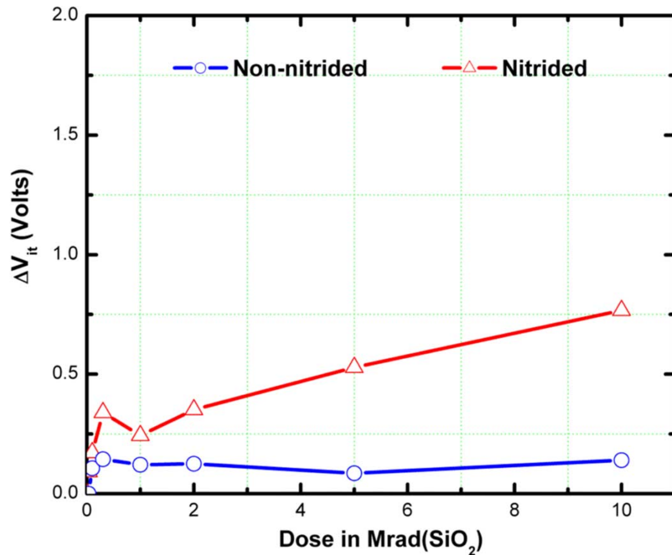

Fig. 6. Voltage shifts (ΔV_{it}) as a function of dose in Mrad(SiO_2) for nitrided and non-nitrided samples positively biased at 1.5 MV/cm.

oxygen vacancy density that is expected from the extremely high oxidation temperatures necessary to grow SiO_2 on SiC. Previous electron-paramagnetic resonance, electrical, characterization, and thermally stimulated current (TSC) studies have shown a strong correlation between high oxidation temperatures, high oxygen vacancy densities, and large net positive-oxide-trap charge buildup [27]–[29], at least in the absence of the charge compensation processes observed in the non-nitrided devices above in Figs. 3 and 5. Indeed, detailed TSC studies of nitrided oxides have shown a significant enhancement of O-vacancy related hole trapping in reoxidized nitrided oxides for Si MOS devices [30].

We now discuss other mechanisms unique to SiC for the enhancement in midgap voltage shifts in the nitrided devices that is suggested by recent experimental and theoretical work on the SiC/SiO_2 materials system. Oxidation of SiC to form SiO_2 necessitates the removal of C (typically in the form of CO that leaves the growing oxide) [31]. Some of the C, however, remains at the interface and forms defect structures. Nitridation in NO plays a significant role in passivating the fast interface traps, presumably by removal of π-bonded carbon, and also is known to eliminate slow trap centers in the near interfacial region of SiC [32], [33]. This reduction occurs over the entire band gap of SiC, although most drastically near the conduction band edge. This pronounced reduction of the density of interface and near-interface electron traps at nitrided interfaces means there is less compensation of the positive charge trapped in the bulk of the oxide and hence no evidence of turnaround for the nitrided capacitors. Moreover, extensive theoretical calculations [34], done using density-functional theory (local-density approximation with generalized gradient corrections for exchange-correlation, ultra-soft pseudo-potentials, plane-wave basis sets, and large supercells; details of the supercells are reported in [29]), combined with available experimental evidence and prior analysis, have led to the conclusion that the SiO_2/SiC interface contains a transition layer that can best be described as a Si-C-O bonded amorphous network composed of Si-O-Si bridges, and direct Si-Si, C-C, and Si-C bonds [34]. Si atoms would be primarily fourfold-coordinated because C atoms would preferentially occupy sites with threefold coordination, in which case they can be referred to as C dangling bonds (amorphous carbon has both three-and four-coordinated C; amorphous SiC contains C dangling bonds but there is no evidence for Si dangling bonds). Thus, the primary defect structures that can produce localized energy levels in the SiC band gap are isolated C dangling bonds, C dangling-bond complexes (e.g., a C-C bond where both C atoms are threefold coordinated), and Si-Si bonds (the latter are true defects in the SiC/SiO_2 interface, whereas they appear as defects at the Si/SiO_2 interface only when they are longer than normal Si-Si bonds). C dangling bonds have localized levels in the SiC band gap. Si-Si bonds, depending on the bond length, may have both a bonding and an antibonding level in the SiC band gap (bottom and top of the band gap, respectively).

It has further been proposed that nitrogen passivation of interface traps occurs because it is energetically favorable for N to replace threefold-coordinated C and Si atoms (N always prefers threefold coordination, whereas C assumes both, with a slight preference for three, as in graphite versus diamond). The result is a Si-C-N-O bonded interlayer [34]. New calculations, using density functional theory suggest that the threefold-coordinated N at the SiC/SiO_2 interface results in a localized level at $\sim$ 0.5 eV from the valence band edge of SiC due to the N lone pair. This lone pair can trap holes under ionizing radiation, thereby enhancing the effects of increased positive charge trapping in the NO passivated samples.

Finally, we note that it is likely that the nitrogen also reduces the densities of interface defects that appear as fixed charge in SiC devices, but would show up as interface traps in Si devices, consistent with observations of the effects of nitridation on oxides on Si [35]–[37]. The absence of charge compensation via interface-trap buildup would show up as increased midgap voltage shifts in the nitrided devices.

D. Annealing Studies

Owing to the similar densities in the range of 10^{12} cm^{-2} for both positive and negative charges, the compensation effect explains the apparent superior radiation hardness of non-nitrided SiC MOS structures as described elsewhere [38]. This counterbalance between the two charges in the non-nitrided samples was verified from isochronal annealing studies [20] conducted at $+5$ V bias as evident from the CV curves in Fig. 7. The figure shows pre-irradiation and post-irradiation CV curves measured after 10 Mrad(SiO_2). The elevated temperature annealing studies were performed after two weeks of room temperature annealing with all of the positive charges annealed at 150°C. A significant portion of the negative charges annealed at higher temperatures ($\sim$ 300°C). This was confirmed from the isochronal annealing measurements. The CV curves begin to shift towards positive voltages with every 25°C temperature increase (all curves not shown), indicating a decrease in the net trapped positive oxide trap charge. Finally, at 150°C, the CV curves no longer shift with increasing temperature, and the curve remains on the positive side of the pre-irradiation curve

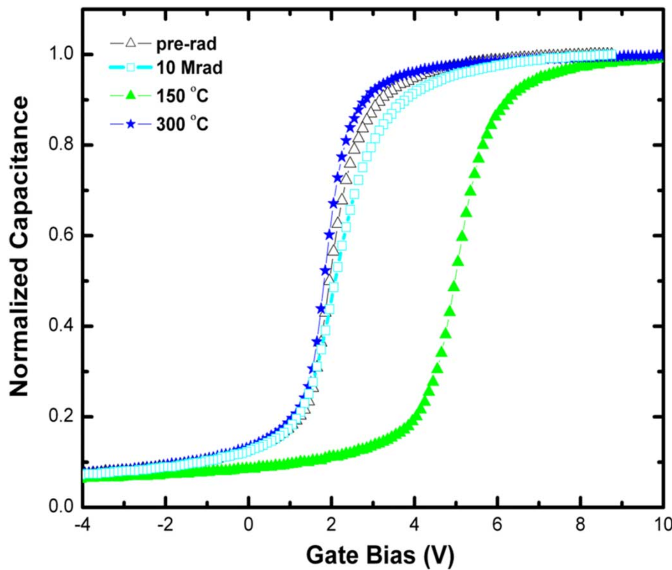

Fig. 7. CV curves plotted for the annealing cycles for non-nitrided capacitors with pre-irradiation (–△– open triangles), 10 Mrad(SiO2) (–□– open teal squares), 150°C anneal (–▲– closed green triangles) and 300°C anneal (–★– closed blue stars) indicating the compensation effect.

until significantly higher temperatures are reached (direct annealing to 300°C, as described further).

This validates the hypothesis of the existence of both positive and negative charges, with only the negative contribution present at 150°C. The CV curves still exhibited stretchout, compared to pre-irradiation curve, even after annealing at 150°C. The temperature was further increased directly to 300°C, this time with no bias applied, and the CV curve shifted back to its pre-irradiation position and the radiation-induced stretchout disappeared. This confirms the annealing of interface trapped charge at higher temperatures and is consistent with earlier reports [21], [23]. The possibility of electron injection during the annealing cycles was probed by biasing the pre-irradiated devices at $+5$ V for 10 min at 100°C and no change in the CV behavior was observed.

Annealing studies were also conducted on nitrided samples, with the detrapping of most of the predominant positive charge observed at 150°C. The loss of the stretchout and return of the CV curve to its pre-irradiation position (curves not shown) was verified by annealing at 300°C. Hence the post-irradiation annealing studies confirm the presence of positive and negative charge contributions to the CV behavior in the SiC MOS capacitors.

IV. Conclusion

The total ionizing dose response of nitrided and non-nitrided SiO_2/SiC capacitors under positive bias was studied. Negative charge trapping in non-nitrided SiO_2/SiC devices was found to be significantly higher than for typical SiO_2/Si MOS structures. The high oxidation temperatures required to grow SiO_2 on SiC lead to high oxygen vacancy densities. For the nitrided MOS capacitors, higher net positive charge build-up was observed, consistent with a lower density of interface and near-interface electron traps. Theoretical calculations also suggest a nitrogen lone pair present in the proximity of the valence band edge of SiC may increase positive trapped charge in the nitrided devices. It is also likely that these devices exhibit a decrease in interface defects that would appear as interface traps in Si devices, but function as negative fixed charge in SiC owing to its wider band gap.

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