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# Atomic state and characterization of nitrogen at the SiC/SiO<sub>2</sub> interface

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We report on the concentration, chemical bonding, and etching behavior of N at the SiC(0001)/SiO<sub>2</sub> interface using photoemission, ion scattering, and computational modeling. For standard NO processing of a SiC MOSFET, a sub-monolayer of nitrogen is found in a thin inter-layer between the substrate and the gate oxide (SiO<sub>2</sub>). Photoemission shows one main nitrogen related core-level peak with two broad, higher energy satellites. Comparison to theory indicates that the main peak is assigned to nitrogen bound with three silicon neighbors, with second nearest neighbors including carbon, nitrogen, and oxygen atoms. Surprisingly, N remains at the surface after the oxide was completely etched by a buffered HF solution. This is in striking contrast to the behavior of Si(100) undergoing the same etching process. We conclude that N is bound directly to the substrate SiC, or incorporated within the first layers of SiC, as opposed to bonding within the oxide network. These observations provide insights into the chemistry and function of N as an interface passivating additive in SiC MOSFETs. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4861626>]

## I. INTRODUCTION

Silicon carbide (SiC) is a wide bandgap semiconductor with materials properties well-suited for high-power, high-temperature applications.<sup>1</sup> The performance of SiC MOSFETs is limited by interface defects formed under high temperature oxidation. Interface defect concentrations for 4H-SiC/SiO<sub>2</sub> following dry oxidation (dry O<sub>2</sub>) are orders of magnitude larger than those that form during SiO<sub>2</sub> growth on Si using similar procedures. Introduction of interfacial nitrogen (N) using a nitric oxide (NO) anneal<sup>2,3</sup> reduces the large interface state density and improves the SiO<sub>2</sub>/SiC channel mobility, and thus device performance. Earlier measurements have shown that the N accumulates in a very narrow layer (<1.5 nm) at the oxide/semiconductor interface<sup>4</sup> with a coverage in the sub-monolayer range.

Recently, Tochihara and Shirasawa<sup>5</sup> and Kosugi *et al.*<sup>6</sup> performed x-ray photoemission studies on NO annealed SiC/dielectric structures. They found a strong N 1s signal after the oxide was mostly etched away indicating that N incorporates very near the SiC/SiO<sub>2</sub> interface. The nitrogen areal density was estimated to be  $\sim 10^{14}/\text{cm}^2$ . They confirmed that N incorporation results in a reduction in the density of interface traps by about an order of magnitude.

Although elemental depth profiles across the interface for these systems have been reported by our group and others,<sup>4,7</sup> the atomic level bonding and chemistry of nitrogen incorporation is not well-understood. In addition to the use of NO, successful nitrogen incorporation and passivation using a nitrogen (N<sub>2</sub>) plasma<sup>8</sup> has been reported. We also report preliminary results on the plasma-formed system indicating a similar bonding configuration.

In this report, we quantified the areal density and investigated chemical environment of nitrogen at the SiO<sub>2</sub>/SiC interface formed by NO anneals, by N<sub>2</sub> plasma nitridation, and by direct nitridation in a very high temperature N<sub>2</sub> (g) anneal. The interfacial N content, measured by X-ray photoelectron spectroscopy (XPS), medium energy ion scattering (MEIS), and dynamic secondary ion mass spectrometry (SIMS) are in approximate agreement. This quantification of buried layers (via SIMS) and etched surfaces (via XPS and MEIS) demonstrate that, within error ( $\sim 10\%$ ) all of the interfacial nitrogen presents prior to etching remains after the buffered oxide etch (BOE). Finally, we discuss possible structural models, supported by theoretical computations, for N bonding at the SiC/SiO<sub>2</sub> interface.

## II. DESCRIPTION OF SAMPLE FABRICATION AND APPARATUS

The emphasis in this work is on results for the NO annealing process, currently the dominant one used in SiC

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MOSFET research and production. For comparison purposes, silicon carbide and silicon samples were processed in parallel using NO (g). Wafers of 4H-SiC obtained from Cree, Inc. (miscut by  $\sim 4^\circ$ ) were used. Nitrogen was introduced via three different processes: (1) NO (g) anneals at  $1175^\circ\text{C}$  of previously dry oxidized (at  $1150^\circ\text{C}$ ) SiC with oxide thickness in the range of 50–60 nm, (2) N plasma exposure to oxidized SiC at  $1160^\circ\text{C}$ , and (3)  $\text{N}_2$  (g) exposure to clean SiC at temperatures from 1250 to  $1600^\circ\text{C}$ . Details of the various sample exposures are listed in Table I.

XPS studies were performed in a Thermo K-Alpha system with a monochromatic Al  $K\alpha$  x-ray source. The Au  $4f_{7/2}$  peak, as well as C and Si substrate peaks, was used for energy referencing. Additional compositional analysis employed SIMS and MEIS.<sup>8</sup> NO annealed SiC samples measured by SIMS showed no detectable N within the “bulk” region of the oxide (within the sensitivity limit of SIMS  $\sim 10^{17}/\text{cm}^3$ ) and an accumulation of N at the interface, consistent with earlier reports by TEM, SIMS, and MEIS.<sup>4,7</sup>

### III. QUANTIFICATION AND PHOTOELECTRON MEAN FREE PATH

Wide energy range XPS spectra of NO-annealed SiC/SiO<sub>2</sub> samples, etched to leave  $\sim 1.5$  nm of oxide, and spectra from the same sample etched to completely remove all the oxide, are shown in Fig. 1. In the case of “full” oxide removal, the intensity of the N 1s peak increases relative to Si (and O) peaks since the overlayer SiO<sub>2</sub> no longer attenuates the outgoing N 1s photoelectrons. All such etches were performed in a 7:1 buffered HF solution (BOE) unless otherwise stated. Note the presence of Si 2p photoemission intensity close to 104 eV, which indicates substantial remaining oxide in the partially etched sample.

The N coverage can be quantified with XPS peak intensities, but the accuracy is limited by the uncertainty in the attenuation length of the relevant photoelectrons. We have used MEIS, further supported by SIMS and earlier reports using nuclear reaction analysis (NRA)<sup>9</sup> for quantification. SIMS provides a measure of the total nitrogen content in the films (without a BOE removal of the oxide layer), and MEIS gives an independent and more accurate measure of the nitrogen content on etched (or thin un-etched) samples. The available evidence implies that after BOE etching the

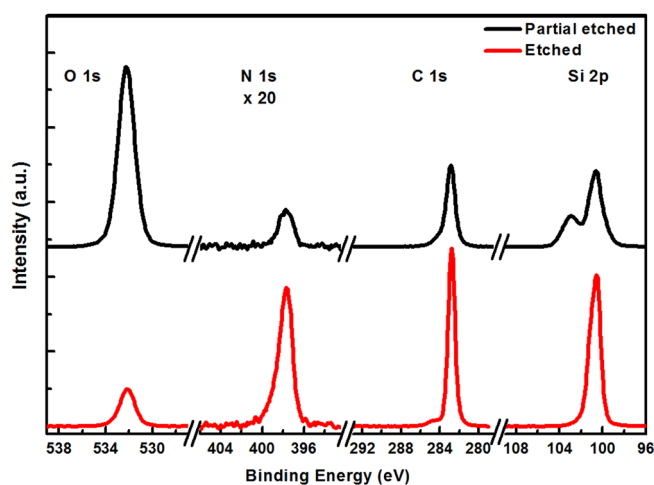


FIG. 1. Wide energy range XPS spectra of a NO annealed SiO<sub>2</sub>/SiC sample partially etched (black) to  $\sim 1.5$  nm of oxide on SiC and completely etched (red), with the N 1s intensity magnified 20 times.

nitrogen is retained, which is also consistent with the result reported by Kosugi *et al.*<sup>6</sup>

Accurate quantification of the N content on the fully etched sample was achieved with MEIS using a 100 keV proton beam in a channeling direction (the  $\langle 0001 \rangle$  axis).<sup>7</sup> Fig. 2 shows the (a) nitrogen portion of the XPS spectra, and (b) the MEIS spectra of a 2 h NO annealed SiC sample. The MEIS measurement yielded an interfacial N areal density of  $4.0(\pm 0.6) \times 10^{14} \text{ cm}^{-2}$ , which agrees (within experimental error) with the SIMS result of  $6.0(\pm 2.0) \times 10^{14} \text{ cm}^{-2}$ .<sup>10</sup> A surface N density of  $4.0 \times 10^{14} \text{ cm}^{-2}$  corresponds to  $\sim$ one third of a monolayer of surface Si atoms on SiC. Using the MEIS and XPS results from the same sample, the Si  $2p_{3/2}$  photoelectron attenuation length in SiC ( $\lambda_{\text{Si/SiC}}$ ) is calculated to be  $\sim 2.1 (\pm 0.3) \text{ nm}$ , assuming all the nitrogen is at the bare surface. Comparing MEIS and XPS results from multiple samples yields an average  $\lambda_{\text{Si/SiC}}$  as  $\sim 2.2 \text{ nm}$ . The combination of results, both absolute values of the N coverage, and the extraction of the mean free path (mfp), indicates that the NO process is well controlled and reproducible. The result also shows that there is no detectable removal of nitrogen during the BOE etching. Fully etched samples are used in most of the XPS analyses that follow.

Our calculated mfp for Si  $2p_{3/2}$  photoelectron attenuation Si is somewhat smaller than the literature value of

TABLE I. Sample preparation and N, O amounts at the SiC/SiO<sub>2</sub> interface prepared by different methods. All the samples were etched in BOE for 5 min before examination by XPS.<sup>a</sup>

	Substrate	N Process	Oxide thickness (nm)	Mobility ( $\text{cm}^2/\text{V}\cdot\text{s}$ )	N amount ( $10^{14}/\text{cm}^2$ )	O amount ( $10^{14}/\text{cm}^2$ )
Fig. 3(a) (Fig. 1)	4H-SiC(0001)	NO, $1175^\circ\text{C}$ , 1 atm, 2 h	50–60	$\sim 40$ (Refs. 2 and 3)	4.0	14.0
Fig. 3(b)	Silicon (100)	NO, $1175^\circ\text{C}$ , 1 atm, 2 h	50–60	...	...	...
Fig. 6	4H-SiC(0001)	$\text{N}_2$ plasma, $1160^\circ\text{C}$ , 4 h	50–60	$\sim 55$ (Ref. 8)	4.1	10.4
Fig. 6	4H-SiC(0001)	$\text{N}_2$ plasma, $1160^\circ\text{C}$ , 8 h	50–60	...	10.0	9.9
Fig. 6	6H-SiC(0001)	$\text{N}_2$ , $1600^\circ\text{C}$ , 5 min	50–60	...	11.1	12.4
Fig. 6	6H-SiC(0001)	$\text{N}_2$ , $1350^\circ\text{C}$ , 30 min	...	...	10.3	5.4
Fig. 6	6H-SiC(0001)	$\text{N}_2$ , $1250^\circ\text{C}$ , 30 min	...	...	12.4	7.6

<sup>a</sup>The N processes on 4H-SiC involved starting with a  $\sim 50$  nm thermal oxide (SiO<sub>2</sub>) grown on SiC(0001) at  $1150^\circ\text{C}$ . For 6H-SiC, a bare (no oxide) sample was used for the  $\text{N}_2$  exposure. The Si substrates also have a 50 nm thermal oxide prior to NO exposure.

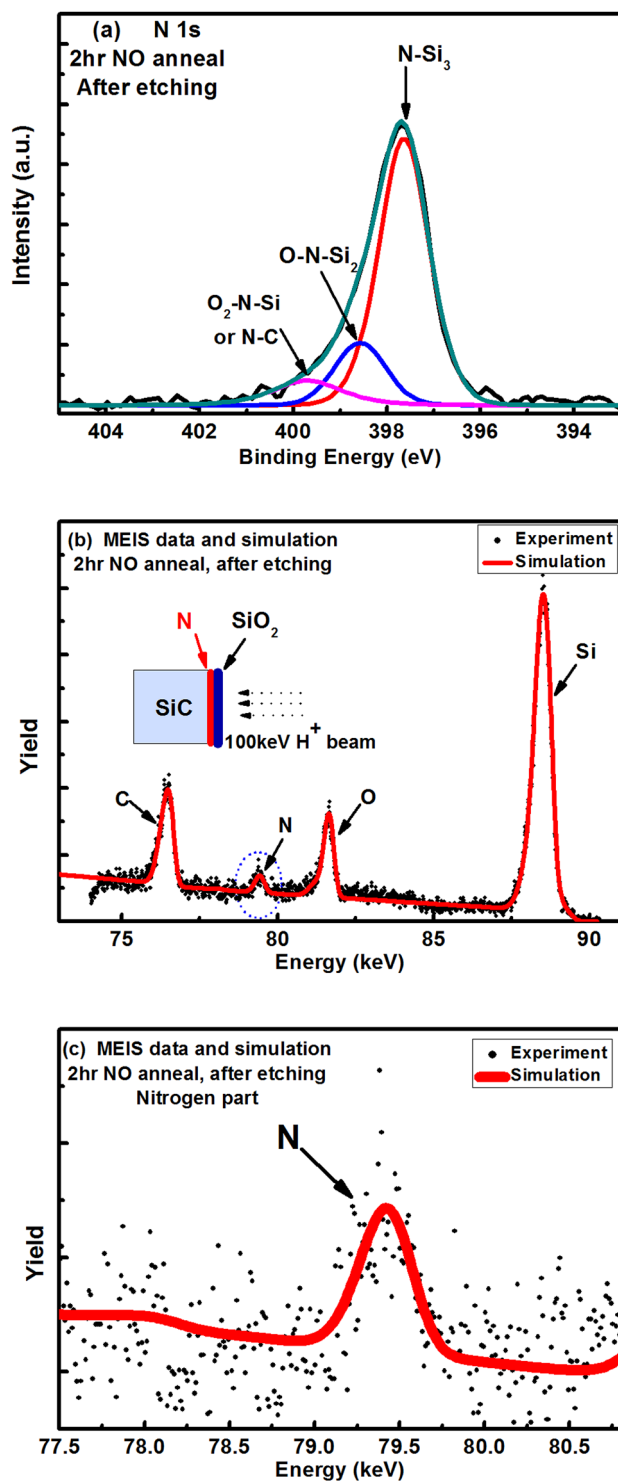


FIG. 2. (a) N 1s XPS spectrum with possible peak assignments, (b) MEIS full spectrum, and (c) Nitrogen part of the MEIS spectrum of 4H-SiC annealed in NO for 2 h, followed by 5 min BOE etching.

2.9 nm (Ref. 11) estimated from an average of the mfp's of Si and C listed in the NIST database.<sup>12</sup> Our result, however, is quite reasonable given that SiC has a significantly higher density than Si and C. Using this value of the mean free path,  $\lambda_{\text{Si/SiC}}$ , the oxygen areal density on the freshly etched sample is estimated to be  $1.4 \times 10^{15} \text{ cm}^{-2}$ , close to one monolayer of oxygen ( $1.2 \times 10^{15} \text{ cm}^{-2}$ ). The majority of the oxygen signal comes from the non-etchable portion of the

initial oxide described in the work of Dhar *et al.*,<sup>13</sup> with some adventitious oxygen due to exposure to the ambient atmosphere.

The MEIS result not only provides accurate quantification but also indicates that the nitrogen is confined to within  $\sim 1$  nm of the surface, consistent with earlier reports of a sharp interfacial N profile. The comparison of the N content via SIMS, done without pre-chemical etching, and MEIS and XPS performed after complete etching indicates that all of the interfacial nitrogen content is preserved in the wet etching process, at least within the sensitivity of these techniques ( $\sim 10\%$ ).

#### IV. COMPARISON OF N ETCHING BEHAVIOR ON SiC AND Si INTERFACE

To understand the N bonding differences between Si and SiC MOS, Fig. 3 reports XPS data for samples that are etched in BOE. Fig. 3(a) compares the N 1s XPS spectra for NO annealed SiO<sub>2</sub>/SiC samples partially and completely etched. The spectra are normalized to the same incident x-ray flux. A quantitative analysis, using 2.2 nm as the Si 2p electron escape length in the SiC (calculated from XPS and MEIS data), indicates that there is no detectable N removal in the case of the “completely” etched SiO<sub>2</sub> overlayer on SiC. Fig. 3(b) shows the same sequence for the silicon system (Si/SiO<sub>2</sub>) indicating complete removal of the N (within the XPS sensitivity limit) after the SiO<sub>2</sub> layer is etched by BOE. In the NO annealed Si/SiO<sub>2</sub> system, it was shown that N accumulates primarily at the interface.<sup>14,15</sup> The figure focuses on the N 1s signal in both cases, indicating that the binding energy of the N 1s for SiC/SiO<sub>2</sub> does not change

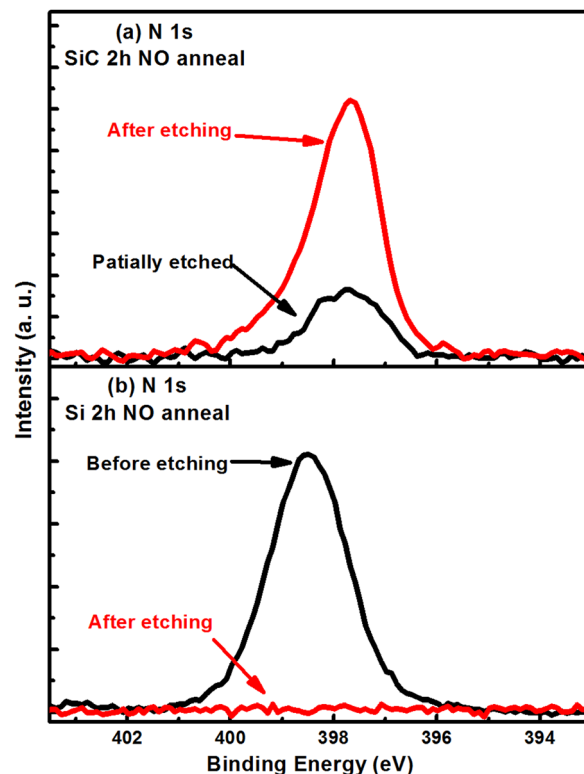


FIG. 3. XPS spectrum of before and after 5 min BOE etching from NO annealed (a) SiC and (b) Si. The increase in the signal strength in (a) is due to the elimination of attenuation by the overlayer.



upon etching, while the N signal in the Si/SiO<sub>2</sub> system (prior to its removal during etching) is indeed shifted in energy relative to N bound at the SiC interface.

We conclude that N is bound to SiC in a manner which minimizes removal during an HF etch of the oxide, quite unlike the behavior observed on Si. Furthermore, the data show that the NO anneal introduces more nitrogen at the interface when grown on a Si sample (for the same NO exposure, the N content in the Si sample is about twice that observed at the SiO<sub>2</sub>/SiC interface), although no nitrogen is detected after the BOE etch of the Si sample. The different chemical behavior of N at Si and SiC interfaces under the same etching conditions and the different N binding energies that we observe by XPS indicate that N is bonded differently in the two systems.

Note that a BOE process etches Si<sub>3</sub>N<sub>4</sub> at a rate of ~2 nm/s (under conditions similar to our SiC/SiO<sub>2</sub> etching), and thus, a thin pure nitride should easily be etched if present in our films, ruling out the possibility that N atoms are incorporated into a stable bulk-like nitride on SiC. Our results are consistent with experimental results<sup>5,6,16,17</sup> and a theoretical model<sup>18,19</sup> which implies that instead of pure Si<sub>3</sub>N<sub>4</sub> or a simple SiNO layer, the N is directly involved in bonding to the SiC substrate at the interface, or possibly embedded within first layer or two of the substrate, forming a stable, BOE-etch-resistant interfacial region.

In an earlier report, Dhar *et al.*<sup>13</sup> measured the residual oxygen following etching of thermal oxides on both Si and SiC using isotopically labeled O<sub>2</sub> analyzed by NRA.<sup>13</sup> The results confirm earlier findings for Si which show that BOE etching of oxide on Si leaves a hydrogen terminated surface. Surprisingly, etching of the oxide on SiC leaves a residual oxide monolayer on SiC.<sup>13</sup> As a possible explanation, the authors noted (i) that etching at the SiO<sub>2</sub>/Si interface requires the insertion of F into the Si-Si bond,<sup>20</sup> and (ii) that this insertion mechanism may not be operative in the SiC/SiO<sub>2</sub> case due to the higher stability of the Si-C bond relative to Si-Si.<sup>13</sup> Analogously, we suggest that this last layer of N-Si at the SiC interface is also resistant to etch on SiC due to the stability (and resulting lower reactivity toward HF) of the Si-C bond relative to the Si-Si bond.

Other possible explanations for the enhanced stability of N at the SiC interface include: (i) differences in the formation energy, and hence the etching kinetics, of etchable intermediates on Si and SiC, or (ii) the formation of a stable interface phase such as a carbon nitride or oxy-nitride.<sup>21,22</sup> However, the surface excess carbon reported by Zhu *et al.*<sup>7</sup> using MEIS is  $\sim 1.8 \times 10^{14} \text{ cm}^{-2}$ , which sets a limit to this type of C<sub>x</sub>N<sub>y</sub> phase. An additional possibility is that some of the N might be incorporated into the near surface of the substrate (but within the escape depth of XPS) such that oxide etching does not apply. It has been reported that an N-doped near surface layer in SiC may result in “counter doping” and improved electrical properties.<sup>23,24</sup>

## V. BONDING STATE OF N: EXPERIMENTAL

To provide further insight into the chemical state of nitrogen at the SiC/SiO<sub>2</sub> interface, the N 1s spectra were fit

with a set of three Gaussians representing three different bonding configurations (Fig. 2(a)). The fit includes a main peak centered at a binding energy of 397.5 eV and secondary peaks centered at ~398.4 eV and ~399.5 eV. Comparing these N 1s peaks to previously reported values indicates possible nitrogen bonding environments.<sup>25</sup> However, surface/interface dipoles and calibration methods together can result in significant variations of binding energy values between experiments.<sup>26</sup> Therefore, caution must be exercised when comparing experiments that do not use a common reference.

Benefited from the extensive work published concerning the N 1s signals of oxy-nitride thin films on silicon,<sup>27</sup> the dominant N 1s peak binding energy for oxynitrides of varying nitrogen content range from 397.0 to 398.0 eV and are attributed to nitrogen bound to three silicon nearest neighbors. The lower binding energy value observed is associated with N within a Si<sub>3</sub>N<sub>4</sub>-like near interfacial environment whereas the higher value is associated with N still bound to three Si atoms but within a SiO<sub>2</sub> environment, with the number of second nearest neighbor oxygen atoms being an important determining factor.

Higher binding energy N 1s peaks are less well understood, with peaks at ~399 eV attributed to nitrogen bound to one oxygen and two silicon atoms, and peaks at ~400 eV attributed to nitrogen bound to one silicon and two oxygen. A recent study of complex nitrogen molecules on silicon surfaces<sup>28</sup> corroborates these assignments. In addition, N bound to two silicon and one carbon was found to produce a N 1s peak at 398.4 eV suggesting an alternative bonding possibility for XPS peaks in this range. While the above results provide a starting point for understanding our N 1s peaks, calibration and interface issues prevents a definitive comparison to our XPS results. Below we describe the calibration method used here to carefully compare competing nitrogen bonding configurations with respect to theoretical estimates.

## VI. BONDING STATE OF N: THEORETICAL CALCULATION

To further elucidate the nature of nitrogen bonding at the SiC/SiO<sub>2</sub> interface, first principles electronic structure calculations have been performed on realistic interface models. Our theoretical calculations employ the VASP electronic structure package<sup>29</sup> to calculate core level energies<sup>30</sup> within the frozen valence approximation. We have studied numerous interface structures with typical super-cell sizes  $\sim 1.0 \times 1.0 \times 2.0 \text{ nm}$  with between 100–300 atoms, including 5 layers of a SiC(0001) substrate with an oxygen-nitrogen cap. For each model, atomic positions are initially relaxed to their lowest energy positions with  $T=0 \text{ K}$ . We compute the relative difference between the N 1s core level and the bulk C 1s level, which provides a common reference when comparing to experiments as absolute core levels are not accurate. In order to calibrate the method, we use a system where both the microstructure and N 1s core level binding energies are known. Shirasawa *et al.*<sup>16–19</sup> have discovered a crystalline oxygen-nitrogen overlayer on the Si face of SiC(0001). Experimentally, the XPS core level of the N 1s level is 398.7 eV with a core level difference between C 1s and N 1s

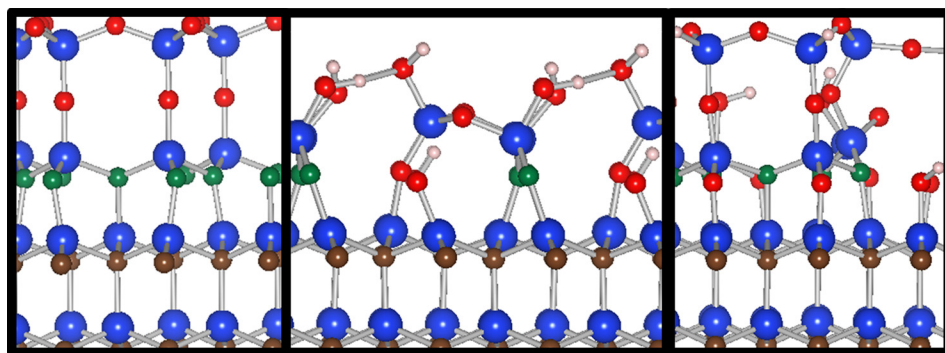


FIG. 4. Model 1, Model 2, and Model 3. Ball and stick figures of the SiC/Oxynitride interfaces (before etching) with Si (blue), C (brown), N (green), O (red), and hydrogen (white).

being 114.8 eV.<sup>5</sup> This latter difference is also found in the present samples and is used to calibrate our theoretical calculations. In Fig. 4, Model 1 is a reproduction of the structure reported by Shirasawa *et al.* that used in our calibrations. We estimate a numerical uncertainty of 0.2 eV for our reported N 1s core levels. The structures in Figs. 4 and 5 represent the oxide and SiC interface prior to the HF etching. They better represent the MOS structure. In these cases, the nitrogen above the interface (wholly within the oxide) is expected to be removed.

### A. Unstrained layers

Our experiments on NO processed samples suggest an inter-layer with about 1/3 mono-layer coverage of nitrogen consistent with the previously determined range of 0.1–0.4 monolayers.<sup>6</sup> Coincidentally, a 1/3 monolayer of N perfectly passivates all the silicon dangling bonds on the SiC(0001) surface (if each N atom were bound to three Si atoms below it).<sup>31</sup> However, this surface precludes any oxide from growing and is not a relevant model for nitrogen at the SiC/SiO<sub>2</sub> interface. We have investigated the properties of realistic models with nitrogen coverages similar to those observed experimentally. In Fig. 4, Model 2 shows an interlayer with a 1/2 monolayer coverage of nitrogen. The interlayer forms a two dimensional crystal with a primitive unit cell of 0.45 nm by 1.03 nm including 3 nitrogen atoms. Using the calibration mentioned above, we can compare our calculations directly to our experiments. Theoretically, the average N 1s XPS level is 397.0 eV for Model 2, close to our experimental result for the main XPS peak of 397.5 eV. In Model 2, the nitrogen interlayer involves rows of nitrogen atoms, each with three silicon nearest neighbors, bonding directly on top

of SiC(0001). The average N-Si distance is 0.176 nm, close to the 0.174 nm value in bulk silicon nitride. The second nearest neighbors of the nitrogen atoms include nitrogen, carbon, and oxygen atoms. Because of the agreement with XPS and the low strain of the Si-N bonds, Model 2 is an attractive model of the Si-N-O interlayer. However, the 0.5 monolayer of N is slightly larger than the observed coverage indicating that the actual interlayer is more complex than the crystal structure presented in Model 2.

### B. Strained layers

To investigate the properties of nitrogen in a strained interlayer, we constructed Model 3 which is shown in Fig. 4. There is a 5/12 monolayer of nitrogen atoms bonded directly to the SiC surface in this model. For Model 3, we calculated the N 1s core level energy for each N atom in the model. For 4 of the 5 nitrogen atoms, the N 1s core level is  $397.4 \pm 0.2$  eV, while for the remaining one it is 397.7 eV. In this latter case, the nitrogen is under considerable tensile strain, with a Si-N bond elongated by 5%, to 0.182 nm. As in Model 2, the second nearest neighbors include nitrogen, carbon, and oxygen atoms. With only nitrogen second nearest neighbors, bulk silicon-nitride (Si<sub>3</sub>N<sub>4</sub>) does not capture the nitrogen bonding environment at the SiC/SiO<sub>2</sub> interface.

### C. Nitrogen containing secondary peaks

Our proposed nitrogen bonding environments from Models 2 and 3 are consistent with the main N 1s peak that we report in Fig. 2. However, the secondary peaks reported in Fig. 2 are likely due to different local chemical environments. Nitrogen bound to oxygen at the interface may

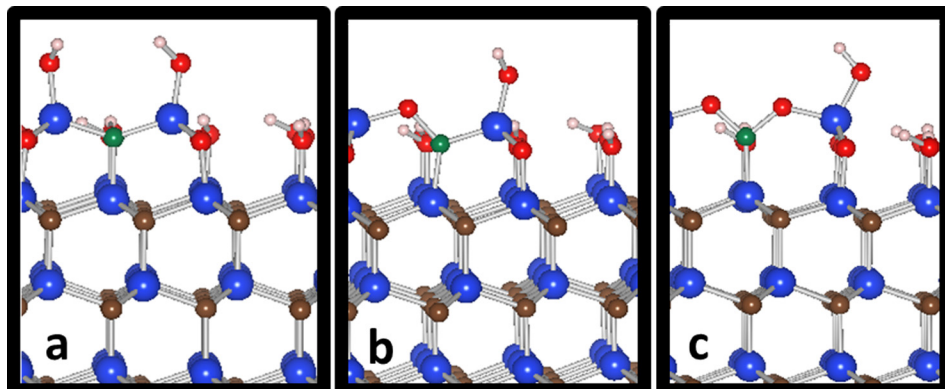


FIG. 5. Ball and stick figures of the SiC surface with a single nitrogen adsorbed with three different oxidation states. Si (blue), C (brown), N (green), O (red), and hydrogen (white).

explain the observed secondary XPS peaks. Therefore, we have created Si-N-O molecular structures on a SiC(0001) surface in order to test the influence of nearest neighboring oxygen on the N 1s binding energy. In Fig. 5, ball and stick structures of the models are shown for nitrogen on top of SiC with silicon nearest neighbors including (a) zero oxygen, (b) one oxygen, and (c) two oxygen nearest neighbors. Other surface silicon atoms are passivated with OH bonds only. The respective theoretical N 1s binding energy is found to be 397.1 eV, 398.5 eV, and 400.3 eV for the structures of Figs. 5(a)–5(c), respectively. These results are systematically lower than the corresponding N 1s peak values reported.<sup>28</sup> The different results may be due to calibrations used N XPS on Si substrate versus SiC substrate. Also, Si and SiC surfaces will have different interface dipoles which would affect the XPS values.

In case (a) where nitrogen has only three silicon neighbors, the N 1s binding energy is 397.1 eV, within the range 397.0–397.4 eV found for relaxed nitrogen in Models 2 and 3 above. These surface results agree with the previous results that include an oxide cap, indicating that the N 1s binding energy is mainly sensitive to nearest neighbor effects. In case (b), the N 1s binding energy 398.5 eV is close to the observed secondary peak at 398.4 (see Fig. 2). In Fig. 2(a), the XPS N 1s binding energy data are fit with three Gaussians. The highest energy peak is reported at 399.5 eV. This tertiary Gaussian is much broader than the other two with a relatively small maximum, suggesting one or more low probability configurations are involved. In Fig. 5 case (c), we present nitrogen bound to two oxygen atoms. In this case, the N 1s binding energy is calculated to be 400.3 eV, which is 0.8 eV higher than the value of the experimentally determined tertiary peak. Overall, nitrogen with oxygen bonds are close to the experimental secondary peaks. However, the concentration of NO bonds after an anneal >1000 °C is likely to be low; therefore, other candidate structures need to be considered.

#### D. Substitutional nitrogen

As the interfacial layer grows, EPR experiments indicate that nitrogen atoms can replace carbon<sup>32</sup> or fill silicon vacancies<sup>33</sup> below the interface, i.e., occupy substitutional sites in SiC. Estimates from low temperature magnetic resonance studies place the concentrations of ionized nitrogen substituting for C within SiC at  $\sim 5 \times 10^{12} \text{ cm}^{-2}$  or about 1% of the total interfacial N. Near interface substitutional nitrogen has also been invoked to explain threshold voltage shifts in NO annealed devices.<sup>14,32</sup> Starting with Model 2, we have considered two distinct cases, both involve nitrogen substituting for carbon in the first layer below the SiC/SiO<sub>2</sub> interface. In our calculations, we find such neutral and ionized nitrogen atoms have N 1s binding energies of 398.4 eV and 399.3 eV, respectively. These configurations are likely to contribute to the higher energy, secondary peaks observed in the XPS peak fitting (Fig. 2(a)).

#### E. Modeling summary

While interlayer Model 1 in Fig. 4 has been realized on SiC surfaces by Shirasawa *et al.*, Models 2 and 3 in Fig. 4

are more likely models for nitrogen incorporation at actual SiC/SiO<sub>2</sub> interfaces. To be clear, the models in Fig. 4 represent the situation just before an HF etch of the last layers of oxide. Examining the chemical reactions involved in HF etching is beyond the scope of the present study. However, for Models 1–3, molecular dynamics simulations at elevated temperatures (between 300 K and 2000 K) were performed to explore the stability of each model. For each simulation, we equilibrated the models at the given temperature and then recorded position data. In all simulations, there is no observation of Si-N bond dissociation. For the T = 1000 K simulations, the average Si-N bond lengths and standard deviations are reported in Table II, along with XPS core level results discussed above. In all three models, each nitrogen forms three strong bonds with bond lengths and angles close to those observed in crystalline silicon nitride. The Si-N bonds in Models 2 and 3 may be in a more stable configuration than those in Model 1, based on the lower average bond lengths and lower bond length deviations. Each oxygen forms a bridging bond between two silicon with bond lengths and angles similar to those found in crystalline and amorphous silicon dioxide. These simulation results encourage confidence in the quality of interface Models 2 and 3, as representative of actual interfaces. Our N 1s XPS calculations indicate the main observed peak is from a configuration of N bound to three Si atoms. The effect of second nearest neighbors appears to be minimal. The observed secondary XPS peaks may be due to N-Si bonds under tensile strain and/or substitutional nitrogen below the SiC/SiO<sub>2</sub> interface.

#### VII. ALTERNATIVE METHODS OF N INCORPORATION

Above we have reported a detailed theoretical and experimental analysis of the N 1s XPS data for samples grown using standard NO processing.<sup>2,8,34</sup> We also examined nitrogen introduced by two new processes: (i) oxidized SiC exposed to a nitrogen plasma,<sup>8</sup> and (ii) non-oxidized SiC exposed to pure N<sub>2</sub> at high temperature (1250 ~ 1600 °C). Fig. 6 shows the N 1s XPS spectral region of SiC prepared by (i) a high temperature N<sub>2</sub> anneal, (ii) an 8 h N<sub>2</sub> plasma, (iii) a 4 h N<sub>2</sub> plasma, (iv) a standard NO anneal (as in Fig. 2(a)), and (v) a bare 4 H-SiC sample. All the samples were etched in BOE for 5 min to remove the oxide layer and retained the N species with similar N 1s peak shapes and similar binding energies (although the total nitrogen peak areas differed). This implies that N atoms occupy essentially

TABLE II. Summary of theoretical simulation data for three interface models for N incorporation. See text for more details.

Model number	Nitrogen coverage	N 1s core level XPS (eV)	T = 0 K Si-N distance (nm)	Average Si-N distance (nm) 1000 K	Si-N stand. dev. (nm) 1000 K
1	1.0	398.7	0.177	0.178	0.0017
2	0.5	397.0	0.176	0.174	0.0013
3	5/12	397.4	0.176	0.177	0.0006
Experiment	1/3	397.5	...	...	...



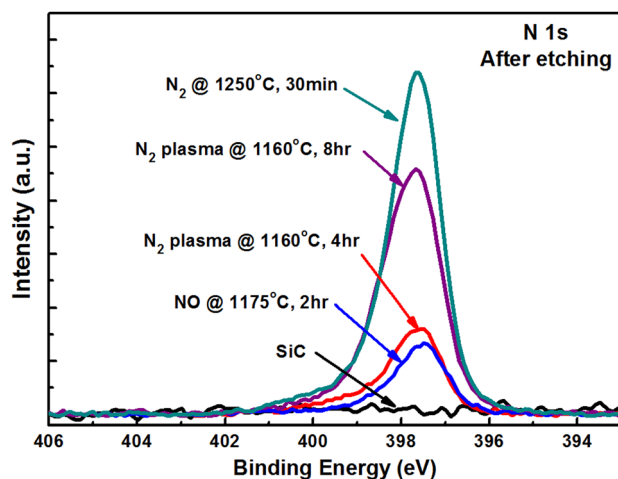


FIG. 6. N 1s XPS spectrum of SiC with different nitridation treatments, followed by 5 min BOE etching to remove all the oxide.

the same local chemical environment at the interface regardless of the nitridation method (close to one monolayer). Both the  $N_2$  plasma method and the high temperature  $N_2$  anneal resulted in approximately three times as much N at the interface as the standard NO anneal as reported in Table I.

Note that there is relatively little oxygen present before the HF etch on both the plasma and  $N_2$  anneal samples. After the HF etch, the NO sample continues to show a significant oxygen signal, much greater than the plasma and  $N_2$  samples after etch. This indicates that this “unetchable” oxide layer associated with NO processing, first reported by Dhar *et al.*,<sup>13</sup> is intrinsic to the NO process and may play a role in the electrical characteristics of devices fabricated via the different processing conditions studied here.

The continuous growth of the NO oxide might limit the efficiency of this nitridation process as a passivating agent. It is well-known that pure oxidation without any N creates a poor electrical interface. Our data indicate that these two alternative nitridation methods might be superior to the traditional NO anneal because they result in a higher N to O ratio at the  $SiO_2/SiC$  interface.

## VIII. SUMMARY

In conclusion,  $SiO_2/SiC(4H-Si)$  face) structures with nitrogen added by an NO anneal, a  $N_2$  plasma, and high temperature anneals in  $N_2$  were examined by XPS following BOE etching. In all cases a significant fraction of the N added, varying from 1/3 to 1 monolayer (where 1 monolayer is defined as the density of Si atoms in a single SiC (1000) atomic plane), was bonded to the substrate at the interface and was not susceptible to etching. This is in sharp contrast to the behavior of N on silicon surfaces, where complete etching of N occurs in similarly prepared samples. All nitridation methods resulted in similar photoemission spectra in the N 1s XPS region, indicating similar nitrogen bonding at the interface. Both N 1s peak fitting and a bonding model are suggested to describe the N bonding at the interface.

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