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Bonding at the SiC-SiO$_2$ Interface and the Effects of Nitrogen and Hydrogen

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Unlike the Si-SiO$_2$ interface, the SiC-SiO$_2$ interface has large defect densities. Though nitridation has been shown to reduce the defect density, the effect of H remains an open issue. Here we combine experimental data and the results of first-principles calculations to demonstrate that a Si-C-O bonded interlayer with correlated threefold-coordinated C atoms accounts for the observed defect states, for passivation by N and atomic H, and for the nature of residual defects.

Bonding configurations at interfaces and the nature of possible interface defects are central issues in determining the suitability of thin-film structures for electronic devices. One of the reasons for the dominance of Si in microelectronics is the nearly defect-free interface with its native oxide, SiO$_2$. The SiC-SiO$_2$ interface has been studied extensively because of its potential use in high-power, high-temperature electronic devices. Its promise lies in the fact that SiC is the only wide-gap semiconductor with a stable native oxide, again SiO$_2$. However, SiC-SiO$_2$ interfaces have large densities of electrically active interface defects that are generally attributed to carbon clusters [1–3]. Oxidation of Si-terminated SiC faces has been studied more extensively because C-terminated faces result in higher defect densities [2]. In recent years, several groups achieved partial passivation by N [4–7]. In contrast, annealing in an H$_2$ atmosphere at moderate temperatures ($\sim$400 °C), which is very effective at passivating Si dangling bonds at Si-SiO$_2$ interfaces, produces no measurable effect [2,8]. There are conflicting reports about high-temperature ($\sim$1000 °C) H$_2$ annealing [9,10]. In more recent work, C dangling bonds were identified by the electron-paramagnetic resonance (EPR) signature at SiC-SiO$_2$ interfaces formed on *porous* SiC [11]. These defects are successfully passivated by H$_2$ at moderate temperatures [12], but their densities relative to non-EPR active interface defects are not known. Atomic-scale understanding of the intrinsic interface defects, the role of N, and the behavior of H has remained elusive.

Theory has so far focused on the key atomic-scale oxidation step, which entails either C or CO release in the oxide and the role of N in passivating interface defects [5,13,14]. More recently, Knaup *et al.* [15,16] reported theoretical studies of both the atomic-scale oxidation reactions and possible defects at SiC-SiO$_2$ interfaces and attributed individual peaks in the experimental interface-state densities to particular C-related defects. The effect of H or N on these defects was not investigated.

In this Letter we first report results of a systematic experimental study of hydrogenating SiC-SiO$_2$ interfaces formed on Si-terminated SiC faces in metal-oxide-semiconductor (MOS) structures. We find that H$_2$ has essentially no effect on the density of electrically active interface defects (D_{it}) unless it is passed through a transition-metal layer such as Pt, where H$_2$ is known to crack into atomic H. We further show that nitridation followed by hydrogenation yields complementary passivation and a substantial reduction of D_{it}. We also report first-principles calculations of possible interface defects and the effect of H and N. A key result is that isolated C dangling bonds can be passivated by H$_2$, whereas "correlated" C dangling bonds on neighboring threefold-coordinated C atoms can only be passivated by monatomic H. We then demonstrate that, instead of the usual view of a density of distinct defects, e.g., large carbon clusters, the SiC-SiO$_2$ interface is best viewed as a bonded Si-C-O interlayer (one to two atomic layers), where *correlated* C dangling bonds are primarily responsible for the observed D_{it}. The wide variation of local topologies renders these defects undetectable by EPR. A much lower density of isolated C dangling bonds is EPR active as in amorphous SiC [17], requiring large surface areas for detection, realized only by using porous SiC [11,12]. We also propose that the effect of nitridation is to convert the Si-C-O bonded interlayer into a Si-C-O-N bonded interlayer with a concomitant reduction in threefold C atoms (N replaces threefold C). We further propose that, when atomic H is added, the Si-C-O-N bonded interlayer is converted to a Si-C-O-N-H bonded interlayer, with a further reduction of interface states. The remaining interface states are attributed to a distribution of Si-Si bonds in the interlayer.

Experiments were performed on MOS capacitors fabricated on n-type (0001) Si-face 4H-SiC substrates. The samples had $\sim$10 μm-thick epitaxial layers with N doping concentration of $\sim$10^{16} cm^{-3}. Dry oxidation at 1150 °C for 4 h was used to grow oxides of thickness $\sim$40 nm. On

some samples, the oxidation was followed by a post-oxidation anneal in flowing NO (500 sccm) at 1175 °C for 2 h. The as-oxidized and NO annealed samples were metallized with a Au/Mo stack or Pt deposited by dc sputtering. The capacitor areas were defined by photolithography. Samples which had Pt as the gate metal (as-oxidized or NO annealed) were further annealed in pure H_2 (flow rate: 500 sccm) at 500 °C for 1 h. The presence of a catalytic Pt is critical for the dissociation of H_2 molecules and subsequent incorporation of H atoms at the SiC-SiO_2 interface. Secondary ion mass spectrometry (SIMS) and nuclear reaction analysis measurements have been used to determine the amount and distribution of H incorporated *via* the Pt-assisted annealing [18] (for SIMS measurements, deuterium was used instead of H for higher sensitivity). The results revealed an incorporation of $\sim 2.5 \times 10^{14}$ cm^{-2} of H in the interfacial or near-interfacial region, with a distribution having a full width at half maxima of less than 3.5 nm, the depth resolution of SIMS.

The processing sequence outlined above yielded four kinds of samples with distinct interfacial compositions: (1) As-oxidized (Mo/Au gate); (2) NO only: Oxidation followed by NO post-oxidation annealing (Mo/Au gate); (3) H only: Oxidation followed by post metallization annealing in H_2 (Pt gate); and (4) NO + H: NO post-oxidation annealing followed by post metallization annealing in H_2 (Pt gate). Densities of interface defects were extracted from the dispersion between high-frequency (100 kHz) and quasistatic (hi-lo) capacitance-voltage (CV) measurements in accordance with the standard simultaneous hi-lo CV technique [19]. Room temperature measurements were used to profile D_{it} from ~ 0.1 to 0.6 eV below the conduction band edge (CBE), whereas measurements at 300 °C were necessary to profile from 0.6 eV below the CBE up to midgap [20]. Typical results are shown in Fig. 1. By comparison with the "as-oxidized" D_{it} profile, the extent of passivation induced by the different processes can be evaluated. Notably, the significant defect passivation associated with N ("NO only" sample) is observed in the entire energy range, with the effect being more dramatic near the CBE. On the other hand, near the CBE (at $E_C - E \sim 0.1$ eV), the "H only" process results in about a factor of 2 reduction in D_{it}, a relatively small effect compared to the NO effect. However, deeper in the gap (i.e., $E_C - E > 0.6$ eV), atomic H has a larger relative effect on defect passivation. Finally, the results for nitridation followed by hydrogenation (NO + H sample) reveal the most effective defect passivation. Near the CBE, a $\sim 30\%$ reduction in D_{it} is observed compared to the NO only case. Deeper in the gap, the effects of the additional atomic H passivation is substantial, where the reduction is almost an order of magnitude.

Calculations were performed using density-functional theory [21,22]. An energy cutoff of 396 eV and the Γ point in the Brillouin zone were used for the calculations. The interface was modeled by a supercell (repeated slabs,
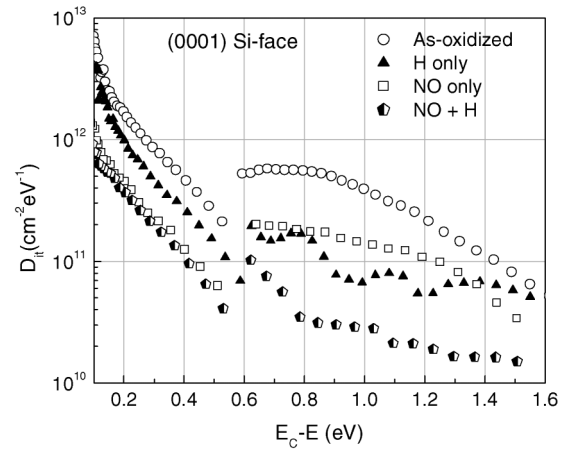

FIG. 1. SiC-SiO_2 interface-state density profiles in the upper half of the 4H-SiC band-gap for the different interface treatments. The horizontal axis, $E_C - E$ denotes the energy from the CBE. The discontinuities and slope changes at ~ 0.6 eV are a reflection of the temperature dependence of electron emission from interface traps. The error bars on the points amount are roughly a factor 2 in the D_{it} values.

separated by a vacuum region of 10 Å) containing a (4 × 4) surface cell with three (0001) double-layers of 4H-SiC (48 Si and 48 C atoms) and two SiO_2 layers (16 Si atoms and 32 O atoms). The abrupt interface was modeled as in Ref. [15]. All 16 Si atoms on the Si-face surface of SiC are bonded to O atoms in SiO_2. The dangling bonds of the C atoms at the bottom layer of SiC and the Si atoms at the top of the SiO_2 layers were terminated by H atoms. The SiO_2 layers and the top four SiC layers were allowed to relax until the forces on the atoms were smaller than 0.05 eV/Å.

The elementary oxidation step at an advancing SiC-SiO_2 interface when an O_2 molecule arrives involves ejection of a C atom as a single C or CO interstitial while O atoms form Si-O-Si bridges, as shown in earlier work [13,15,23]. As in the oxidation of Si, volumetric constraints also require the occasional emission of a Si atom. The key difference in the case of SiC is the fate of the emitted C or CO. Most leave through the growing SiO_2, but inevitably a fraction remain stuck at the interface when oxidation stops [14,24,25]. Our initial goal was to determine the fate of the excess carbon, which has been generally believed to form distinct C clusters [1,2], possibly including graphitic clusters [3,15].

First, we track the fate of a single C interstitial emitted at the interface. Right at the interface, it prefers to be bonded on the oxide side. The most stable configuration [Fig. 2(a)], with the C atom bonded to two Si atoms and a "dangling" O atom, has only a doubly occupied level in the gap [0.5 eV above the valence band edge (VBE)], and can act only as a hole trap. Another configuration [Fig. 2(b)], in which the C atom forms a Si-O-C-Si bridge and is slightly bonded to an additional Si atom in the oxide network, is metastable in the neutral state (higher in energy by 0.5 eV), but it is 0.3 eV lower in energy when it traps an electron near the
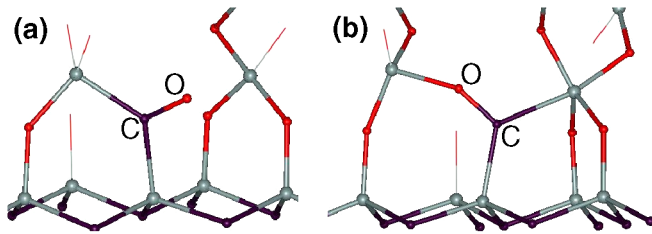
FIG. 2 (color online). Schematics of (a) the lowest-energy configuration: C takes the place of O and O is pushed out resulting in a C-O bond. (b) A slight-higher-energy configuration: C shares the O site resulting in a Si-O-C-Si bridge.

CBE. In addition to the full level in the lower part of the band gap (0.3 eV above the VBE), it has an empty level in the upper part of the gap (0.3 eV below the CBE).

We studied other metastable defect configurations due to a single excess C atom. We found, however, that, in any of the configurations, the excess C atom can capture an H_2 molecule and be fully passivated, with no gap states. The net result is that isolated excess C atoms would be passivated by H_2 molecules. Since our experiments on MOS capacitors find that H_2 molecules are not effective at passivating the as-oxidized SiC-SiO$_2$ interface, we conclude that most C atoms are not incorporated in the interface as single interstitials. A similar analysis of a single CO molecule at an otherwise abrupt interface found that the CO molecule binds to the interface with a binding energy of 0.35 eV. However, the resulting configuration has no levels in the gap, thereby it is either not present or plays no significant role.

Further explorations resulted in the following. An extra C atom substituting for an interface Si atom amounts to a C cluster (the central C atom would have up to 3 C neighbors and at least an O neighbor). Such a defect is unstable because the C-C bonds are too long. In contrast, placing 2 C atoms to share a nominal Si site yields a stable structure [Fig. 3(a)]. The two central C atoms are threefold coordinated and each produces a level in the gap (about 1 eV below the CBE). Note that the three neighbors of each of the 2 C atoms define different planes. Indeed, if we passivate each of the 2 C atoms with a H atom, we find that the 2 C-H bonds point in opposite directions [Fig. 3(b)], showing that a large energy barrier would be involved if an H_2 molecule is introduced to passivate the defect (passivation of the 2 C dangling bonds is not a one-step process because of the distance). Further, passivating only one of the 2 C atoms by an H_2 molecule, letting the other H to migrate (hopping from O to O in the oxide) is not energetically favored, with an energy cost of ~0.4 eV. Therefore, H_2 molecules are not effective in passivating correlated C dangling bonds. In contrast, truly isolated C dangling bonds can be passivated by an H_2 molecule (with the other H migrating away) with a substantial energy gain (~1.0 eV). The different local geometries of isolated C dangling bonds and correlated pairs of C dangling bonds are indeed quite different. The net conclusion is that iso-
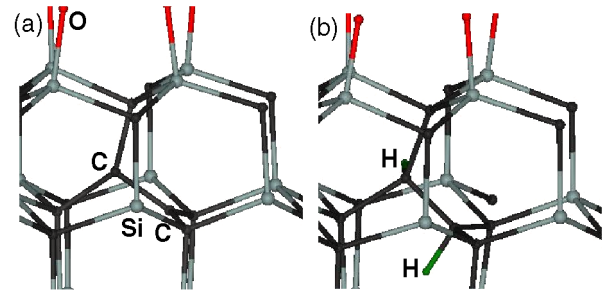

FIG. 3 (color online). (a) Schematic of 2 C atoms on the SiC side of the interface (a C-C dumbell replaces a single Si atom). (b) The same defect passivated by 2 H atoms (each C forms a C-H bond).

lated C dangling bonds can be passivated by H_2, but correlated C dangling bonds cannot. We are therefore able to account for the seemingly contrasting data reported here for MOS capacitors and in Ref. [12] on oxidized porous SiC: EPR detects a signal only from isolated dangling bonds, which can be passivated by H_2. The correlated C dangling bonds, with much more variation in geometry and backbond structure, are more likely to give a smeared out EPR signal (in amorphous SiC only the isolated C dangling-bond EPR signal is observed [17]). The two sets of data, therefore, tell us that the dominant defects in MOS capacitors, detected by electrical measurements, are correlated C dangling bonds.

We studied a wide range of other defects and their reactions with H_2 and H. Our net conclusion is that isolated C dangling bonds with various backbond combinations have a level in the midgap region (the case of two O backbonds is an exception) and can typically be passivated by either H or H_2, whereas the different local geometries of correlated C dangling bonds can only be passivated by monatomic H. Graphitic rings also have levels in the gap that can be passivated, but steric constraints make them unlikely. Thus, we conclude that excess C at the interface, which has been documented by various experiments [26–29], results in a bonded Si-C-O interlayer. One can think of this interlayer as amorphous SiC in which an O has been inserted in most Si-Si bonds. As is the case in amorphous diamond and in amorphous SiC [17], there is a mix of threefold and fourfold C. Isolated threefold C atoms are the C dangling bonds detected by EPR. The data and calculations suggest that correlated threefold C atoms are dominant in the interface layer that forms in MOS capacitors (the same may be true in oxidized porous SiC, but no electrical data are available; the EPR signal from a large porous structure is relatively weak, suggesting that isolated C dangling bonds are not dominant). The energy levels of correlated threefold C atoms in the Si-C-O interlayer span the midgap region and give rise to the observed D_{it}. This result is consistent with the fact that features in the measured D_{it} curve are broad and variable and contrasts with assignments made in Ref. [16], where the interface was assumed abrupt with specific distinct defects.

We now turn to N and show that it can also passivate the interlayer in an altogether different way. Calculations show that N can replace a threefold C (or Si) and remove the gap state due to C (or Si). Thus, N is an effective passivator of both C and Si "dangling bonds". However, a threefold N induces an energy level (due to its lone pair state) in the gap (~ 0.5 eV above the VBE) when it has Si-N or C-N backbonds. When N has O-N backbonds, on the other hand, it does not have any states in the gap (the results account for the fact that N is effective at passivating interface states near the top of the gap, and less effective in the lower part [5]). The net result is a bonded Si-C-N-O interlayer, which still has residual threefold C and Si, required by thermodynamics. Subsequent H treatment at lower temperatures leads to further passivation because it is a different process (attachment of H, which has no barrier, as opposed to replacement, which entails a barrier). The final result is a bonded Si-C-N-O-H interlayer, which, inevitably, has residual defects with levels spanning the gap.

In addition to excess C, defects due to Si-Si bonds also make the interface trap density larger than that at the Si-SiO$_2$ interface where suboxide bonds (Si-Si bonds on the oxide side of the interface) exist. The bonding-antibonding splitting of these defects is very large compared with the Si band gap if the Si-Si bond is of normal length. Only unusually long Si-Si bonds have small enough bonding-antibonding splittings to result in "tail states" at the band edges as in amorphous Si. In contrast, at the SiC-SiO$_2$ interface, all Si-Si bonds are defects. Calculations show that the Si-Si bonding level is near the top of the SiC valence bands and moves into the band gap for longer Si-Si bonds. The antibonding level remains in the conduction bands near the edge, but the uncertainty in the calculations is too large to tell for sure. We found that very long Si-Si bonds are effectively passivated by 2 H atoms. In addition, most Si-Si bonds can be passivated by N, which can be inserted in a Si-Si bond to form a Si-N-Si bridge, with a localized state at the VBE. This localized level contains only one electron, whereby every such defect would become negatively charged in n-type SiC. Such a process can be ruled out because no such charging is observed. Even for normal-length Si-Si bonds, on the other hand, an N atom can replace a Si atom resulting in a threefold N (no levels in the gap) and a dangling Si bond. Since the Si-Si bond length provides enough room, even 2 N atoms can replace both Si atoms and form two threefold N defects that have no states in the gap. Thus, N is more effective than H at passivating the Si-Si interface states near the band edges, in accord with the experimental data. Inevitably, however, thermodynamics dictates a residual density of unpassivated Si-Si defects that is higher than that at the Si-SiO$_2$ interface.

In summary, we have combined experiment and theory to arrive at atomic-sale understanding of SiC-SiO$_2$ interfaces and the effect of N and H in reducing the interface defect densities. The techniques employed here are suitable for further study of the role of other elements in reducing defect densities at SiC-SiO$_2$ interfaces and other stable semiconductor-insulator interfaces.

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