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Comparison of nitrogen incorporation in SiO₂/SiC and SiO₂/Si structures

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The nitrogen content of SiO₂/SiC (4H) structures annealed in NO and N₂O has been measured using nuclear reaction analysis. Samples were annealed in ¹⁵N¹⁸O or ¹⁵N₂O at 1000 °C at a static pressure of 10 mbar for either 1 or 4 h. Annealing in N₂O incorporates ~10¹³ cm⁻² of N and annealing in NO incorporates ~10¹⁴ cm⁻², both of which are an order of magnitude lower than in SiO₂/Si. In the NO anneal, N is predominantly incorporated near the SiO₂/SiC interface with an atomic concentration of ~0.5%. As in the nitridation of SiO₂/Si, two features are observed in SiO₂/SiC after the NO anneal: a surface exchange of O in the oxide with the gas phase and NO diffusion and reaction at the interface. The surface exchange reaction in SiO₂/SiC is similar to SiO₂/Si, but there is a large difference in the incorporation of N at the interface. © 2000 American Institute of Physics. [S0003-6951(00)03605-6]

Silicon carbide is in the early stages of development for use in metal-oxide-semiconductor (MOS) power devices. Like Si, SiC thermally oxidizes to form SiO₂, however, the oxidation kinetics and oxide interface are different from Si and are still not well understood. The oxidation rate of SiC is more than a factor of 10 lower than that of Si and the interfacial quality and carrier mobility of SiC are inferior to Si.^{1,2} Refinements in cleaning and oxidation techniques have improved the oxide and interfacial quality of SiO₂/SiC, but more work remains to be completed before reliable devices can be made.^{3,4} Oxynitride films on Si have better device reliability, dopant diffusion resistance, and dielectric quality than pure oxide films.^{5,6} Methods for manufacturing oxynitride films include annealing oxides in N₂O or NO, with NO thought to be the species responsible for incorporating N into the oxide.^{7,8} Nitrogen is typically incorporated near the SiO₂/Si interface^{8,9} at concentrations of ~10¹⁵ cm⁻², although the actual profile is a complicated function of the gaseous species and the temperature cycle. The atomic process for the incorporation of N in the oxide is thought to involve NO interstitial diffusion through the oxide to the interface where it reacts, leaving N and O and promoting new film growth.¹⁰ Initial studies of oxynitrides on 6H-SiC have shown improved MOS interfacial quality after a NO anneal by reducing the interface state and fixed charge densities, but with a worse quality after a N₂O anneal.^{11,12} These results are surprising considering that N incorporation at the SiO₂/Si interface does not decrease the interface trap density. Using secondary ion mass spectrometry (SIMS), it has been

found that a NO anneal incorporates N near the SiO₂/SiC (4H) interface, but the amount of N has not been determined.¹³ In this letter we determine the amount and location of N and O incorporated in SiO₂/SiC samples after annealing in ¹⁵N¹⁸O and ¹⁵N₂O using nuclear reaction analysis (NRA) and compare the results with SiO₂/Si reference samples.

Silicon-faced (8° off axis) 4H-SiC wafers with a *p*-type substrate and epitaxial layer, doped 2×10¹⁶ cm⁻³, were used in this work. For comparison, *n*-type (100) Si wafers with a resistivity of ≥10 Ω cm were used. All samples were etched in a 10% HF solution before oxidation and were thermally oxidized in a resistively heated quartz tube furnace. The SiC samples were oxidized in wet oxygen for 30 min at 1150 °C, and the Si samples were oxidized in dry oxygen (<2 ppm H₂O) for 25 min at 900 °C. The oxide thickness for the SiC substrates was ≈30 nm and ≈20 nm for Si. The samples were then annealed in 99.7% ¹⁵N¹⁸O or ¹⁵N₂O at a static pressure of 10 mbar for either 1 or 4 h.

The areal densities of ¹⁵N, ¹⁸O, and ¹⁶O were determined by nuclear reaction analysis using the reactions ¹⁵N(*p*, αγ)¹²C at *E_p*=1 MeV, ¹⁸O(*p*, α)¹⁵N at *E_p*=730 keV, and ¹⁶O(*d*, *p*)¹⁷O at *E_d*=810 keV, respectively.^{10,14} The thickness of the films could then be determined based on the equivalent thickness relationship 10¹⁵ (O+N) atoms/cm² = 0.226 nm.¹⁰ The ¹⁵N and ¹⁸O depth profiles were determined by nuclear resonance profiling (NRP) using the resonances in the reactions ¹⁵N(*p*, αγ)¹²C at 429 keV and ¹⁸O(*p*, α)¹⁵N at 151 keV, respectively, and a tilted sample geometry (*ψ*=65°). The measured excitation curves (γ or α yield versus incident proton energy) around the resonance energy were converted into concentration versus depth profiles using the SPACES code.¹⁵

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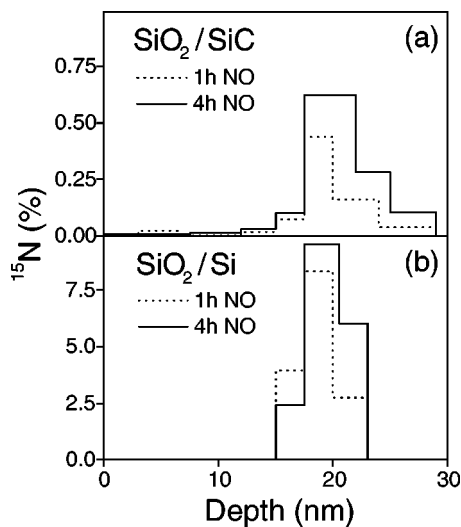


FIG. 1. Concentration profiles of ^{15}N in (a) SiO_2/SiC and (b) SiO_2/Si annealed in 10 mbar of $^{15}\text{N}^{18}\text{O}$ at 1000°C for 1 h (dotted) and 4 h (solid). The origin corresponds to the surface, the SiO_2/SiC interface is at ≈ 30 nm, and the SiO_2/Si interface is at ≈ 20 nm.

The obtained depth profiles of ^{15}N in the SiO_2/SiC samples [Fig. 1(a)] resemble the profiles in the SiO_2/Si samples [Fig. 1(b)]. Nitrogen is concentrated primarily near the SiO_2/SiC interface, but unlike in SiO_2/Si , it is centered at a shallower depth. The width of the N profile is also wider in the SiO_2/SiC samples than in the SiO_2/Si samples. Possible reasons for this behavior include unusual roughness or an anomalous oxide region immediately adjacent to the SiC substrate. For example, a region with carbon impurities or unusual stress might produce these results. These depth profiles, determined by NRP, provide independent verification of the SIMS results in Ref. 13, which also showed N located near the interface, without the inherent uncertainty of ion beam induced displacement of N.

The ^{15}N areal density in the SiO_2/SiC samples is $\sim 10^{14}$ cm^{-2} for both anneal times in $^{15}\text{N}^{18}\text{O}$ (see Table I), and the maximum N concentration is $\sim 0.5\%$ [see Fig. 1(a)]. Both of these values are much smaller than the ones for SiO_2/Si samples, where the ^{15}N areal density is $\sim 10^{15}$ cm^{-2} and the maximum concentration is $\sim 10\%$. The rate of N incorporation in SiO_2/SiC and SiO_2/Si scales with their oxidation rates, which suggests that the rate of Si–N bonding at the interface is also governed by the same factors as the oxidation rate in each material.

The ^{18}O depth distributions in the SiO_2/SiC samples [Fig. 2(a)] show a gradient of ^{18}O in the oxide from the surface to the interface. These ^{18}O profiles, as well as the ^{18}O areal densities (Table I), strongly resemble those of the Si

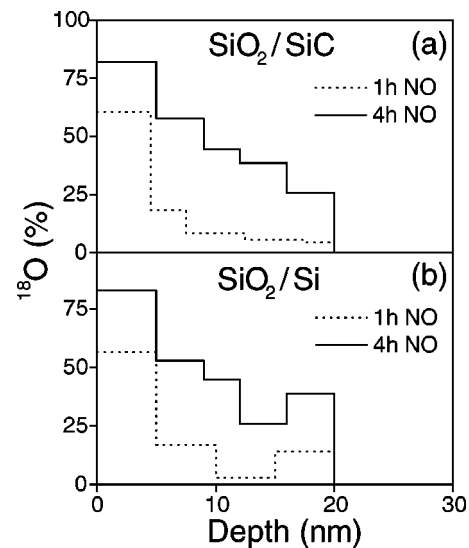


FIG. 2. Concentration profiles of ^{18}O in (a) SiO_2/SiC and (b) SiO_2/Si annealed in 10 mbar of $^{15}\text{N}^{18}\text{O}$ at 1000°C for 1 h (dotted) and 4 h (solid). The origin corresponds to the surface, the SiO_2/SiC interface is at ≈ 30 nm, and the SiO_2/Si interface is at ≈ 20 nm.

samples [Fig. 2(b)]. In the SiO_2/Si samples, however, there is noticeable ^{18}O accumulation at the interface, while there is little or no new oxidation in the SiC samples. These results again confirm the difference in the oxidation rates of SiC and Si, but also indicate that the surface exchange mechanism is identical for oxides on SiC and Si. Since the exchange reaction is solely a characteristic of the oxide and not the substrate, this is further evidence that the oxide on SiC behaves chemically as the oxide on Si.

In the SiO_2/SiC samples annealed in $^{15}\text{N}_2\text{O}$, the amount of N incorporated is $\sim 10^{13}$ cm^{-2} , which is near the detection limit of NRA and prevents resonance profiling. This amount of incorporated N is again an order of magnitude smaller than the amount of N in the SiO_2/Si samples, which is $\sim 10^{14}$ cm^{-2} .

These results are particularly meaningful considering the electrical properties of oxynitrides on SiC reported in Refs. 11 and 12. In their work the authors show that rapid thermal annealing of SiO_2/SiC in NO at 1100°C significantly decreases the interface trap density D_{it} , while N_2O anneals actually increase D_{it} . Our work shows a small but definite incorporation of N near the SiO_2/SiC interface from the NO anneal and considerably less N from the N_2O anneal. It is known that during thermal exposure to NO at temperatures >1000 K, the NO concentration remains fairly constant, with small amounts of N_2 and O_2 formed.¹⁶ Conversely, N_2O readily decomposes into N_2 ($\approx 60\%$), O_2 ($\approx 25\%$), and ($\text{NO} \approx 15\%$), and the dominant reaction for annealing oxide films in N_2O is the dry oxidation of the substrate.¹⁷ Evidently annealing in N_2O not only incorporates very little N because of the low NO concentration, but also leads to a poor quality, dry oxidation of the SiC, which is known to produce a higher interface trap density.^{1,2} The reoxidation technique (annealing SiO_2/SiC in wet oxygen at 950°C) is known to dramatically improve the interfacial quality without any appreciable new oxide growth.⁴ The incorporation of N at the SiO_2/SiC interface may offer benefits similar to the

TABLE I. $^{15}\text{N}^{18}\text{O}$ anneal time, incorporation of $^{15}\text{N}^{18}\text{O}$ isotopes, and final film thickness of SiO_2/SiC and SiO_2/Si samples. The $^{15}\text{N}^{18}\text{O}$ anneal was performed at 1000°C with a static pressure of 10 mbar.

Substrate material	$^{15}\text{N}^{18}\text{O}$ anneal time (h)	Areal density (10^{15} cm^{-2})		Film thickness (nm)
		^{15}N	^{18}O	
Si	1	1.6	19.6	20.3
Si	4	2.2	44.6	22.8
SiC	1	0.1	15.9	28.9
SiC	4	0.2	51.0	27.6

reoxidation anneal, which also could explain the consequences of the NO and N₂O anneals.

The results described here also address the interesting question of the mechanisms of nitrogen incorporation at the interfaces of SiO₂/semiconductor systems. It is not obvious that N should incorporate at the interface of either the Si system or the SiC system. The clear observation that the interface is the preferred location in Si has given rise to a number of suggestions for the driving force for this phenomenon. One suggestion is a stress reduction mechanism that supposes the stress between Si and its oxide is reduced by incorporation of an interfacial silicon nitride species, since nitrides are associated with the opposite sign of stress to oxides.¹⁸

These results on SiC are consistent with the stress argument for the following reason: Stress in these systems is driven mainly by the large difference in Si concentration between the substrate and the dielectric. The concentration of Si in SiC, $4.8 \times 10^{22} \text{ cm}^{-3}$, is comparable to the density of Si, $5 \times 10^{22} \text{ cm}^{-3}$, and is approximately twice the concentration of Si in SiO₂, $2.2 \times 10^{22} \text{ cm}^{-3}$. On the other hand, the density of Si in pure Si₃N₄ is $4.4 \times 10^{22} \text{ cm}^{-3}$. Therefore, it is reasonable to assume that the Si and SiC systems have the same stress. If the driving force for N interfacial accumulation is stress reduction, N is expected to be found at both the SiO₂/Si and SiO₂/SiC interfaces, which is indeed the case. Nevertheless, more sophisticated analysis is required, as it is clear that ~ 1 monolayer of nitride is not sufficient for total stress reduction. Another point of view argues that interfacial N is the result of the strong Si bonding at the SiO₂/Si interface.¹⁹ Our results would be consistent with such a view provided that N bonding at the SiC interface is appropriately weaker.

In summary, SiO₂/SiC samples were annealed in ¹⁵N¹⁸O or ¹⁵N₂O at a pressure of 10 mbar at 1000 °C for either 1 or 4 h. Annealing in N₂O incorporates very little N, $\sim 10^{13} \text{ cm}^{-2}$, while annealing in NO incorporates N near the SiO₂/SiC interface, with an areal density of $\sim 10^{14} \text{ cm}^{-2}$ and an atomic concentration of $\sim 0.5\%$. These values are an order of magnitude lower than comparably prepared SiO₂/Si samples. As in SiO₂/Si, a surface exchange of O in the gas phase with the oxide and NO diffusion and reaction at the SiO₂/SiC interface are observed after a NO anneal. The sur-

face exchange reaction for SiO₂/SiC appears to be similar to SiO₂/Si, confirming that the oxides themselves are chemically identical. However, the rate of N incorporation in SiO₂/SiC is lower than in SiO₂/Si, comparable to the different oxidation rates of Si and SiC. The incorporation of N near the interface provides a possible explanation for the better electrical characteristics of NO, compared to N₂O, annealed SiO₂/SiC structures. These results also strengthen the argument that stress reduction is responsible for nitrogen incorporation in oxide–semiconductor systems.

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