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International Conference on Silicon Carbide and Related Materials 1999,
Research Triangle Park, North Carolina, October 10-15, 1999,
Submitted to meeting *Proceedings*

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under
Contract No. DE-AC05-96OR22464
with the
U.S. DEPARTMENT OF ENERGY
Oak Ridge, Tennessee

October 1999

ATOMIC-SCALE ENGINEERING OF THE SiC-SiO₂ INTERFACE

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Keywords: oxidation, interface structure, interface traps, nitrogen

Abstract: We report results from three distinct but related thrusts that aim to elucidate the atomic-scale structure and properties of the SiC-SiO₂ interface. a) First-principles theoretical calculations probe the global bonding arrangements and the local processes during oxidation; b) Z-contrast atomic-resolution transmission electron microscopy and electron-energy-loss spectroscopy provide images and interface spectra, and c) nuclear techniques and electrical measurements are used to profile N at the interface and determine interface trap densities.

Introduction: The native oxide of SiC is SiO₂, but the properties of the SiC-SiO₂ interface fall far short of those of the Si-SiO₂ interface for MOSFET applications. We have initiated a program to investigate the atomic-scale properties of the SiC-SiO₂ interface aiming to identify the causes and possible remedies for the observed behavior. We employ a combination of first-principles calculations, atomic-resolution microscopy, electron-energy-loss spectroscopy, and analytical and electrical measurements as functions of process variation. In this paper we report initial results of these investigations.

Theory: We have pursued first principles calculations (density functional theory, local density approximation for exchange-correlation, pseudopotentials, plane waves) with several objectives.

a) Global bonding arrangements at the interface: Systematic studies of the Si-SiO₂ interface for (001) Si revealed that a totally abrupt interface is possible and energetically preferred. Suboxide bonds (i.e. Si-Si bonds on the oxide side are energetically unfavorable because insertion of an O atom in such a bond generally allows more relaxation to occur via a pivoting action about the O site). In contrast, for SiC-SiO₂, an abrupt interface is not possible for topological reasons. Even in the case of cubic SiC and its (001) surface, the bond lengths are too small to accommodate an abrupt interface. The hexagonal phase is even worse because the surfaces resemble the Si (111) surface [known to have a much rougher interface than (001) surfaces] and the bond lengths are again not suitable. In fact, there is an experimental study¹ that found that depositing a monolayer of O on SiC saturates the bonds in a way that does not allow for the growth of an oxide. Our modeling studies confirm this result and further establish that a substantial interface layer with mixed bonding including Si-Si bonds is absolutely necessary. This result is fully consistent with the EELS data reported below.

b) Atomic-scale processes during oxidation and interface defects: We performed calculations investigating the atomic-scale steps that lead to precipitation of O atoms in the form of SiO₂ particles in SiC.² These studies allowed us to deduce several important results about the oxidation of SiC: i)

whereas during Si oxidation, Si interstitials are emitted, during SiC oxidation the emission of either Si or C interstitials is energetically unfavorable. On the other hand, C atoms are removed by being captured by O atoms into CO molecules. The latter are not stable in SiC but are stable and mobile in SiO₂. Thus we have identified the atomic-scale processes that lead to the removal of C in the form of CO, as observed experimentally. We further find that the activation energy for diffusion of CO in SiO₂ is much smaller than that for the diffusion of O₂ in SiO₂ (0.5 eV versus 1.5 eV) so that the rate-limiting step for oxidation is the supply of O or the interface reaction. Similarly, during reoxidation, the rate-limiting step for the possible removal of C precipitates at the interface is again the supply of O. Our calculations further reveal that the oxidation process does not leave dangling bonds. The only likely interface defects are centers involving threefold-coordinated O that are reminiscent of the “thermal donors” in Si³ and C interstitials from the break-up of departing CO molecules. Both these defects introduce localized energy levels in the upper part of the SiC band gap. We also expect Si-Si bonds at the interface to introduce localized states at both ends of the SiC band gap. Thus, there are several candidates for the observed large densities of interface defects, especially at the edges of the band gap in 4H material.

Microscopy:

Sample preparation: We report investigations of two samples, both oxidized thermally at 1100 °C and one reoxidized at 900 °C. Prior to preparing them for the TEM, the samples were coated with a layer of amorphous silicon (a-Si in Fig. 1 a) for protection. The reoxidized sample showed im-

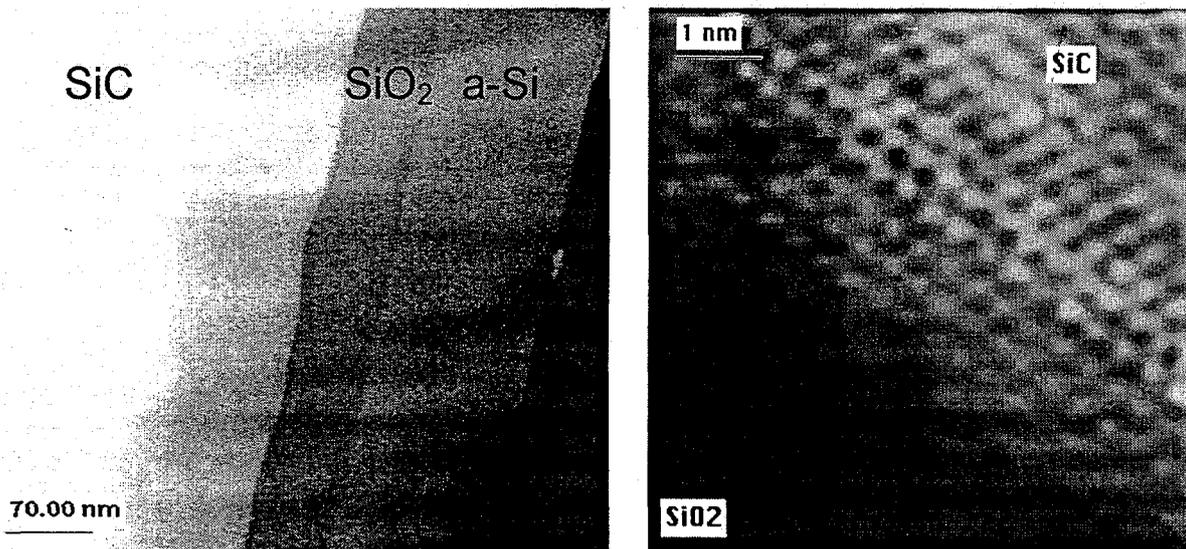


Fig. 1. Z-contrast images of the SiC-SiO₂ interface with a) low and b) atomic resolution. In the reoxidized sample (a) we see a faceting not observed in normally oxidized samples (b). On the atomic scale, both samples reveal a roughness of about one monolayer.

proved electrical properties after the additional heat treatment (see below for details).

Z-contrast images obtained from the reoxidized sample revealed a strong faceting (Fig. 1a). We attribute this faceting to an accumulation of steps originating in the miscut of the SiC-4H substrate. The faceting is not periodic; large plane areas (mostly, but not only, of the (0001) plane) are alternating with areas as shown in Fig. 1a where many facets accumulate. An atomic column resolution investigation of both samples showed a roughness of only about one monolayer.

We also performed electron energy-loss spectroscopy (EELS) on the same samples. The spectra were obtained while the beam (diameter of about 0.3 nm) was scanned along a line across the inter-

face . In Fig. 2 we compare the results of a reoxidized SiC-SiO₂ interface with corresponding data from a (111) Si-SiO₂ interface. In the case of the Si-SiO₂ interface spectrum, the slowly rising onset is attributed to a suboxide layer (SiO_x), namely one or two layers of mixed Si-Si and Si-O-Si bonds. In contrast, for the SiC-SiO₂ interface, a mixed spectrum persists over an interface layer of order 3 nm, suggesting an extended amorphous region whose stoichiometry remains unclear. This result is consistent with the theoretical studies described above. It is notable that, despite the extended mixed phase, the crystalline-amorphous interface has minimal roughness, one to two monolayers, as revealed by the micrograph in Fig. 1b.

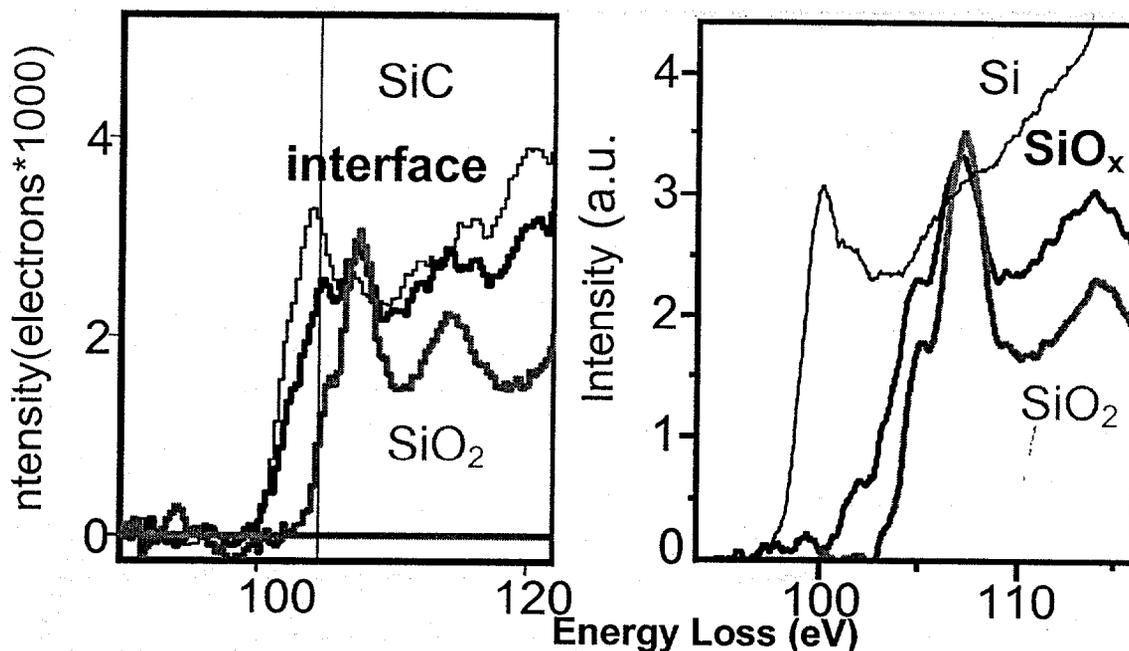


Fig. 2. EELS spectra of Si-L_{2,3} edges from the SiC-SiO₂ interface and the Si-SiO₂ interface. In each case we show the two bulk spectra plus a typical interface spectrum.

Analytical and electrical measurements: Recent experimental work found that incorporation of N in SiC-SiO₂ structures may have a beneficial effect on the interface trap density.⁴ We have studied the incorporation of N for oxides grown in (i) N₂O (1100 °C) and (ii) O₂ (1100 °C), subsequently annealed in ¹⁵N¹⁸O (1000 °C). The N₂O grown sample reveals an exceedingly slow growth rate (compared to pure O₂) and a non-stoichiometric oxide. As a result we have concluded that growth in N₂O is not a useful way of incorporating nitrogen into the SiC/SiO₂ structure.

The annealed samples were investigated using isotope-sensitive nuclear techniques to determine the N content and profile. As shown in Fig 1, there is a clear indication of interfacial N, corresponding to ~10¹⁴ N/cm². These values are considerably smaller than the corresponding N accumulation for the Si-SiO₂ system. This is consistent with the fact that the SiC interface is less reactive than the Si interface. Complementary measurements (not shown) of the ¹⁸O exchange reaction (from the ¹⁵N¹⁸O annealing gas) with the oxides shows exactly the same reaction rate for both the Si and SiC structure. This is another sensitive demonstration of the fact that the bulk oxides of these two materials are chemically and physically similar, though the interfaces are distinctly different.

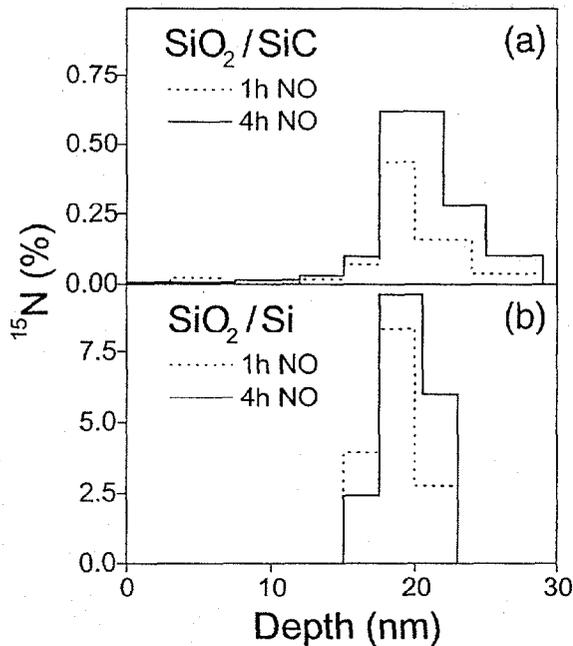


Fig. 3. Concentration profiles of ^{15}N after annealing in 10 mbar of $^{15}\text{N}^{18}\text{O}$ at 1000 °C for 1 h (dotted) and 4 h (solid). The origin corresponds to the surface, the SiC-SiO₂ interface is at ~30 nm, and the Si-SiO₂ interface is at ~20 nm.

doping. This correlation of D_{it} with doping suggests that information about states in the upper part of the band gap obtained from n-type material may not be applicable to p-type material. Reoxidation was found to reduce D_{it} in p-type but not in n-type material.

This work was supported in part by a joint grant from the Defense Advanced Research Projects Agency (MDA972-98-1-0007 and the Electrical Power Research Institute (WO806905).

Electrical measurements have been performed on a series of samples to evaluate the effect of N incorporation both with and without reoxidation. As is well known,⁵ reoxidation reduces the density of interface traps (D_{it}). We have found that nitridation does not have any effect on D_{it} , with or without reoxidation. Though further reduction of D_{it} would have been desirable, the result that N can be incorporated without an increase in D_{it} is important because N is known to enhance reliability.⁶

Finally we report briefly on samples grown epitaxially and oxidized in a furnace. Different ratios of propane to silane were used and the resulting D_{it} in the upper part of the band gap for 6H-SiC is shown in Fig. 4. When the Si/C ratio is small, doping by the ambient N is suppressed and the material is essentially intrinsic. Thus, the observed improvement in D_{it} may in fact be due to the lower

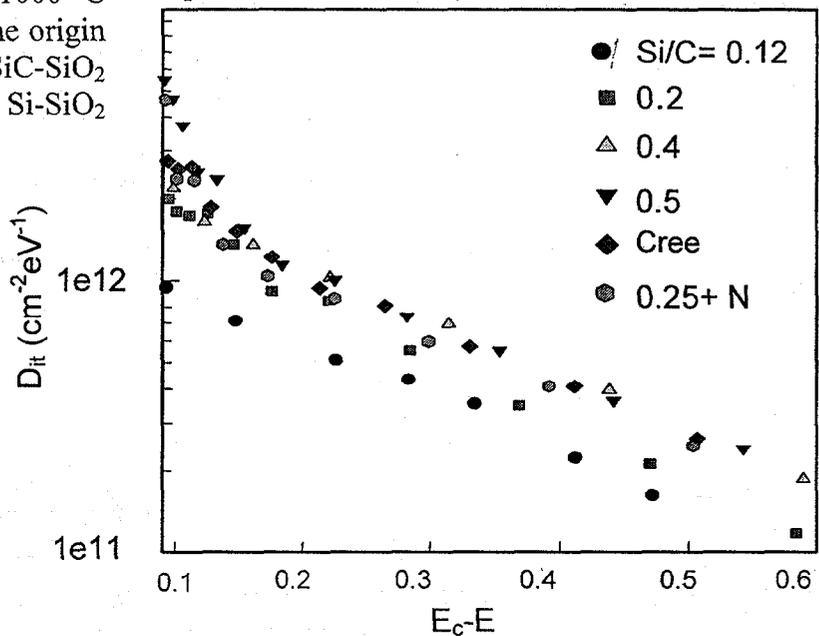


Fig. 4. Interface State Density vs Si/C Ratio for 6H-SiC

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