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## ADVERTISEMENT



## Transition layers at the SiO<sub>2</sub>/SiC interface

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The electrical performance of SiC-based microelectronic devices is strongly affected by the densities of interfacial traps introduced by the chemical and structural changes at the SiO<sub>2</sub>/SiC interface during processing. We analyzed the structure and chemistry of this interface for the thermally grown SiO<sub>2</sub>/4*H*-SiC heterostructure using high-resolution transmission electron microscopy (TEM), *Z*-contrast scanning TEM, and spatially resolved electron energy-loss spectroscopy. The analyses revealed the presence of distinct layers, several nanometers thick, on each side of the interface; additionally, partial amorphization of the top SiC surface was observed. These interfacial layers were attributed to the formation of a ternary Si–C–O phase during thermal oxidation. © 2008 American Institute of Physics. [DOI: 10.1063/1.2949081]

Silicon carbide is the only known wide-bandgap semiconductor with a native SiO<sub>2</sub>, which makes it suitable for metal-oxide-semiconductor (MOS) high-power and highfrequency devices.<sup>1</sup> However, interface trap densities at the  $SiO_2/SiC$  interface (~ low to mid- $10^{11}$  cm<sup>-2</sup>) remain one to two orders of magnitude higher than those typically found at the SiO<sub>2</sub>/Si interface ( $\sim$  low to mid -10<sup>10</sup> cm<sup>-2</sup>) and degrade the channel mobility.<sup>2</sup> According to recent studies, the likely sources of interface traps in SiC MOS field effect transistors include (i) excess carbon, 3-6 (ii) interface defects due to the presence of threefold coordinated O and C interstitial atoms, and (iii) point defects, such as Si vacancies, that extend into the SiC underneath the SiO<sub>2</sub>/SiC interface.<sup>8</sup> In addition, it has been calculated that fixed oxide trapped charge densities exceed 10<sup>12</sup> cm<sup>-2</sup>.<sup>9</sup> Switching oxide traps that contribute to threshold voltage instability exceed  $2 \times 10^{11}$  cm<sup>-2</sup>.<sup>10</sup>

The SiO<sub>2</sub>/SiC MOS structures used in the present study were fabricated on N-doped n-type 4H-SiC wafers with a 5-µm-thick Si-face-terminated homoepitaxial layer, doped at approximately mid-10<sup>15</sup> cm<sup>-3</sup>. The oxidation was performed at 1200 °C in pure oxygen, followed by an Ar annealing at 1100 °C and a 950 °C wet reoxidation annealing.<sup>11</sup> The structure and composition of the SiO<sub>2</sub>/SiC interfaces were characterized using high-resolution transmission electron microscopy (HRTEM), Z-contrast scanning TEM (STEM), and electron energy-loss spectroscopy (EELS). Cross-sectional TEM specimens were prepared by standard mechanical grinding and ion milling methods. The specimens were ion milled at a low angle  $(\sim 5^{\circ})$  during the final stage to achieve larger thin and uniform areas. Immediately before loading the specimen into the microscope, a 0.5 kV cleaning at 15° in the ion mill (Fischione model 1010) was carried out in order to minimize the surface contamination due to its exposure to air (no oxygen plasma cleaning was applied). HR-TEM images were acquired at ARL with a JEOL 2010F TEM operated at 200 kV; Z-contrast images and EELSs were simultaneously obtained at NCSU with a JEOL 2010F TEM operated at 200 kV in STEM mode, providing an electron-probe size close to 1.5 Å. The EEL spectra were collected by rastering the electron beam over a rectangular area to minimize the radiation dose and the beam-induced carbon contamination at any given point in the vicinity of the interface. Each spectrum was acquired from a rectangular region of  $7.7 \times 1.2$  nm<sup>2</sup>. The following conditions were applied during EELS acquisition: 0.5 eV/channel, convergence angle of  $\sim 19$  mrad, and collection angle of  $\sim 25$  mrad at zero projection lens current. The probe size, condensor lens aperture size, and acquisition time were optimized for enhanced EELS spectra. We applied an improved method<sup>12</sup> to quantify all the EELS spectra following Ref. 13. Hydrogenic ionization cross sections and inverse power-law background fitting were used for the quantification.

Low-magnification TEM images reveal a sharp  $SiO_2/SiC$  interface, free of voids or contamination. The thickness of the  $SiO_2$  layer is 62 nm. However, HRTEM images display visible contrast variations across the  $SiO_2$  layer which can be attributed to a structural and/or compositional variance within the  $SiO_2$ . Additionally, the top surface of the SiC epilayer exhibits signs of partial amorphization. The HRTEM image from the  $SiO_2/SiC$  interface region,



FIG. 1. HRTEM image of the  $SiO_2/4H$ -SiC interface revealing the transition layers A (4.8 nm) and B (3.3 nm) on the  $SiO_2$  and SiC sides of the interface, respectively.

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FIG. 2. (Color) (a) *Z*-contrast STEM image of the SiO<sub>2</sub>/4*H*-SiC interface. Each of the EEL spectra is collected from a rectangular area of 7.7  $\times$  1.2 nm<sup>2</sup> and the arrow indicates the sequence of the area scans (from 1 to 9). Spatially resolved EEL spectra containing the (b) Si-*L*<sub>2,3</sub> edge (99 eV), (c) C-*K* edge (284 eV).

taken along the [1100] direction, shown in Fig. 1, reveals the presence of transition layers A ( $t_A \approx 5$  nm) and B ( $t_B \approx 3$  nm) on the SiO<sub>2</sub> and SiC sides of the interface, respectively. These layers exhibit dissimilar contrast which likely reflects their structural and/or compositional differences. The thickness ratio,  $t_B/t_A=0.6$ , for these transition layers is consistent with the well-known model for the oxidation of Si.<sup>14</sup> According to this model, an oxide of thickness *d* consumes a layer of Si 0.44*d* thick. Application of this model to the oxidation of SiC yields a thickness ratio of 0.66 for the consumed SiC and the resulting SiO<sub>2</sub> layers, which agrees well with the observed ratio  $t_B/t_A=0.6$ . Overall, these observations indicate the expected occurrence of a chemical reaction during the thermal oxidation process.

Spatially resolved EELS analyses confirmed chemical modifications of the interfacial region (Fig. 2). In particular, analyses of energy-loss edge onset for the Si- $L_{2,3}$  (102 eV in SiC and 105 eV in SiO<sub>2</sub>) revealed chemical shifts of approximately 2 eV, consistent with the presence of a ternary Si–O–C phase in the vicinity of the SiO<sub>2</sub>/SiC interface.<sup>15</sup> On the SiC side of the interface, a measurable shift to higher energy (about 1 eV) of the C-*K* edge (284 eV) is observed at the interface, as compared to the bulk SiC; on the SiO<sub>2</sub> side,



FIG. 3. Low angle annular dark field STEM image of the  $SiO_2/SiC$  interface. Note the nonuniform thickness of the brighter band at the top SiC surface that can be correlated with the nonuniformity of the excess carbon at these regions.

a shift of the O K and Si- $L_{2,3}$  edges by approximately 2 eV is measured. These shifts of the edges for the major elements present at the interface suggest a chemical and structural modifications of the SiC in the vicinity of the SiC/SiO<sub>2</sub> interface. The chemical shifts of both Si- $L_{2,3}$  and C-K edges are consistent with the presence of O and/or excess C atoms at the SiC near the interface. These additional atoms would increase the number of valence electrons causing core level shift to lower energies due to Coulombic repulsion. In a simplified picture where valence electrons do not relax significantly this core electron level shift to a lower energy would increase the distance between the initial (core) state below the valence band edge and the final state, the conduction band edge, while leaving the overall energy-loss near-edge structure unchanged.<sup>16</sup>

Low angle annular dark field STEM imaging of the  $SiO_2/SiC$  interface (Fig. 3) reveals a layer at the SiC surface (1-2 nm thick) which exhibits a distinctly brighter contrast and can be identified with the structurally degraded layer *B* in the HRTEM images (Fig. 1). More detailed studies using high angle annular dark field (HAADF) STEM imaging (i.e., *Z*-contrast) combined with EELS (Fig. 4) provided quantitative profiles of the C/Si and O/Si concentration ratios across the interface. The O/Si ratios were measured at a position far away from the interface on the SiO<sub>2</sub> side, and that ratio was reset to 2:1 and all other O/Si values were scaled accord-



FIG. 4. (Color online) (a) HAADF image of the  $SiO_2/SiC$  interface. (b) Profiles of the C/Si and O/Si ratios as measured using EELS. Note the increased carbon content on both sides of the interface which correlates with the interfacial transition layers displaying a distinct contrast in Fig. 1.

ingly; on the SiC side the C/Si ratios were found to be approximately 1:1 and were measured directly from the experimental results, thus no rescaling was necessary. This difference indicates that the specimen surface contamination with carbon may not be as serious as the contamination of the specimen surface with oxygen. The O/Si ratio in the SiO<sub>2</sub> retained its bulk value to approximately 1 nm of the interface (the resolution limit of the present area scans). The C/Si ratio decreased from 0.6 at the interface to zero at a depth of approximately 4 nm into the oxide. In addition, the C/Si ratio exhibited nonstoichiometric behavior up to 4 nm into the SiC (i.e., approximately four unit cells of 4H-SiC), with a peak value of approximately 1.3 found for the first two area scans. Overall, the chemical profiles, i.e., the C/Si and the O/Si ratios, and the core level shifts suggest that thermal oxidation of SiC results in the incorporation of excess C into both the SiC surface and SiO<sub>2</sub> with the formation of a Si–O–C layer approximately 4 nm thick on both sides of the interface.

The experimental evidence from our studies indicates (i) the presence of transition layers on both sides of the SiO<sub>2</sub>/SiC interface, (ii) an excess of C in both transition layers (and possibly a decrease of Si in the SiC), and (iii) a structural degradation or amorphization of the top few atomic layers of the SiC at the interface. These results correlate well with previous experimental and theoretical studies by other groups. For example, one of the earlier EELS/Z-contrast studies of the SiO2/SiC interface by Pantelides et al.<sup>7,17</sup> reported a mixed EEL spectrum associated with Si-Si and Si-O-Si bonds determined from the Si-L2.3 line over a 3 nm range at the interface which, they suggested, indicates the presence of an extended amorphous region of unclear stoichiometry. The oxidation of SiC occurs by oxygen diffusion through the SiO<sub>2</sub> layer and the subsequent binding of O to the Si atoms. Simultaneously, the residual C can either be released as CO gas or form graphite; alternatively, C can form interstitial defects on both sides of the interface.<sup>7</sup> More recently, a study by Chang *et al.* using HAADF STEM indicated a bright line at the SiO<sub>2</sub>/SiC interface, which they attributed to a high defect concentration in the outermost atomic layers of the crystalline SiC that could be associated with lattice distortions around the defects.<sup>6</sup> The oxidation process can also be accompanied by the release of Si atoms from SiC, thus forming vacancies within SiC, as supported in the earlier work by Muelhoff, who suggested a sublimation of Si as the reason for graphitization of the SiC surface.<sup>18</sup> More recent studies by Lenahan, using spin-dependent recombination analysis, suggested the presence of Si vacancies in the SiC near the interface.<sup>8</sup> Thus, formation of C interstitials and release of Si could both contribute to a structural degradation and even amorphization of the SiC surface during the oxidation reaction.

Analytical studies using EELS and energy-filtered TEM by Chang *et al.*,<sup>3–6</sup> revealed an increased C/Si ratio at localized regions in the vicinity of the SiC/SiO<sub>2</sub> interface upon oxidation. This excess C had an estimated equivalent graphite layer thickness of 0.34-3.4 nm. These estimates also correlate well with the 5 and 3 nm thick transition layers, respectively, that we observe on the SiO<sub>2</sub> and SiC sides of the interface. Also, earlier angular-resolved x-ray photoelectron spectroscopy studies of the C-*K* binding energy revealed

more detailed stoichiometric changes in the vicinity of the  $SiO_2/SiC$  interface and pointed to a few distinct Si–O–C phases at this interface.<sup>15</sup> All of the above analyses by other groups show good correlation with the presence of transition layers at the  $SiO_2/SiC$  interface, as observed by TEM.

In summary, experimental evidence from our combined TEM/EELS studies revealed transition layers, approximately 5 and 3 nm thick, on the  $SiO_2$  and SiC sides of the interface, respectively. The thickness ratio for these layers is consistent with an oxide of thickness d consuming a SiC surface layer of thickness 0.6d, under the assumption of steady state oxidation. The transition layer on the SiC side of the interface is highly disordered, indicating that the oxidation process involves structural degradation of the top few atomic layers of SiC. According to spatially resolved EELS, the transition layer on the SiO<sub>2</sub> side contains C, whereas the top layer of SiC contains excess C and, possibly, small amounts of O. These results suggest formation of a ternary  $SiO_xC_y$  phase(s) in the vicinity of the  $SiC/SiO_2$  as a by-product of the oxidation reaction. The excess C in the SiC near the interface is believed to be present in the form of interstitial atoms. Further studies that analyze the individual stages of SiC oxidation are needed to verify these conclusions. Similarly, more work is needed to correlate the compositional/structural changes with the interfacial traps that affect the electrical performance of SiC MOS devices.

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