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Structure and stoichiometry of (0001) 4H–SiC/oxide interface

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The 4H–SiC/SiO_2 interface is a major obstacle that hampers SiC device applications. The nature of the transition region stoichiometry and structure need to be elucidated to both understand and improve such devices. In this paper, we use medium energy ion scattering on device grade structures to examine critical aspects of this dielectric/semiconductor structure. Our findings indicate no excess C greater than 1.8×10^{14} cm^{-2} from the oxide surface down to a few monolayers beneath the SiC/SiO_2 interface, setting limits on the previously predicted nonstoichiometric transition region on the dielectric side. © *2010 American Institute of Physics*. [doi:10.1063/1.3481672]

The 4H polytype of silicon carbide (SiC) is a promising candidate for high temperature and high power metal-oxide-semiconductor device applications. A major advantage is that it forms the same oxide (SiO_2) as Si, which makes most of the processing techniques in the Si industry applicable to SiC devices. However, the quality of the 4H–SiC/SiO_2 interface achieved so far is far from satisfactory. Many investigators have reported a large number of interface defects and low inversion channel mobility. A nitric oxide (NO) anneal on a thermally grown oxide can significantly reduce the interface trap density and improve the inversion channel mobility.[1,2] However, the performance is still below expectation.

A controversial topic regarding the 4H–SiC/SiO_2 interface is the physical description of the atomic structure of the interface and the possibility of excess carbon at that interface. Recent reports have discussed imperfections of the 4H–SiC/oxide interface on both the oxide side[3–5] and on the semiconductor side of the interface.[6,7]

In this paper, we report a detailed investigation at the interface using medium energy ion scattering (MEIS) (Ref. 8) on device quality structures. MEIS is capable of accurate depth profiling of different elements beneath the surface. Therefore, not only can we identify the concentrations of different species but also their locations with monolayer-scale depth resolution. To clarify, this report is only concerned with the existence of excess carbon, possibly in the form of a Si–C–O layer, from the oxide surface down to a few monolayers beneath the SiC/SiO_2 interface. Many reports concluded or inferred the existence of significant amounts of carbon and a Si–C–O layer,[3–5,9,10] while other recent papers are in contradiction with the existence of such a layer.[11–15]

Our latest MEIS results definitively rule out a significant Si–C–O like layer (Si–C–O–N in case of NO anneal) and suggest a near-ideal interface in terms of carbon stoichiometry and structure. Earlier MEIS-related reports, which focused on oxygen adsorption and kinetics on different faces, different polytypes and studied oxides formed under nondevice conditions,[16,17] did not specifically address excess carbon at or near the interface. Another MEIS report[10] did not properly account for surface contamination. In light of these variable results, and because of the considerable attention currently being given to the control of carbon at the SiC/SiO_2 device interface, it is critical to report observations that give further elucidation on this topic. Note that these results do not rule out submonolayers of C as the cause of the electrically-active interface defects ($\sim1\times10^{13}$ cm^{-2}) present at submonolayer concentrations but do reveal that the carbon substructure at the interface as being both structural and chemically abrupt on the monolayer scale.

All samples in this work were diced from (0001) face on-axis, n-type 4H–SiC wafers with additional chemical-mechanical polishing (surface roughness <0.2 nm) from Cree, Inc. The results reported are consistent with our measurement on 8° off-axis epitaxial samples but on-axis samples are preferred due to better ion channeling. They were cleaned by the standard Radio Corporation of America (RCA) procedure, and then oxidized in dry O_2 at 1150 °C to an oxide thickness of ~200 Å. In some cases this was followed by a NO anneal (1 atm, 1175 °C, 2 h). The conditions are consistent with the device fabrication procedure in order to form a similar interface. The oxides were then etched to a desired thickness of ~50 Å in diluted buffered oxide etchant (BOE). The thickness during etching was monitored by an ellipsometer. After etching, samples were loaded into the MEIS chamber for measurement. As explained below, leaving a thin oxide is critical to the experiment.

A 100 keV H^+ beam was used in the MEIS experiments. The incident beam was aligned to the ⟨0001⟩ axis of the SiC substrate to measure the surface peaks in channeling mode.[18] All the spectra are taken at 127.5° backscattering angle.

Since all samples were exposed to atmosphere before MEIS analysis, the total measured carbon possibly contained a contribution from extraneous surface carbonaceous species, similar to that reported by Dhar *et al.*[10] X-ray photoelectron spectroscopy (XPS) indicated that indeed a significant per-

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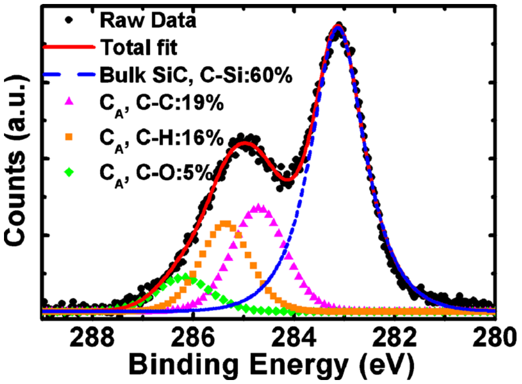

FIG. 1. (Color online) XPS spectrum of C 1*s* from bare SiC sample using Al Kα radiation with 53° exit angle. The adventitious carbon peaks account for at least 40% of the total signal.

centage of the total carbon is from the buildup of surface carbon-containing species during air exposure (Fig. 1). Binding energies associated with adventitious carbon are in agreement with values in the literature.[19] Therefore, in order to measure the SiC substrate carbon surface peak free of contamination, all oxides were etched down to ~50 Å in diluted BOE. The MEIS depth resolution is more than adequate to then separate the substrate carbon surface peak from the surface carbon.

The oxides are then further etched to bare substrate to measure the Si surface peak and N content. In agreement with Dhar *et al.*,[20] all spectra show about one monolayer (~5 Å) of residual O after etching (and about half monolayer of N in NO treated samples).

Before a discussion of the results, we briefly review the expected surface peak intensity in channeling on 4H–SiC. A full discussion of channeling surface measurement can be found elsewhere.[18,21]

In the absence of an oxide, the scattering spectrum with the incident beam in a channeling direction is dominated by "surface peaks" associated with scattering from the top Si and C monolayers encountered by the beam, with some possible addition due to the thermal motions of the closest underlying layers. In the presence of an amorphous SiO_2 overlayer, there will be an additional Si signal and an O signal. The 4H SiC structure is basically hexagonal and has a stacking fault of four bilayers, namely, ABCB, ABCB, … (A, B, and C stands for different bilayer positions). In a real 4H–SiC wafer, there are also four possible surface terminations associated with the Si-face (namely, ABCBA, BCBA, CBA, and BA).[22] For all surface terminations, there is always one monolayer of Si atoms and two monolayers of C directly exposed to the incident ion beam along ⟨0001⟩ direction. The Si atoms directly underneath the top two C monolayers will also make some contribution to the measured Si surface peak due to the thermal motion. The intensity of the surface peak is a function of the two-dimensional root mean square thermal vibration amplitude ρ, and the shadow cone R_M.[21] $\rho_{(Si)}$ is 0.0517 Å using a Debye temperature of 1300 K, and R_M is 0.0775 Å for these experimental conditions. Hence the expected C and Si surface peak intensity in an ideal single crystal correspond to 2.43×10^{15} cm^{-2} and 2.85×10^{15} cm^{-2}, respectively, as reported by Dhar *et al.*[10] (One monolayer of atoms in the surface plane corresponds to 1.21×10^{15} cm^{-2}). Therefore, if there is any excess carbon at the interface region within the depth resolution, which is about 20 Å (full width at half maximum) with the presence of 50 Å of oxide, it would result in a higher measured C surface peak intensity.

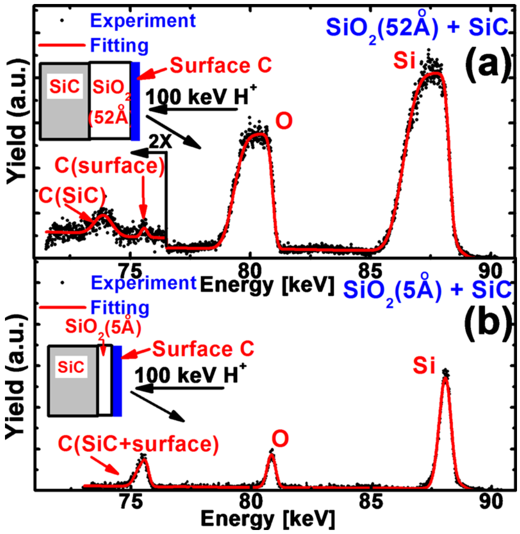

FIG. 2. (Color online) (a) (top) MEIS spectrum of as-oxidized SiC with 52 Å oxide. The substrate carbon surface peak is well separated from the surface carbon; (b) (bottom) MEIS spectrum of as-oxidized SiC with ~5 Å oxide.

Figures 2(a) and 2(b) show the MEIS spectrum of the as-oxidized (0001) SiC with 52 Å oxide and ~5 Å oxide (the spectra of bare SiC and the NO treated sample are not shown). The experimental surface peaks are calculated from the simulated fitting, which also shows that no C is detected in the oxide region. The accuracy of the surface peak evaluation is about 1.8×10^{14} cm^{-2}.

Table I lists the C surface peak of the bare SiC (unprocessed, RCA cleaned only), as-oxidized (dry O_2 at 1150 °C) and NO treated (dry O_2 at 1150 °C followed by 2 h NO anneal at 1175 °C), respectively. Both the as-oxidized and the NO treated sample are measured with ~50 Å oxide, and the C surface peak from SiC agrees well with the surface peak prediction. This means that no excess C is detected at the interface region (within a few monolayers) within 1.8×10^{14} cm^{-2}. This is the main experimental conclusion from this report.

The Si and O surface peaks are measured from the same samples with ~5 Å oxide. The measured Si surface peak consists of Si from the thin oxide on the surface and from the SiC substrate. Hence, we estimate the Si from the SiC substrate assuming the oxide has perfect SiO_2 stoichiometry. This estimation for both the as-oxidized and NO treated samples (2.88×10^{15} cm^{-2} and 2.78×10^{15} cm^{-2}, respectively) is consistent with the theoretical calculation (2.85

TABLE I. MEIS measured C surface peak of 4H–SiC samples with ~50 Å oxide (except bare SiC) after different processes. The calculated C surface peak is listed for comparison.

Conditions	Oxide thickness (Å)	Measured C_{SiC} (cm^{-2})	Calculated C_{SiC} (cm^{-2})
As-oxidized	52	2.35×10^{15}	2.42×10^{15}
NO treated	47	2.31×10^{15}	2.42×10^{15}
Bare SiC	⋯	4.60×10^{15} (with surface C)	2.42×10^{15}

$\times 10^{15}$ cm^{-2}), indicating the validity of our assumption and a near perfect surface structure. Within our detection limit, this observation rules out the possibility of a highly nonstoichiometric transition region, both with and without N passivation.

A number of recent studies have addressed the question of the SiC interface structure. (i) Wang *et al.*[5] presented a theoretical discussion concluding that the SiC/SiO$_2$ interface is best viewed as a "bonded Si–C–O interlayer, encompassing one to two atomic layers."[5] Such a model would suggest a larger carbon surface peak with an excess of $\sim 1 \times 10^{15}$ cm^{-2} over the ideal structure. This model is ruled out by the present results. (ii) Virojanadara and Johansson[11–13] reported XPS studies, with a detailed analysis of the C 1*s* spectrum in a sample with a thin covering oxide. They conclude that "…no carbon clusters or carbon containing byproduct could be detected at the interface of samples…"[13] XPS does not provide any structural information on atomic sites. Assuming that XPS has a sensitivity of $\sim 1 \times 10^{14}$ cm^{-2}, these XPS results are in excellent agreement with the findings reported here—namely, an interface stoichiometry free of excess C ($< 1.8 \times 10^{14}$ cm^{-2}). While the XPS analysis reveals the interface chemistry these current MEIS results show that the interface is not only chemically abrupt but structurally nondistorted within the surface plane. (iii) A recent oxygen sensitive ion scattering report from Corrêa *et al.*[3] originally interpreted the existence of residual oxygen found after HF etching as being in the form of a nonetchable Si–C–O interfacial layer at the buried interface. However, Dhar *et al.*,[20] identified this monolayer of oxygen left at the interface as a remaining layer of oxygen simply bonded to surface SiC. A Si–C–O layer would have contributed to substantial excess C, which is ruled out by the MEIS results. (However a very thin layer (~20 Å) of with stoichiometry such as Si$_{1-x}$C$_x$O$_2$ and $x < 0.08$ cannot be ruled out based on the error reported above.) The results reported here, taken with the experimental findings cited above, lead to a consistent picture of the interface as described above.

The mechanism of nitrogen passivation and its positive effects on the electronic properties of the interface are still not resolved. For NO treated samples, an amorphous carbon containing Si–C–O–N layer is not detected, however, epitaxial Si–O–N layers may possibly form. It has been reported that under certain conditions N forms an ordered structure at the interface, tying up dangling bonds.[23] However this structure does not alter the surface peak prediction. Our calculations indicate essentially no blocking effect of the Si atoms or C atoms by N atoms in this specific model, hence all the surface peak intensities should remain unaffected by the presence of nitrogen. Again the main result is the absence of excess C at the level of $\sim 1.8 \times 10^{14}$ cm^{-2}.

Our result is similar in spirit to earlier data for the Si(111)/SiO$_2$ interface,[24] which showed minimal in-plane distortions when measured along the normal direction. The similarity between the hexagonal structure of 4H–SiC and Si (111) suggests a commonality in structural distortions of the underlying substrate.

In conclusion, for all the samples oxidized under device conditions, the fact that both the measured Si and the C surface peaks agree with the theoretical prediction indicate a laterally near-perfect SiC surface structure. The results indicate no excess carbon greater than 1.8×10^{14} cm^{-2}, from the oxide surface down to about few monolayers beneath the SiC/SiO$_2$ interface. Monolayer-scale interfacial Si–C–O and Si–C–O–N type of structures are not observed. This does not rule out the possible existence of excess C less than 1.8×10^{14} cm^{-2}, sufficient to effect electrical properties but does reveal the interface as being both structurally and chemically abrupt on a macroscopic scale.

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