Suppression of interface state generation upon electron injection in nitrided oxides grown on 4H-SiC

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The flatband voltage stability of SiO_2/SiC metal-oxide-semiconductor capacitors upon electron injection can be enhanced by the introduction of nitrogen in a thermal gate oxide. We show that it is due to the suppression of negative charge buildup in interface states during injection. We discuss the role of nitrogen in this effect and how it might be linked to the passivation of interface defects. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2790374]

Among wide band gap semiconductors that can be used in high power devices, silicon carbide stands out as one of the most promising materials because, like silicon, it has a stable native oxide, namely SiO_2. However, the poor quality of the as-grown $SiO_2/4H$-SiC interface results in a surface mobility that is two orders of magnitude smaller than the bulk mobility. This reduction has been attributed to the complexity of the interface and to the resulting large number of defect levels in the energy gap.[1–6] It has been shown, however, that the incorporation of nitrogen greatly decreases the density of interface states,[5–13] subsequently enhancing device performance. Moreover, nitridation leads to improved reliability.[14–17] Indeed, negative charge buildup upon electron injection is much less pronounced in nitrided oxides than in unpassivated oxides where most of the charge is thought to be trapped in generated acceptor states.[18–20] Further progress requires understanding of the impact that the passivating nitrogen has on the aging of the devices.

In this letter, we demonstrate that the origin of the nitrogen-induced reliability improvement lies in the suppression of interface state generation upon electron injection into NO-annealed oxides. The results are discussed in terms of specific defects responsible for negative charge trapping in the as-grown oxides and the ability for nitrogen to passivate them.

The studied oxides were grown on the Si-face of *n*-type (5×10^{15} cm^{-3} N doping) 4H-SiC wafers purchased from Cree, Inc. The RCA cleaning sequence was performed prior to the oxidation in dry O_2 at 1150 °C for 4.5 or 8 h, yielding SiO_2 thicknesses of 40 and 60 nm, respectively. The samples were then annealed in Ar for 30 min. One of the thicker oxides was subsequently passivated in NO at 1175 °C for 2 h. Finally, semitransparent Al electrodes, having a 500 μm diameter and a thickness less than 30 nm, were evaporated onto the oxides.

Electrons were photoinjected from the metal at a current density of approximately 5×10^{-7} A/cm^2 using focused radiation of a 100 W mercury lamp (see Fig. 1). The applied oxide field necessary to achieve the injection under these conditions was less than −2 MV/cm. The flatband voltage variation and the density of interface states (between 0.2 and 0.6 eV below the SiC conduction band edge[21]) were monitored through simultaneous quasistatic and high-frequency (100 kHz) capacitance-voltage (*CV*) measurements[22] using a Keithley Model 82 CV system.

The hysteresis of the high-frequency *CV* curves is used to detect the energetically deep interface states and slow border states. The *CV* trace is obtained from the following measurement sequence. The semiconductor interface is first driven from accumulation into deep depletion. Then, the capacitors are exposed to a low intensity UV-light pulse leading to the formation of an inversion layer and to the detrapping of deep/slow states by hole capture.[23] Finally, the semiconductor surface potential is swept from depletion toward accumulation.

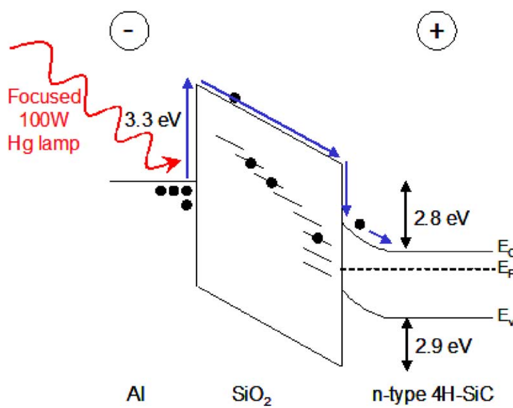

FIG. 1. (Color online) Schematic of the electron injection conditions and of the resulting charge trapping in the bulk of SiO_2 and at the SiO_2/SiC interface. The energy values refer to the relevant band offsets between the metal, the insulator, and the semiconductor.

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The effective charge density per unit area N_{eff} trapped upon injection is calculated from the flatband voltage shift ΔV_{fb} using the relation $N_{eff}=C_{ox}\Delta V_{fb}/q$ and is plotted in Fig. 2 for the different samples. C_{ox} is the oxide capacitance per unit area and q is the elementary charge.

The different trapping rates of the two unpassivated oxides for doses below 2×10^{16} cm^{-2} reveal the contribution of bulk electron traps. For larger doses, the similar slopes indicate a thickness independent electron trapping phenomenon occurring at the interface. Therefore, the effective charge can be expressed by $N_{eff}=N_{ot}+N_{it}$ to include the bulk (ot) and interface contributions (it). Assuming a single process in the dielectric, both the cross section σ_{ot} and the effective density of oxide traps per unit area N^*_{ot} can be deduced from first order kinetics,[24]

$$N_{eff}(\rho_e)=N^*_{ot}(1-e^{-\rho_e\sigma_{ot}})+N_{it}(\rho_e), \quad (1)$$

where ρ_e is the injected charge density and $N_{it}(\rho_e)$ describes the trapping occurring at the interface. Noticing that only the first term of Eq. (1) is thickness dependent, one finds that the difference between the effective trapped charge densities in the unpassivated oxides directly scales with

$$\Delta N_{eff}\propto(1-e^{-\rho_e\sigma_{ot}}), \quad (2)$$

regardless of the positions of the bulk-trapped charge centroids which yield the proportionality constant. From Eq. (2), we find the cross section $\sigma_{ot}\simeq1.3\times10^{-16}$ cm^2.

The *CV* hysteresis before and after electron injection [shown in Fig. 3(a)], indicates that some of the trapped negative charge can be released upon creation of an inversion layer, revealing its proximity to the interface. Also, the fact that the postinjection hysteresis can be cycled, and is wider than the initial one, indicates that there is a new/different trap level that can be occupied by electrons. Finally, because the hysteresis widening occurs toward positive voltages, these traps are identified as acceptor states.

Using the width of the hysteresis to deduce the apparent increase in interface states in both of the unpassivated samples, as described in Ref. 20, we find that N_{it} approaches 10^{12} cm^{-2} for the larger doses. This result is consistent with the previously reported values and proves that a large part of the observed voltage shift is related to the trapping in the generated interface states.

Note that the density of interface states with levels between 0.2 and 0.6 eV is also enhanced by electron injection. This results in a change of the *CV* curve stretch-out. However, the increase in the density of fast states is at most

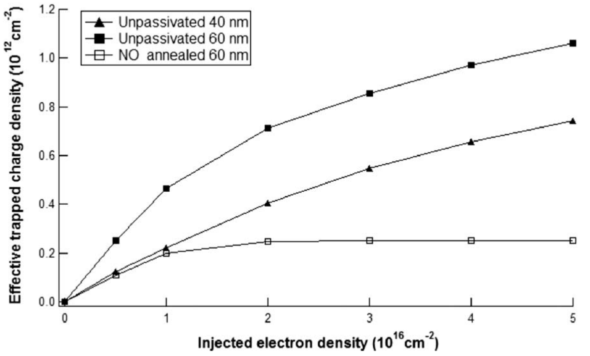
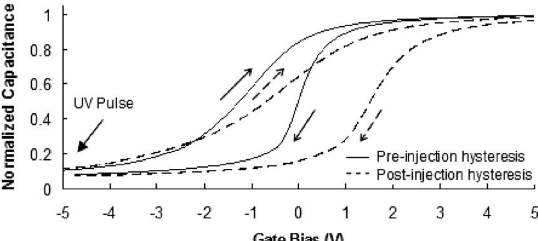


FIG. 2. Effective density of trapped charge, deduced from the flatband voltage shift, as a function of the injected electron density. The trapped charge saturates in the nitrided oxide.



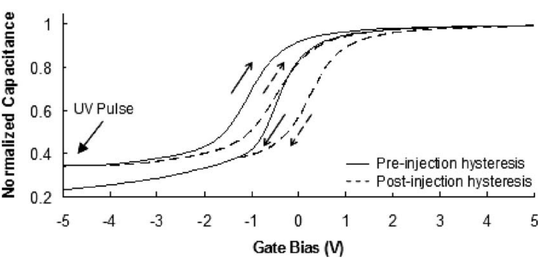


FIG. 3. *CV* hysteresis of the 60 nm unpassivated (a) and nitrided (b) oxides before and after injection of 5×10^{16} electrons/cm^2. The constant hysteresis width observed in panel (b) shows that interface states are not generated in the nitrided sample.

10^{11} cm^{-2} for the studied doses and does not contribute to the hysteresis, which is mostly sensitive to deep interface states and slow border states.

It is clear that the net electron trapping in the 60 nm nitrided oxide is greatly reduced. Also, there is a saturation of the captured charge for doses above 2×10^{16} cm^{-2}, suggesting the absence of interface state buildup. Moreover, the curve can be fitted by a single exponential [first term of Eq. (1)] and leads to $N^*_{ot}=2.4\times10^{11}$ cm^{-2} and $\sigma_{ot}=1.9\times10^{-16}$ cm^2. This capture cross section is close to the one found for the unpassivated samples, which suggests that the trapping still occurs in the bulk of the oxide but not at the SiO_2/SiC interface.

The evolution of the hysteresis shown in Fig. 3(b) confirms this hypothesis since its width remains constant during injection, indicating that no additional interface traps are generated by the injected electrons. The *CV* curve shift is caused by the negative charge trapped in the bulk of the oxide.

The fact that the density of states does not increase in the NO-annealed samples during electron injection is an indication that the degradation of unpassivated interfaces is related to precursor defects. It is clearly of interest to seek a specific atomic level configuration that can display such a behavior. This precursor state has to meet four criteria: (i) it must occur in the SiO_2/SiC interfacial region as evidenced by the *CV* hysteresis, (ii) it must be passivated in the presence of NO at 1175 °C, (iii) it must result in an energy level within the gap of 4H-SiC when exposed to flowing low-energy electrons, and (iv) the induced state cannot be readily passivated by H_2 at 400 °C, as shown by Afanas'ev *et al.*[20]

An analogous behavior during electron injection has been observed in silicon devices passivated with hydrogen. In that case, flowing electrons induce the release of the passivating species, leaving dangling bonds as "new" interface states.[25] Here, we observe degradation of the as-oxidized, unpassivated SiO_2/SiC interface. We note that silicon-like P_b

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TABLE I. Some defects predicted by theory to relax upon electron capture and their ability to be passivated by nitrogen. The induced energy levels are measured from the conduction band edge of 4H-SiC.

Precursor defect	Trivalent Oxygen	Single C interstitial	Pair of C interstitials
	Si, Si, O—Si	Si—C—Si, O	Si—C—O—Si, Si—C—O—Si
Induced level (eV)	0.6[a]	0.3[b], 0.6[c]	<0.1
N passivated	Yes[a]	Yes	Yes
References		6	3,13

[a]From calculation method described in Ref. 6.
[b]Empty level (neutral state).
[c]Singly occupied level (negatively charged state).

centers (Si dangling bonds) have not yet been identified at the studied (0001) SiC surfaces. There is only evidence for carbon dangling bonds from paramagnetic resonance techniques, they result in C–H bonds after intentional hydrogen passivation.[26] We conclude that the effects of electron injection reported here is not associated with adventitious hydrogen bond-breaking.

Instead, we envision that when the unpassivated SiO_2/SiC interface is exposed to a low-energy electron flow, some defects trap a negative charge and then relax to a more stable configuration, generating an acceptor state that can be detected by subsequent measurements without being affected by the probing charge exchange. Accordingly, we now consider defects that have been suggested by theory to meet the criteria listed above. Detailed computational studies on defect relaxation have been published by Wang *et al.*[6] and Knaup *et al.*[3,13] We also performed additional simulations following the method described in Ref. 6. In Table I, we list three defects that, according to calculations, could occur at the interface, have originally no level within the gap of 4H-SiC and are predicted to relax upon electron capture. The calculated states resulting from the trapping of one electron (trivalent oxygen and single carbon interstitial) or four electrons (pair of carbon interstitials) are reported, all appear in the SiC band gap. Moreover, the listed defects are thought to be prone to nitrogen passivation. Of course, each of these configurations requires further examination. In particular, we note that no relationship between fixed positive charge, which we expect to be associated with trivalent oxygen, and electron trapping has been observed.[27] Also, the capture of four electrons, predicted to lead to the relaxation of the pair of carbon interstitials, is likely to be a low-probability event. Further theoretical and experimental work is needed to clearly identify the pertinent atomic configuration.

In conclusion, we have shown that the reduced negative charge trapping upon electron injection in nitrided oxides on 4H-SiC correlates with the absence of interface state generation. In unpassivated oxides, the resulting charge buildup could be due to the trapping of electrons in metastable defects and to the transition of the levels to within the gap after relaxation. Nitrogen can passivate these defects, thus improving the reliability of the NO-annealed oxides.

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