

Charge Trapping Properties of 3C- and 4H-SiC MOS Capacitors With Nitrided Gate Oxides

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Abstract—Silicon-carbide-based MOS capacitors were formed on either 3C (epitaxial on Si) or 4H substrates and using SiO₂ gate dielectrics both with and without interfacial nitrogen. The charge trapping properties of these structures were examined after exposure to ionizing radiation. In all cases interfacial nitrogen results in improved trap density and increased oxide charge trapping. For equivalent nitrogen content, 3C-based devices exhibit more charge trapping than the 4H-based equivalents.

Index Terms—MOS, NO, N₂O, POA, 3C-SiC, 4H-SiC.

I. INTRODUCTION

SILICON CARBIDE (SiC) is a candidate material for high-power and high-frequency electronic devices due to its excellent thermal conductivity and high breakdown field [1], [2]. It is preferred over other wide band gap semiconductors because SiO₂ can be thermally grown to form the gate oxide [3], [4]. In addition, SiC has excellent thermal and chemical stability, a large saturation drift velocity and high bulk electron mobility.

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SiC exists under stoichiometrically equivalent crystalline structures called polytypes. The 4H-SiC polytype has received more attention compared to others due to its greater band gap, combined with a high and more isotropic bulk carrier mobility [5]. Among the other SiC polytypes, cubic silicon-carbide (3C-SiC) is another promising candidate for electronic applications because of its compatibility with Si CMOS technology [6].

Historically, 4H-SiC MOSFETs have suffered from low inversion channel mobilities due to extremely high interface trap densities in un-passivated devices (D_{it} close to the 4H-SiC conduction band-edge $\sim 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$). Annealing in hydrogen, which is a key in improving the quality of the interface in SiO₂/Si is not sufficient in the case of SiC [7]. Nitridation of the SiO₂/SiC interface, via nitric oxide (NO) or nitrous oxide (N₂O) post-oxidation annealing (POA), has emerged as the most effective solution to reduce the pre-irradiation interface trap densities [8]–[14]. Indeed, it significantly improves channel mobility by reducing the D_{it} . Thus, it is of interest to relate the incorporation of nitrogen to the reliability and radiation response of SiC-based devices.

3C-SiC substrate MOS capacitors with as-grown SiO₂ gate dielectrics have been shown to be relatively resistant to ionizing radiation-induced degradation [15]. The radiation response of 4H-SiC MOS capacitors has also been studied recently [16]–[18]. In 4H-SiC devices, it was demonstrated that a NO POA leads to the suppression of interface trap generation due to electron injection, but also enhances the formation of hole traps, yielding large voltage shifts following X-ray irradiation [19]–[21]. Here we report the total dose radiation response of both 3C- and 4H-SiC-based MOS capacitors with oxides grown in either O₂, NO or N₂O, providing a comparison of the reliability of the SiO₂/SiC interface as a function of the oxidized polytype and of the nitridation processes. The voltage shifts induced by x-ray irradiation are detected using capacitance-voltage ($C - V$) measurements and discussed in terms of incorporated nitrogen densities extracted by secondary ion mass spectroscopy (SIMS).

II. DEVICES AND EXPERIMENTS

The devices considered in this study, processed at Griffith University, are n-substrate 3C- and 4H-SiC MOS capacitors. The starting substrates for the 4H-SiC were obtained from Cree Inc., with a high quality SiC epitaxial layer on top. The 3C-SiC was grown on Si, and was obtained from the Institute of Crystal Growth, Germany. Doping densities for 3C- and 4H-SiC are $1.8 \times 10^{16} \text{ cm}^{-3}$ and $2 \times 10^{15} \text{ cm}^{-3}$ respectively. All samples

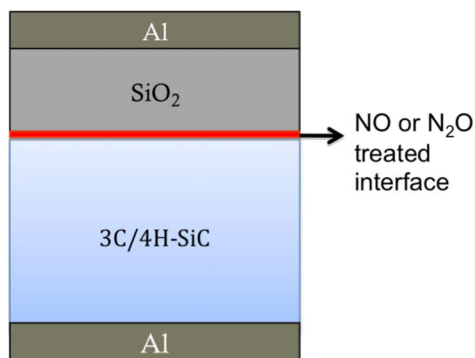


Fig. 1. Schematic diagram of the MOS capacitor structure used in this study.

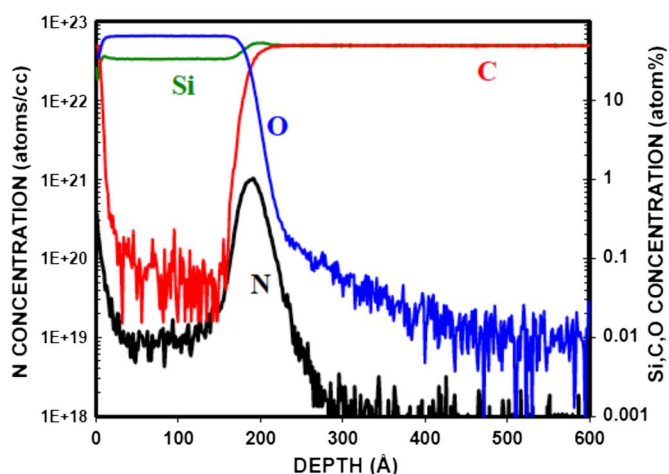


Fig. 2. SIMS profile showing N, O, Si and C concentration (3C-SiC sample with NO treatment).

were cleaned in a mixture of H_2SO_4 and H_2O_2 followed by the RCA process. SiO_2 gate dielectrics are thermally grown on the (0001) Si face of 4H-SiC and on the (001) plane of 3C-SiC. The gate dielectrics were thermally grown using three different processes: 1) dry oxygen at 1185°C ; 2) NO for 2 hours at 1185°C ; 3) N_2O for 1 hour at 1185°C . This yielded oxide thicknesses in the 18–25 nm range. A schematic cross section of the devices is shown in Fig. 1. Aluminum is used for the gate and substrate electrodes.

Irradiation experiments were performed with an ARACOR 10-keV x-ray source at a dose rate of $31.5 \text{ krad}(\text{SiO}_2)/\text{min}$. Different biases were applied to the devices during the radiation experiments. Constant voltage stress (CVS) experiments (no radiation) were performed for a duration corresponding to the radiation time in order to separate the effects of bias and irradiation [22]. High frequency (1 MHz) capacitance-voltage ($C-V$) and conductance-voltage ($G-V$) measurements were performed between successive irradiation or CVS steps to monitor the change in the midgap voltage (V_{mg}) [23]. The interface-trap density between 0.2 and 0.6 eV from the SiC conduction band edge was determined from simultaneous high frequency (100 kHz) and quasi-static $C-V$ measurements made at

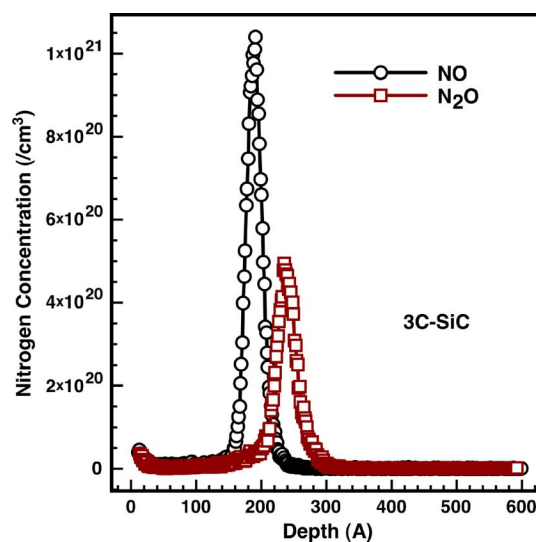


Fig. 3. Nitrogen concentration as a function of depth for 3C-SiC MOS capacitors grown in NO and N_2O .

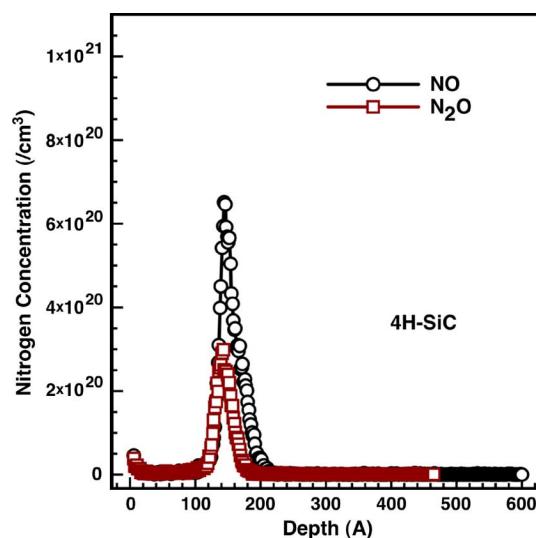


Fig. 4. Nitrogen concentration as a function of depth for 4H-SiC MOS capacitors grown in NO and N_2O .

room temperature. The relation between the gate voltage and the corresponding band gap energy was derived using the Berglund method [24].

SIMS measurements were performed to extract the nitrogen concentrations at the interface. The nitrogen concentrations have been calibrated against a thermal silicon dioxide standard that has been ion implanted with nitrogen. The depth scale has been calibrated against a crater measurement on the same standard sample. Although the absolute values extracted from SIMS are expected to be accurate only within a factor of two, the shapes of the profiles and the relative concentrations between samples provide an excellent basis for direct comparison [21].

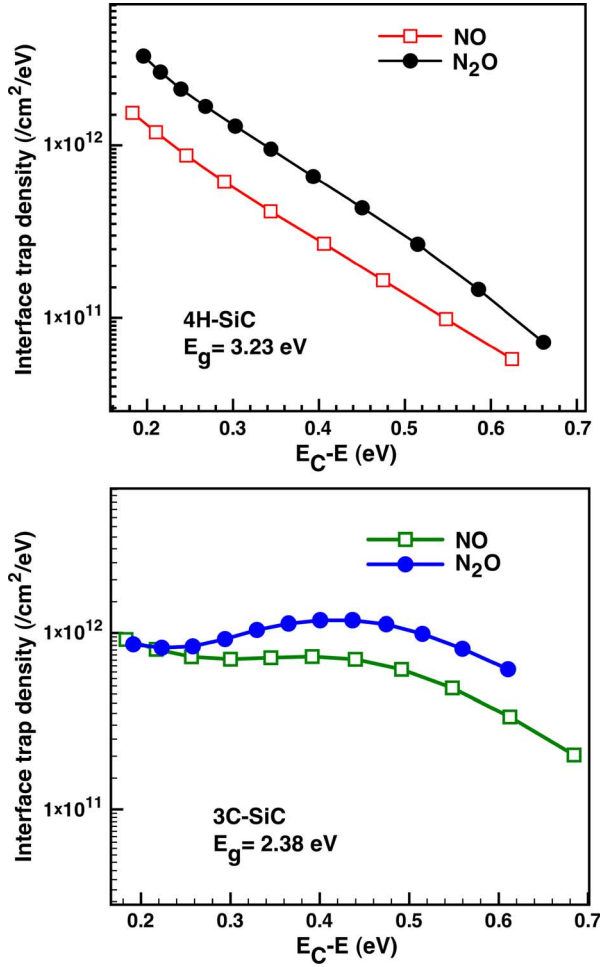


Fig. 5. Interface trap density, D_{it} , as a function of the energy relative to the semiconductor conduction band edges for 4H- and 3C-SiC samples.

III. RESULTS AND DISCUSSION

A. SIMS Profiles

Fig. 2 shows the SIMS profiles for nitrogen (N), carbon (C), oxygen (O), and silicon (Si) for the 3C-SiC sample with NO treatment. Concentrations corresponding to the nitrogen profiles, N, are labeled on the left axis (the depth profile is resolution limited). The C, O, and Si concentrations are plotted in arbitrary units on the right axis.

Comparisons of the nitrogen profiles for the 3C- and 4H-SiC MOS capacitors are shown in Figs. 3 and 4. Although the relative positions of the peaks vary because of the slight variations of the oxide thicknesses, we observe the accumulation of nitrogen at the interface between SiO_2 and SiC. It is evident that NO grown oxides result in a greater N concentration at the interface for both polytypes. Also, 3C-SiC has a greater N concentration for both the NO and N_2O processes as compared to 4H-SiC.

B. Interface-Trap Densities

The pre-irradiation interface-trap density of all devices is shown in Fig. 5. 3C- and 4H-SiC have different energy band gaps. The valence band edges for 3C- and 4H-SiC are at the same level in energy. Interface-trap densities in the SiC band

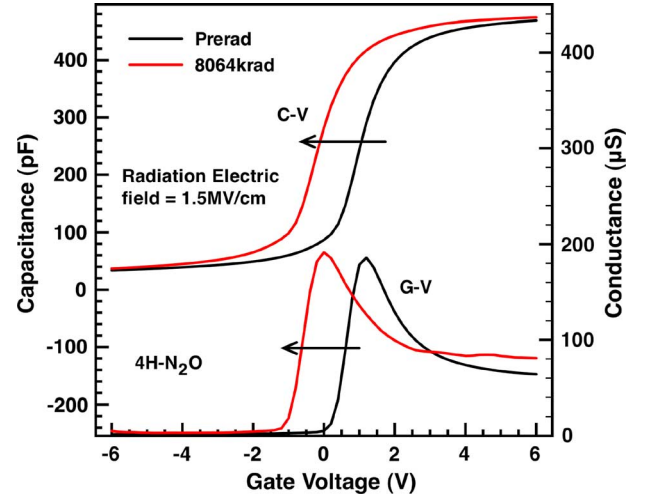


Fig. 6. Capacitance/conductance-voltage characteristics for 4H-SiC MOS with N_2O treatment (arrows in the figure points to the total dose induced shifts).

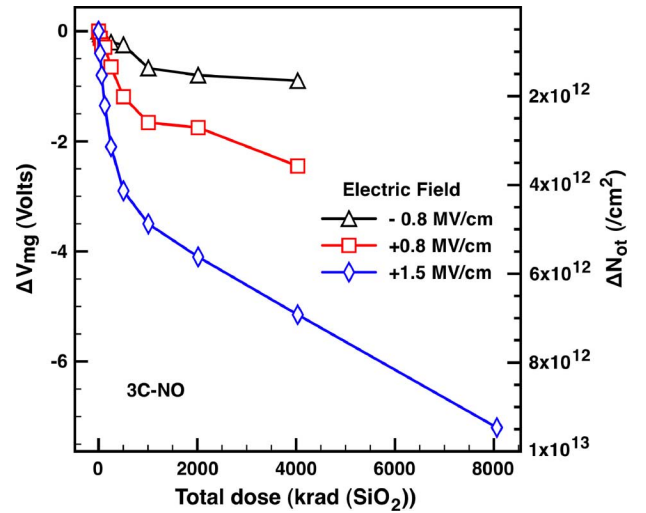


Fig. 7. Shift in midgap voltage as a function of x-ray dose for 3C-SiC MOS capacitors with oxides grown in NO.

gap are asymmetric with a higher density closer to the conduction band edge. The N_2O -grown 3C-SiC and 4H-SiC devices have a greater interface-trap density than the NO-treated devices. This is consistent with previous reports that NO treatment creates a better oxide-SiC interface than N_2O treatment [8]. The interface-trap distribution for the oxides on 3C- and 4H-SiC is different in the band gap.

C. Radiation Effects on Interface-Trap Formation

Fig. 6 shows the $C - V$ and $G - V$ characteristics for N_2O grown 4H-SiC samples before and after 8 Mrad(SiO_2) total dose irradiation (biased at +1.5 MV/cm). The shift of the $C - V$ and $G - V$ characteristics toward more negative voltage indicates net positive charge trapping. No significant stretch-out of the $C - V$ characteristics is observed, indicating negligible interface-trap formation with radiation within 0.6 eV from the conduction band edge (for all radiation biases studied) [25]. No significant $C - V$ stretch-out was observed for other processes as well.

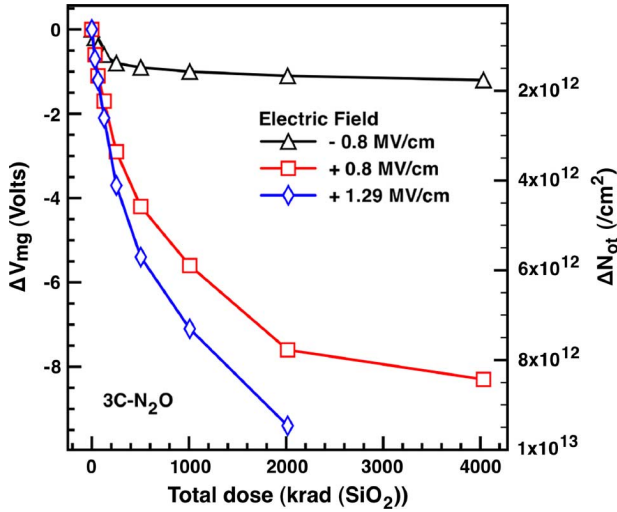


Fig. 8. Shift in midgap voltage as a function of x-ray dose for 3C-SiC MOS capacitors with oxides grown in N_2O .

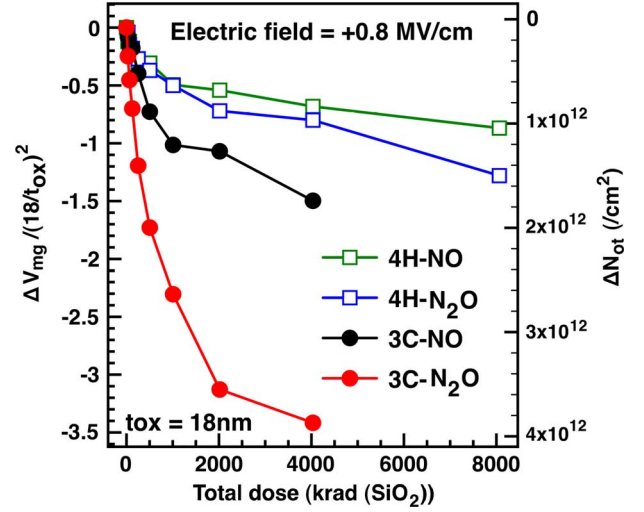


Fig. 10. Normalized midgap voltage shift comparison for NO and N_2O oxidation 4H-/3C-SiC MOS sample.

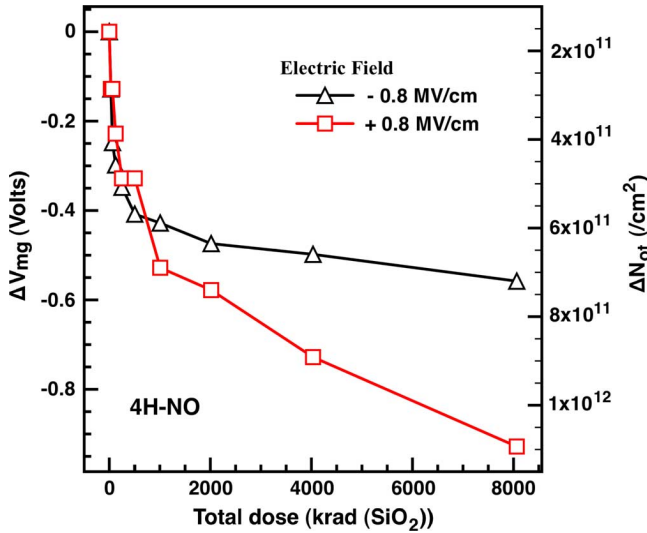


Fig. 9. Midgap voltage shift as a function of x-ray dose for 4H-SiC MOS capacitors with oxides grown in NO.

D. Oxide Trapped Charge

Figs. 7 to 9 show the evolution of the midgap voltage (and the corresponding net trapped charge density) in the various samples upon x-ray irradiation. A constant gate bias corresponding to $+0.8$ MV/cm or -0.8 MV/cm was applied during the exposure. In all cases, a buildup of net positive charge was observed. The following expression has been used to calculate the change in net oxide-trap charge density (ΔN_{ot}):

$$\Delta N_{ot} = -\frac{\Delta V_{mg} C_{ox}}{q} \quad (1)$$

where ΔV_{mg} is the shift in midgap voltage, C_{ox} is the oxide capacitance per unit area, and $-q$ is the electron charge. As expected, the shift is greatest for positive gate bias during irradiation as the holes are pushed toward the oxide/semiconductor interface. Higher shifts are observed at higher fields due to a higher fractional yield of the induced e-h pairs. No significant

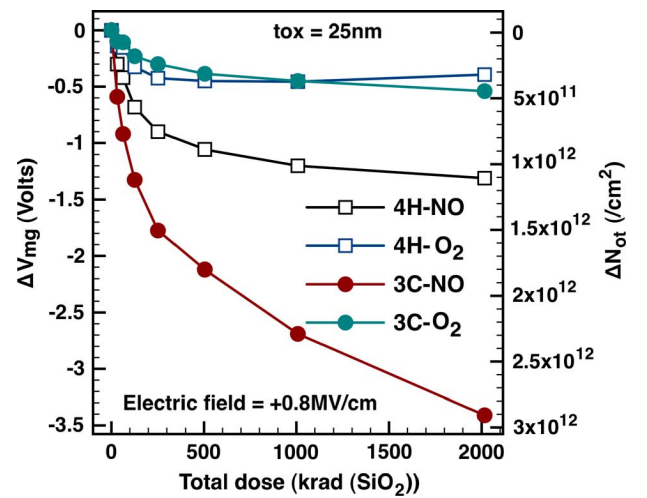


Fig. 11. Midgap voltage shift comparison for NO oxidized and as-oxidized 3C- and 4H-SiC MOS of the same oxide thickness.

stretch-out of the high frequency $C - V$ curves with irradiation and/or CVS is observed, indicating that the density of interface traps generated by irradiation and/or electrical stress is not significant in these devices.

In contrast, a noticeable increase in the stretch-out was reported in previous studies of radiation effects on 3C-SiC MOS devices that did not have a nitrided interlayer [15]. This suggests that nitridation improves the interface by preventing interface-trap generation during reliability stress conditions [26]. However, the flatband voltage shifts can be quite large under positive bias, in agreement with recent observations showing that nitriding the SiO_2/SiC interface increases the density of net positive oxide-trap charge [20], [21].

CVS measurements performed at equivalent positive biases show that there is a relatively small amount of background electron trapping in the 4H-SiC devices, and none is detected in the 3C-SiC devices. Because the magnitude of charge trapping produced by CVS is much smaller than the radiation-induced charge trapping, the compensating effects of electron injection

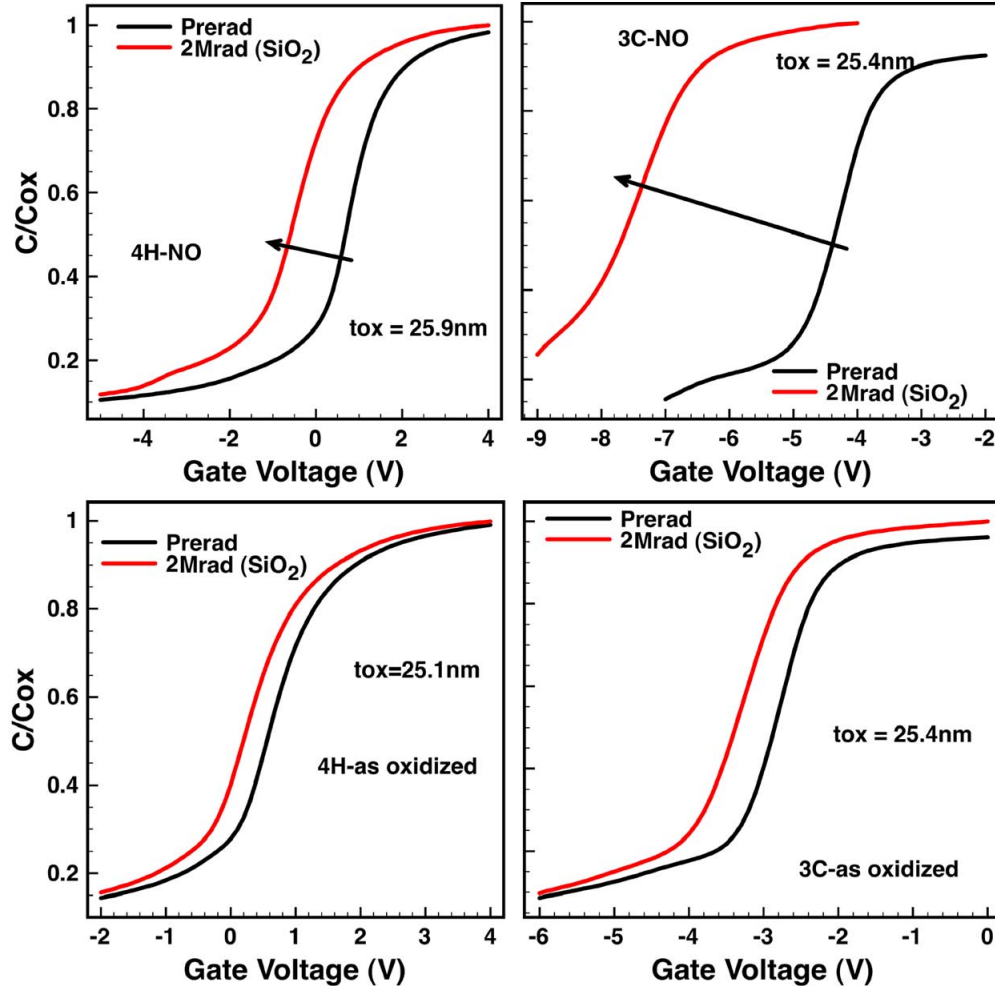


Fig. 12. Capacitance-voltage characteristics for 4H-NO, 3C-NO, 4H-as oxidized, and 3C-as oxidized MOS samples before and after a total dose of 2 Mrad (SiO₂).

into shallow traps [22] are small in these devices, and do not greatly impact the radiation-induced voltage shifts.

Oxides processed on different substrates and with different oxidation conditions had slightly different oxide thicknesses (in the 18–25 nm range), making it difficult to make a direct comparison of the trapped densities. We therefore attempt to normalize the data to compare the charge buildup and the resulting voltage shifts. Assuming that the centroids of the oxide-trap charge distributions are located at similar distances from the SiC/SiO₂ interface and that interface-trap charge densities are small compared to oxide-trap charge densities, it can be shown in the dose range where oxide-trap charge increases monotonically with dose (e.g., below ~ 2 Mrad(SiO₂)) that [27]

$$\Delta V_{mg} \propto t_{ox}^2 \quad (2)$$

for a given oxide field, where t_{ox} is the oxide thickness. Accordingly, the observed trends in charge trapping discussed below are larger than those associated with simple oxide thickness differences.

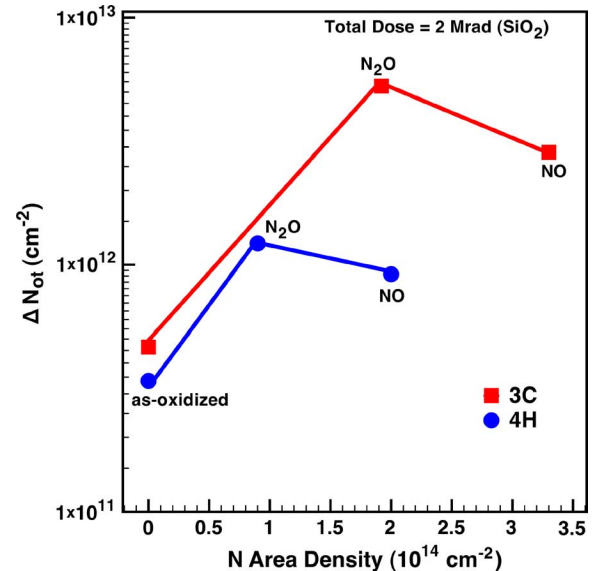


Fig. 13. Comparison of net positive oxide-trapped charge density as a function of nitrogen areal density for the 6 samples (3C-as oxidized, 3C-N₂O, 3C-NO, 4H-as oxidized, 4H-N₂O, 4H-NO).

E. Comparison of Trapped Charge

Fig. 10 compares the midgap-voltage shift for the NO- and N₂O-treated oxides on both substrates. The data for the 3C-SiC (NO and N₂O) and 4H-SiC (NO) devices are normalized with respect to the data for the 4H-SiC (N₂O) devices (oxide thickness = 17.9 nm). A greater density of trapped oxide charge is observed for oxides on the 3C-SiC substrates. This may be because the crystal quality of the CVD-grown 3C-SiC is not as good as the 4H-SiC [28]. The 4H-SiC material is grown by the modified Lely (sublimation) method and has an epi layer grown on top of it by CVD. In the case of 3C-SiC the difference of the crystal lattice constant between Si and SiC leads to a significant density of defects and stacking faults for the 3C-SiC substrates. Other factors that may lead to differences in charge trapping for the two polytypes are the different crystalline structures and orientations, yielding different semiconductor surface properties, as well as the different band gaps (~ 3.23 eV for 4H-SiC and ~ 2.38 eV for 3C-SiC).

The dominant hole trap in nitrided 4H-SiC has been recently linked to defect configurations involving N in the near-interface region [20]. Furthermore, it has been shown for the 4H-SiC case that the trapped charge density is linearly proportional to the N content [21]. The oxide-trap charge density is greater for the N₂O-treated 3C-SiC devices, indicating that the interface quality is not as good as for the NO-treated samples, consistent with the linearity mentioned above. The 3C-SiC samples contain more nitrogen than 4H-SiC samples, as shown above.

The oxidation kinetics of the two nitrogen containing gases, NO and N₂O, are different. Thus their impact on the electrical properties are not the same, as demonstrated by SIMS and D_{it} measurements, and further observed through the differences in positive charge buildup. According to calculations of Gupta *et al.*, the N₂O gas dissociates into NO (15%), O₂ (25.7%) and N₂ (59.3%) at 1130 °C [29]. The molar ratio of O₂ to NO is ~ 0.5 and 3 during NO and N₂O anneals, respectively [30]. The greater O₂ content due to dissociation of N₂O leads to competing reactions. NO incorporates nitrogen and oxidizes the substrate at a lower rate; whereas, O₂ causes a higher oxidation rate. The NO component resulting from the decomposition of N₂O causes the same chemical reactions and effects that occur in the cases of pure NO nitridation, but it is accompanied by substantial additional oxidation, with a correspondingly high defect creation in competition with the beneficial effects of the nitrogen. This competition favors more nitrogen incorporation in the case of NO, and possibly a higher concentration of O vacancies (also efficient hole traps in nitrided oxides [31]) in the N₂O oxides.

To further analyze the role of nitrogen at the interface on charge trapping in nitrided samples, we compared the charge buildup results in as-oxidized and NO-grown samples. Fig. 11 shows the results for both polytypes. In this case no normalization was necessary as the oxide thicknesses were very similar (within 1 nm). It is clearly seen that NO treated 3C samples trap more charge than 4H-SiC samples with the same treatment. The as-oxidized 3C- and 4H-SiC MOS samples trapped much less net oxide-trap charge than those which underwent NO nitridation, directly confirming that the nitridation process leads to higher net positive trapping (Figs. 11, 12). The very small

midgap voltage shifts in as-oxidized samples may either result from less hole trapping, or from compensating deep interface traps at the SiC/SiO₂ interface, which appear as fixed charges in these wide band gap SiC devices [4].

F. Discussion

Fig. 13 shows the shift in oxide trapped charge density vs. the N areal density for both polytypes at a total radiation dose of 2 Mrad(SiO₂). It has been shown previously that increasing the N areal density due to NO post-oxidation anneal results in consistently increasing net positive oxide trapped charge density [20], [21]. We see the same linear trend when comparing the as-oxidized samples to either the NO or N₂O grown oxides, further indicating that N plays a significant role in charge buildup.

In contrast, Fig. 13 suggests that this monotonic trend of increasing trapping with N content is not obeyed in the case where the N has been incorporated by different growth conditions (NO or N₂O). N₂O oxidized samples trap more charge, although they have lower N areal density. This may be attributed to the degraded quality of the interface after N₂O treatment, associated with an increase of O vacancies, as discussed above [31].

The 3C-SiC devices trapped more charge than 4H-SiC devices for any kind of nitridation. The results suggests that greater charge trapping on 3C- as compared to 4H-SiC is at least partly due to greater nitrogen concentration at the interface of 3C-SiC. When looking at a given nitridation process, the trend between charge buildup and nitrogen concentration indicate the origin of the traps may be similar in oxides grown on both polytypes, despite the difference in the crystal structure, orientation, quality, and band gap.

IV. CONCLUSION

Oxides grown on 3C-SiC substrates trap more charge than those grown on 4H-SiC substrates. N₂O-annealed oxides trap more charge for both 3C- and 4H-SiC substrates than do the NO-annealed oxides. N₂O-annealed oxides also have higher interface trap densities before irradiation. No significant generation of interface traps is observed for any of the nitride oxide samples after irradiation within 0.2 and 0.6 eV from the conduction band edge. We link greater charge trapping in the 3C devices compared to the 4H-SiC devices to the greater nitrogen content at the interface for 3C. N₂O follows different reaction kinetics and traps more oxide charge than NO, despite having a lower N concentration at the interface. Additional trapped positive charge in N₂O-treated devices may possibly be correlated to O vacancies in SiO₂.

Although N seems to play a role in the trapping process, we have observed that it is not the only factor to take into account. Indeed, the details of the nitridation and the nature of the substrate are also key parameters defining the quality of the oxide/semiconductor interface.

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