

## Si/SiO<sub>2</sub> and SiC/SiO<sub>2</sub> Interfaces for MOSFETs – Challenges and Advances

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**Abstract.** Silicon has been the semiconductor of choice for microelectronics largely because of the unique properties of its native oxide (SiO<sub>2</sub>) and the Si/SiO<sub>2</sub> interface. For high-temperature and/or high-power applications, however, one needs a semiconductor with a wider energy gap and higher thermal conductivity. Silicon carbide has the right properties and the same native oxide as Si. However, in the late 1990's it was found that the SiC/SiO<sub>2</sub> interface had high interface trap densities, resulting in poor electron mobilities. Annealing in hydrogen, which is key to the quality of Si/SiO<sub>2</sub> interfaces, proved ineffective. This paper presents a synthesis of theoretical and experimental work by the authors in the last six years and parallel work in the literature. High-quality SiC/SiO<sub>2</sub> interfaces were achieved by annealing in NO gas and monatomic H. The key elements that lead to high-quality Si/SiO<sub>2</sub> interfaces and low-quality SiC/SiO<sub>2</sub> interfaces are identified and the role of N and H treatments is described. More specifically, optimal Si and SiC surfaces for oxidation are identified and the atomic-scale processes of oxidation and resulting interface defects are described. In the case of SiC, we conclude that excess carbon at the SiC/SiO<sub>2</sub> interface leads to a bonded Si-C-O interlayer with a mix of fourfold- and threefold-coordinated C and Si atoms. The threefold coordinated atoms are responsible for the high interface trap density and can be eliminated either by H-passivation or replacement by N. Residual Si-Si bonds, which are partially passivated by H and N remain the main limitation. Perspectives for the future for both Si- and SiC-based MOSFETs are discussed.

### Introduction

Silicon has been the semiconductor of choice for microelectronics for decades. It has good semiconductor properties (Table 1). Though other semiconductors, especially III-V compounds have better bulk electron mobilities, Si has remained unchallenged largely for two reasons: ease of processing, including the fabrication of large wafers, currently 300 mm in diameter, and the fact that its native oxide, SiO<sub>2</sub>, is stable and has excellent interface properties. In contrast, III-V compounds do not have stable oxides that can be used as gate dielectrics for metal-oxide-semiconductor field-effect transistors (MOSFETs). Deposited dielectrics have not been particularly competitive either.

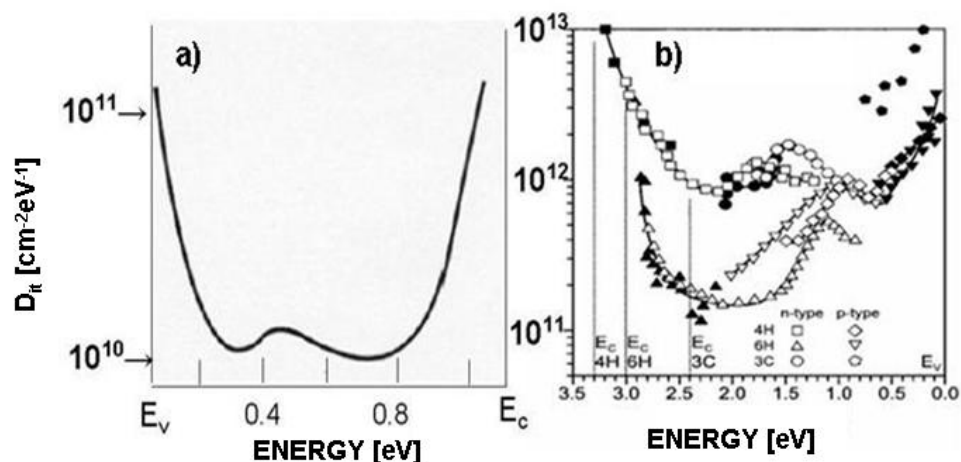


Fig. 1. a) Schematic of the interface trap density in Si/SiO<sub>2</sub> after annealing in hydrogen gas; b) Interface trap-density in SiC/SiO<sub>2</sub> as reported in 1997 by Afanasev et al. (Ref. 1) for several SiC polytypes. Open and filled symbols correspond to two different measurement techniques.

Table 1 Key semiconductor properties of Si and the 4H polytype of SiC.

Material	Energy gap [eV]	Electron mobility [cm <sup>2</sup> /Vs]	Thermal conductivity [W/mK]
Si	1.15	1350	150
4H-SiC	3.3	800	450

Silicon-based electronics are not very good for high-power and high-temperature applications, for which a larger energy gap and higher thermal conductivity are more desirable. Several wide-gap semiconductors have virtually all the necessary properties, but lack a suitable dielectric for the fabrication of MOSFETs. Silicon carbide is unique among wide-gap semiconductors. In addition to good semiconductor properties (Table 1), it has a stable native oxide, none other than SiO<sub>2</sub>, and can, therefore, be singled out as the most promising choice for MOSFETs. Early work in the 1990's, however, found that, despite good bulk electron mobilities, channel mobilities in SiC MOSFETs were unacceptably low. In contrast to Si, where bulk mobilities are only cut by a factor two in the channel adjacent to the Si/SiO<sub>2</sub> interface, channel electron mobilities in SiC were found to be more than two orders of magnitude smaller than their bulk values. The origin of the trouble was traced to very high interface trap densities ( $D_{it}$ ), as illustrated in Fig. 1. Whereas annealing in hydrogen gas has been very effective at reducing  $D_{it}$  to acceptable levels in the case of Si, efforts to do the same for SiC did not pay off [1]. A "re-oxidation" step (continued annealing in oxygen atmosphere at ~950°C after oxidation at ~1150 °C ) led to a reduction of  $D_{it}$  by a factor of 2-3 [2], but the major open question in the later 1990's was why the SiC/SiO<sub>2</sub> interface was so bad relative to the Si/SiO<sub>2</sub> interface and if anything could be done about it.

A great deal has happened in the last 6-7 years. The key experimental finding is that a significant reduction of  $D_{it}$  can be achieved by post-oxidation annealing in NO gas [3-10]. The effect of hydrogen annealing remained fairly controversial, with conflicting reports [1,11-13]. It has recently been demonstrated, however, that, when hydrogen annealing is done after the deposition of a Pt metal layer, which breaks H<sub>2</sub> molecules into monatomic H, the resulting reduction of  $D_{it}$  is substantial. Furthermore, a sequential combination of NO and hydrogen annealing results in further  $D_{it}$  reduction. These latest results are reported at this conference by Dhar et al. [14]. A summary of key results is given in Fig. 2. Theoretical work on the SiC/SiO<sub>2</sub> system has been carried by the principal author's group, only some of which has been published [5,15-19], and by Deák et al. [20-21].

This paper is not a comprehensive review of the literature or points of view. Instead, it represents a synthesis of available results on the two interfaces, Si/SiO<sub>2</sub> and SiC/SiO<sub>2</sub>, aiming to give a

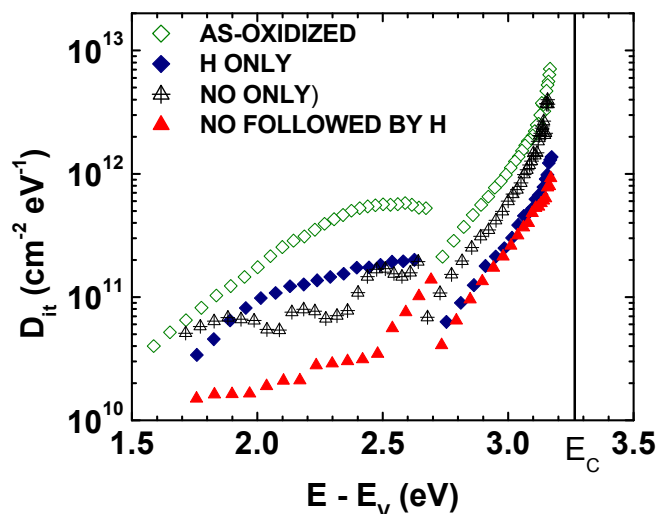


Fig. 2. Measured interface-trap density of states ( $D_{it}$ ) in as-oxidized Si-face (0001) 4H-SiC and the corresponding  $D_{it}$  after annealing in NO only, after annealing in  $H_2$  gas through a Pt metal layer, and after a combination of NO annealing followed by  $H_2$  annealing. For more details on the measurements see paper by Dhar et al. [14].

unified account of why the former has such good properties and the latter does not, and to account for the roles of nitridation and hydrogenation. The synthesis reflects decades of theoretical work on the Si/SiO<sub>2</sub> system by the principal author and extensive recent theoretical/experimental work by the principal author with several of the co-authors in the last seven years. It also reflects combined theoretical/experimental work in the last seven years on the SiC/SiO<sub>2</sub> system, especially the experimental work led by L.C. Feldman at Vanderbilt and J. R. Williams at Auburn that produced successful NO and H treatments [5-7,9,10,14]. The work for the synthesis also benefited from an extensive experimental literature on both interfaces and from extensive theoretical literature on the Si-SiO<sub>2</sub> system. The new synthesis also employed results from published theoretical work on the SiC-SiO<sub>2</sub> system by the principal author's group [5,15-19] and by Deák et al. [20-21]. The latter papers reported theoretical studies of possible C-related defects at the interface and in SiO<sub>2</sub>, investigated several distinct oxidation paths and deduced possible interface defects, relating them to observations.

### Theoretical Methods

This paper contains new theoretical results, especially for the SiC/SiO<sub>2</sub> system. The results were obtained using density-functional theory with the generalized-gradient approximation (GGA) for the exchange-correlation potential, the parameter-free state-of-the-art method for atomic-scale quantum mechanical calculations for materials as in Refs. [15,16]. Minimization of the total energy with respect to atomic coordinates yields local stable structures at the interface. In the GGA, individual energy levels are obtained with lower accuracy than total energies, but they are adequate for our purposes. For the present SiC calculations, we used ultrasoft pseudopotentials, a plane-wave basis set with energy cut-off of 396 eV and supercells containing slabs of six SiC layers (96 atoms), two SiO<sub>2</sub> layers (52 atoms) and 10 Å of vacuum. Surface Si and C atoms were terminated with H atoms. Atomic relaxations were performed using a conjugate-gradients algorithm. The four lowest SiC layers were kept fixed and the forces on all other atoms were reduced to less than 0.05 eV/Å. The theoretical results will not be presented separately, but will be folded into the synthesis of the properties of the two interfaces of interest.

### Microscopy and EELS

Figure 3a,b shows Z-contrast images of Si/SiO<sub>2</sub> and SiC/SiO<sub>2</sub> interfaces taken with a VG Microscopes HB501UX scanning transmission electron microscope (STEM) in S. J. Pennycook's group

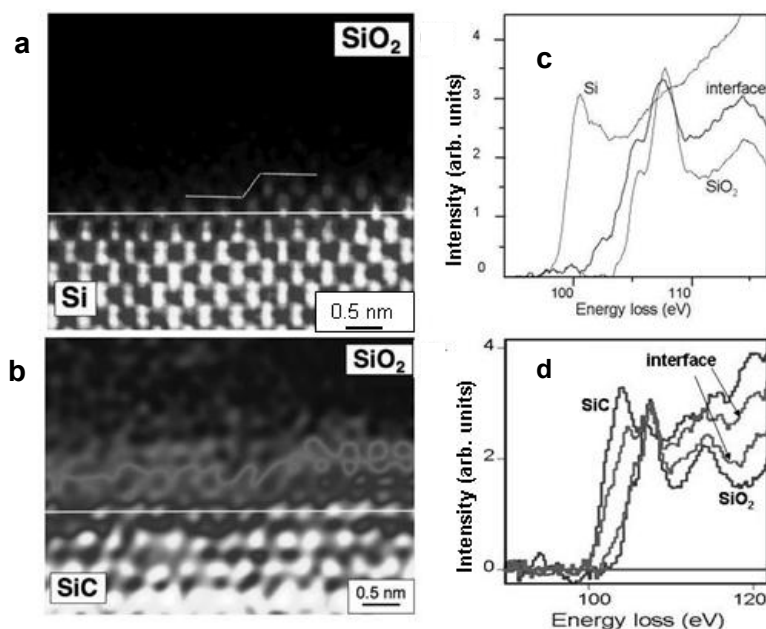


Fig. 3. Z-contrast images and EELS from a Si/SiO<sub>2</sub> interface (a,c) and a 4H-SiC/SiO<sub>2</sub> interface (b,d).

at Oak Ridge National Laboratory. The STEM is operated at 100 kV and is equipped with a field emission gun and a parallel electron-energy-loss-spectroscopy (EELS) system. In both Si/SiO<sub>2</sub> and SiC/SiO<sub>2</sub> interfaces, a step is visible. Such steps are responsible for the roughness that contributes to carrier scattering and mobility degradation in the channel relative to the bulk material. Away from the step, the Si/SiO<sub>2</sub> interface appears very abrupt. In contrast, in the SiC/SiO<sub>2</sub> image, we clearly discern an interlayer, 1-2 atomic layers thick, where the intensity undergoes a transition from values typical in the SiC side to values typical in the SiO<sub>2</sub> side.

The presence of the interlayer is confirmed by electron-energy-loss (EELS) spectra collected from the various regions. In Fig. 3c and 3d, we see the Si L<sub>23</sub> spectra (transitions from the spin-orbit-split Si 2p level to available empty states). In the Si/SiO<sub>2</sub> case (Fig. 3c), we clearly see the spectra from the Si side and the SiO<sub>2</sub> side. In the interface region, we get distinct spectra that correspond to different oxidation states of Si. In Fig. 3d, we again see distinct spectra from the SiC side and the SiO<sub>2</sub> side. In the interface region, however, we get a very wide variation of initial rises (two spectra are shown), indicating very diverse bonding environments for Si atoms.

### Choice of Surface for Optimally Abrupt Interfaces

In this Section we start our journey to understand the atomic-scale structure of Si/SiO<sub>2</sub> and SiC/SiO<sub>2</sub> interfaces, the nature of defects at the two interfaces, and the role of H and N in passivating them.

In Fig. 4a we show a schematic of an “ideal” (001) Si surface, i.e., all atoms occupy their normal bulk positions. The top layer of Si atoms has two back bonds and two “dangling bonds” sticking out in the vacuum making a figure V. Each of these dangling bonds can be bridged to a dangling bond on a neighboring atom. One can have a Si-O-Si bridge on one side and a Si-O-Si-O-Si on the other, as shown in the figure, or even a Si-O-Si-O-Si-O Si bridge. One can then continue growing an oxide. An example of such an abrupt interface is shown in the schematic diagram of Fig. 5. In contrast, if a similar construction is attempted on the (111) Si surface, the bond lengths and bond angles are not as good for an abrupt interface (Fig. 4b).

A large model of a (001) Si/SiO<sub>2</sub> interface was constructed by Pantelides and Long [22] in 1978 using plastic “atoms” and connectors and the resulting structure of the amorphous oxide was found to be comparable with the structure of bulk amorphous SiO<sub>2</sub>. Using a simple force model, Pantelides and Long found that the abrupt interface was energetically preferred. This result was confirmed more recently by first-principles calculations by the principal author’s group [17].

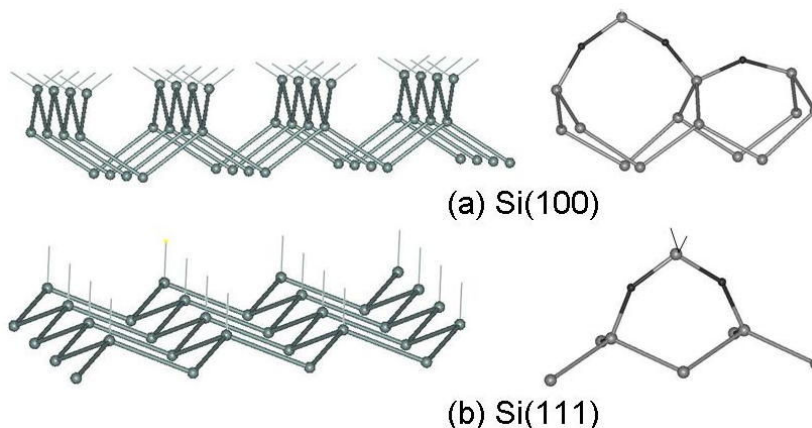


Fig. 4. a) Schematic diagram of a (001) Si surface and the pairs of O bridges that can be accommodated in adjacent dangling bonds. A Si-O-Si-O-Si-O-Si bridge in place of the Si-O-Si-O-Si bridge is also possible. b) Schematic of a (111) Si surface and an attempt to construct O bridges that would lead to an abrupt Si/SiO<sub>2</sub> interface. The bond lengths and bond angles are not quite right in this case. In the case of SiC surfaces, the reverse is true. The (111) cubic face or (0001) hexagonal face work best.

In the case of cubic SiC, the bond lengths and bond angles do not favor an abrupt interface on the (001) surface. One can only have Si-O-Si bridges, which would passivate a clean surface. In contrast, as first noted by Knaup et al. [21], the bond lengths and bond angles are just right for the (111) surface of cubic SiC or the (0001) surface of hexagonal SiC (they are essentially identical).

The above analysis is consistent with observations. In the case of Si, the best-quality Si-SiO<sub>2</sub> interfaces are fabricated on (001) surfaces. In the case of SiC, the best-quality interfaces are fabricated on hexagonal (0001) Si-face surfaces. We will see in the next section, however, that the oxidation process is distinctly different for Si and SiC.

### Atomic-scale Processes During Si Oxidation – Interface Traps

**The Oxidation Process.** Once the oxidation process is initiated, the interface advances as O<sub>2</sub> molecules arrive at the interface, break up, and O atoms are inserted into available Si-Si bonds. Every once in a while, however, a Si atom must be emitted because the density of Si atoms in the oxide is roughly half of the density of Si atoms in crystalline Si. The emitted interstitials have been detected indirectly by their effect on dopant diffusion [23].

In Fig. 6 we show a schematic of an abrupt Si/SiO<sub>2</sub> interface, except for a suboxide bond and an O protrusion. Calculations have shown that, if only a suboxide bond is present at an advancing interface during oxidation, the “next” O atom would insert in the suboxide bond instead of creating an O protrusion (the protrusion costs elastic energy, whereas relaxations in the oxide are easy). Similarly, if the advancing interface has a single O protrusion, the next O atom goes into a Si-Si bond adjacent to the interface (marked by the gray triangle in Fig. 6) instead of extending the existing protrusion into the Si side (e.g., site marked by the black arrow in Fig. 6). Overall, the energetics of oxidation favor an abrupt interface. The above analysis can be extended further to the occasional emission of a Si atom (Fig. 7). Successive insertions of O atoms change a 5-member ring to a 6-member ring while a Si atom is emitted. Thus, oxidation proceeds smoothly without disruptions of the bonding structure. The amorphous nature of the oxide, however, inevitably leads to an occasional bonding mismatch and a “dangling bond”, namely a threefold coordinated Si atom.

Though energetics favor an abrupt interface, the amorphous nature of the oxide and finite temperature-effects (entropy) lead to suboxide bonds and “oxygen protrusions” as the primary intrinsic deviations from an ideally abrupt interface. The result is a mix of Si<sup>+1</sup>, Si<sup>+2</sup> and Si<sup>+3</sup> oxidation states, seen in photoemission data [24]. For all practical purposes there are no other intrinsic defects at the Si/SiO<sub>2</sub> interface (singly-coordinated O, triply coordinated O, and 5-coordinated Si are in principle possible, but there is no firm evidence for them; for a discussion of overcoordinated Si and O at the

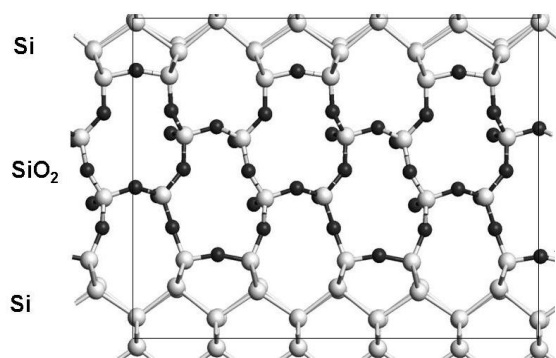


Fig. 5. Schematic of an abrupt (001) Si/SiO<sub>2</sub> interface. An ordered SiO<sub>2</sub> is shown, which allows the construction of superlattices that are useful for calculations.

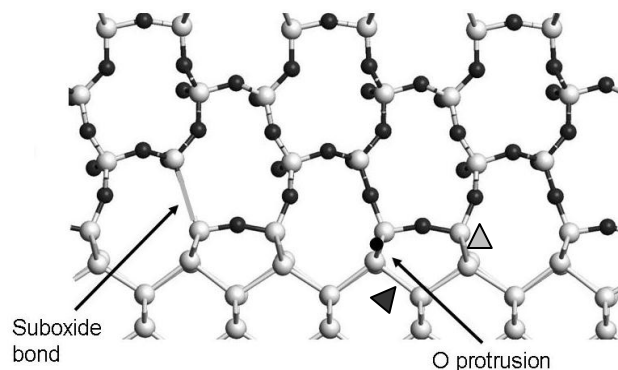


Fig. 6. Schematic of an abrupt Si/SiO<sub>2</sub> interface with one suboxide bond and one oxygen protrusion.

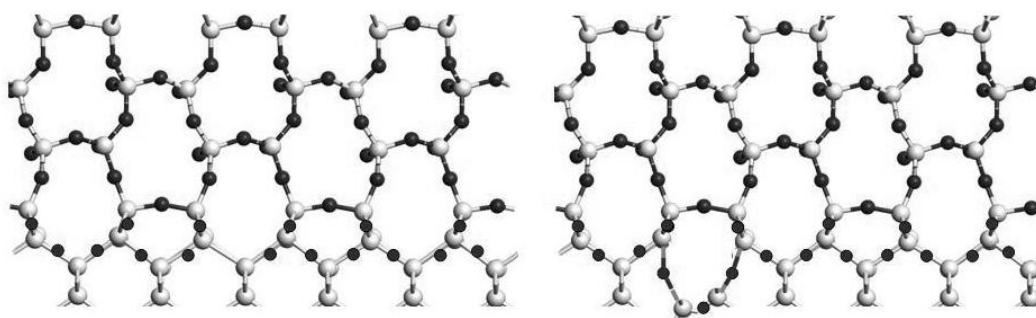


Fig. 7. Schematic of the atomic-scale process of emitting a Si atom during Si oxidation. Left: initial structure; right: structure after insertion of a new O atom and emission of a Si atom.

Si/SiO<sub>2</sub> interface see Ref. 25). Finally, the presence of the oxide, especially the presence of oxygen protrusions, causes strain in the last few atomic layers of crystalline Si [26].

**Interface traps.** The above analysis allows us to account for the observed interface traps (Fig. 1a). The hump in the middle is due to dangling bonds that can be eliminated by annealing in hydrogen gas. The U-shape density is due primarily to suboxide bonds. We note that, in the crystal, Si-Si pairs contribute bonding and antibonding states; the bonding states give rise to the valence bands and the antibonding states give rise to the conduction bands, as shown in Fig. 8 (see Ref. 27). Suboxide bonds, however, vary in length. Longer-than-normal Si-Si bonds result in smaller bonding-antibonding splittings and in localized states at the band edges. These states resemble the “band tail states” in hydrogenated amorphous Si [28], which also arise from longer-than-normal Si-Si bonds.

Suboxide bonds further from the nominal interface layer may be viewed as O vacancies (E<sup>+</sup> centers). They are known as border traps. They trap charge that can be cycled by changing the polarity of externally applied electric fields [29]. The ability of border traps to respond during an electrical measurement depends on the frequency of the measurement signal [30,31].

The high quality of the (001)Si/SiO<sub>2</sub> is due to passivation of dangling bonds by H. H also passivates longer-than-normal suboxide bonds: two H atoms are inserted, forming two electrically inactive Si-H bonds. Normal-length suboxide bonds, on the other hand, can trap a single H, which acts as fixed positive charge [32]. Another H atom can remove such a trapped H by forming H<sub>2</sub> [33]. Despite its beneficial effect, H is also a main agent for the degradation of MOSFETs under normal operating conditions, under irradiation (as in space electronics [34]), or even in storage for extended periods of time (aging of electronics) [35]. The problem is that H atoms can be released from various places in the entire MOSFET (oxide, Si, poly-Si). Holes, generated by irradiation or fields (e.g., in the inversion layer), enhance the release of H, which migrate to the interface and depassivate

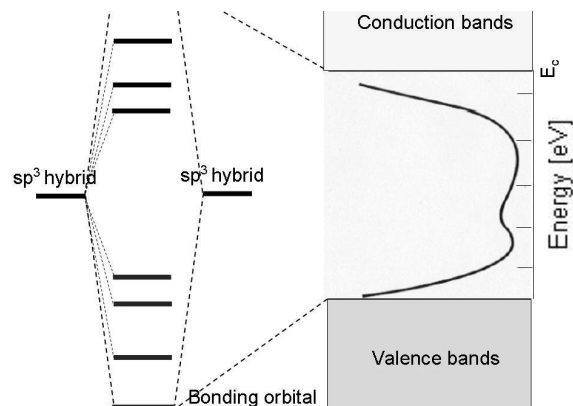


Fig. 8. Schematic of the formation of Si-Si bonding-antibonding states. The outermost bonding-antibonding states give rise to the valence-conduction bands, respectively. Longer-than-normal Si-Si bonds have smaller bonding-antibonding energy splittings (three examples are shown) and can give rise to localized states near the band edges (the same as the band-tail states in hydrogenated amorphous Si).

dangling bonds by forming  $H_2$  molecules [33]. Water molecules in the oxide also contribute to aging and degradation because they form complexes from which H can be released [36].

### Atomic-scale Process during SiC Oxidation

The oxidation of SiC is fundamentally different from the oxidation of Si because the process now entails emission of C atoms. In 1999, using calculations in bulk SiC, Di Ventura and Pantelides [15] identified the key oxidation step. A detailed study of the oxidation process was reported more recently by Deák et al. [20,21]. Combining these results with results of new calculations using supercells with the interface shown schematically in Fig. 9 (no distinction between polytypes can be made at this scale), details of which will be published elsewhere, we arrive at the following. Starting with the abrupt interface shown in Fig. 9(a), the next two O atoms that arrive (Fig. 9(b)) kick a C atom and form two Si-O-Si bridges (Fig. 9(c)). The process is enabled by the fact that the Si-Si distance in SiC is 3.1 Å, essentially the same as the preferred Si-Si distance in a Si-O-Si bridge. The ejection of the C atom can be facilitated by a third O, whereby a CO is emitted. The energy barriers for these processes have not been calculated, but they are likely to be large, acting as the rate-limiting step that is responsible for the high temperatures of SiC oxidation (over 1100°C as compared to 900°C for Si).

We will track the emitted C atom or CO molecule in the next Section. Here we note that the process of ejecting C atoms can continue. Once in a while, a Si atom must also be emitted because the Si density in SiC is also too large compared with that of SiO<sub>2</sub> (it is roughly the same as in Si because the lattice constant of SiC is so much smaller). This process is more complicated than in the case of Si, again because of the C atoms and because one cannot form a C-O-C chain. Overall, although there are several factors that favor an abrupt interface (e.g., it is energetically favorable to “oxidize” suboxide bonds first, emitted Si and C atoms do not enter the SiC side, and arriving O atoms do not enter the SiC side) there are two main factors that cause trouble: a) the disruption of the SiC ring structure by the emission of C and Si atoms and b) the emitted C atoms, some of which are likely to be stuck in the interface region. We conclude that the oxidation process of SiC leads to a more complex interface structure. Indeed, several authors have suggested the existence of some kind of interlayer at the SiC/SiO<sub>2</sub> interface [37,20] and the notion is corroborated by Fig. 3. In the next few sections we will arrive at a detailed description of the interlayer as a bonded Si-C-O network.

### Interface Carbon in SiC/SiO<sub>2</sub> Interfaces – A Bonded Si-C-O Interlayer

In this Section we examine what happens to C atoms that are emitted during oxidation as C atoms or as CO molecules. In 2000, we showed that CO can be trapped in the oxide in the form of O-



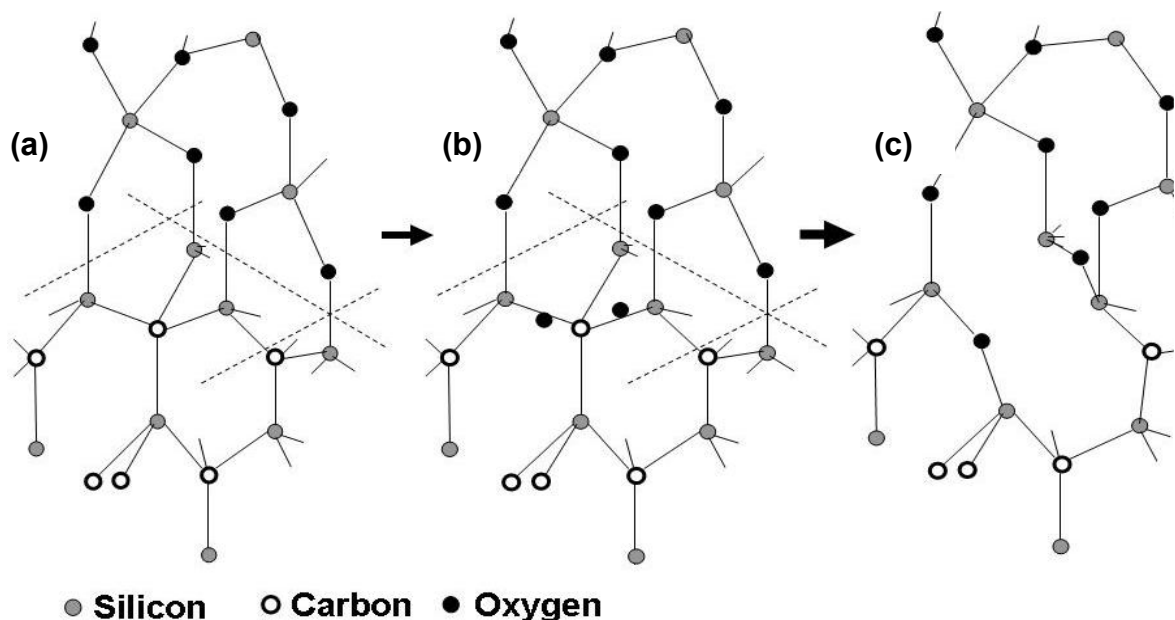


Fig. 9. The basic atomic-scale step for SiC oxidation: a) an initially abrupt interface region; b) two O atoms arrive at the interface as shown; c) a C atom is ejected and two Si-O-Si bridges are formed.

deficient C clusters, while some of it is oxidized into  $\text{CO}_2$ , which leaves the material, as observed. The re-oxidation step that was briefly mentioned in the introduction provides the necessary oxygen to dissolve the O-deficient clusters into  $\text{CO}_2$ , cleaning up the oxide. The re-oxidation step removes some of the C atoms stuck at the interface, but apparently not completely.

The early papers by Afanasev et al. [1] reported several experimental probes of C at the interface and suggested that the interface contains C clusters (e.g., graphitic rings) that are responsible for the mid-gap density of interface traps. More recently, profiles of the EELS C edge have revealed a very large C concentration at the SiC/SiO<sub>2</sub> interface (Fig. 10) [38]. Another observation supporting the existence of large amounts of C at the SiC/SiO<sub>2</sub> interface is that it takes roughly  $5 \times 10^{14} \text{ cm}^{-2}$  N atoms in the interface region to produce measurable passivation of C-related interface traps.

The large concentrations of C atoms observed at the interface and the Z-contrast images and EELS spectra of Fig. 3 strongly suggest that C atoms at the interface should not be viewed as isolated C clusters that act as interface traps. Instead, they should be viewed as part of a bonded Si-C-O interlayer (the notation Si-C-O is not meant to convey stoichiometric 1:1:1 ratios of Si, C, and O atoms). We will now make the same case on theoretical grounds. First we discuss results for single C atoms at the interface and then address the issue of C clusters *versus* a Si-C-O interlayer.

**Single C Atom at the SiC/SiO<sub>2</sub> Interface.** Consider a single C atom at the SiC/SiO<sub>2</sub> interface, say the C atom that is ejected when two O atoms form two Si-O-Si bridges during oxidation. Right at the interface, it can share a C site with another C atom (split interstitial configuration), as shown in Fig. 11a. This defect has two levels in the gap, and can, therefore, behave as both a hole and an electron trap. This configuration, however, is metastable. An alternative configuration on the oxide side of the interface (Fig. 11b) is lower in energy by 1.5 eV. This configuration has only an occupied level in the gap, as shown, and can act only as a hole trap. Something intriguing is, however, possible. There exists yet another configuration (Fig. 11c), which is 0.5 eV higher in energy than configuration b, but, in addition to the full level in the lower part of the band gap, it has an empty level in the upper part of the gap. When it traps an electron from the conduction-band edge, this configuration is 0.3 eV lower than the configuration of Fig. 11b. Clearly, we have a rich structure.

If we inquire about possible hydrogenation of the energetically-preferred neutral configuration of the single C atom described above (Fig. 11b), we find that it binds a single H atom (the Si-CO-Si



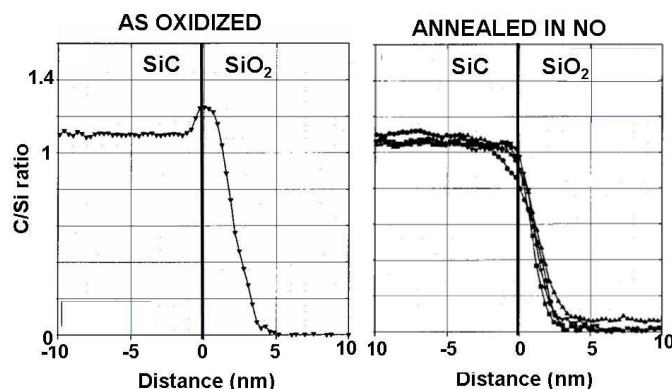


Fig. 10. Profile of the EELS C edge across the SiC/SiO<sub>2</sub> interface before and after nitridation (From Ref. 38).

chain in Fig. 11b becomes a Si-C-O-Si chain and H binds to the O atom in this chain). The new defect has a level in the middle of the gap with a single electron in it (amphoteric trap). Two H atoms, however, truly passivate the defect (both bind to the O atom of the Si-C-O-Si chain), leaving no levels in the gap. The net result is that isolated C atoms would be passivated by H<sub>2</sub> molecules, without the need to break them into monatomic H. Experiments tell us, however, that H<sub>2</sub> molecules are not effective at passivating anything at the as-oxidized SiC/SiO<sub>2</sub> interface. We conclude that C atoms are not incorporated in the interface as single interstitials.

We pursued a similar analysis of a single CO molecule at an otherwise abrupt interface. In that case, the resulting configuration has no levels in the gap. It can bind a single H and acquire an amphoteric level in the gap or two H atoms and have no levels in the gap. Thus, extra CO molecules at an otherwise abrupt interface are either not present or play no significant role.

**Carbon Clusters versus a Si-C-O Interlayer.** An extra C atom in the interface can, in principle, be a “substitutional impurity”, i.e., occupy a nominally Si site. Such a C atom at the nominal interface would be four-fold coordinated: it would have up to three C neighbors and at least one O neighbor, comprising a carbon cluster. However, in such a defect, the C-C bonds would be too long and the configuration is unstable. In contrast, placing two C atoms to share a nominal Si site yields a stable structure. The two central atoms C are threefold coordinated (Fig. 12a) and each produces a level in the gap. We note that the two C atoms do not form a “double bond” known to occur in molecules, e.g. ethylene because their three neighbors define orthogonal or nearly orthogonal planes. Instead, we have a pair of relatively independent “C dangling bonds” as if we had two isolated threefold-coordinated C atoms. Indeed, if we passivate them with H atoms, we find that two C-H bonds point in opposite directions (Fig. 12b), showing clearly that an H<sub>2</sub> molecule would not passivate the defect.

The above result is actually a general trend. We studied several configurations of a threefold-coordinated carbon with different backbones: various combinations of Si, C or O atoms. The threefold-coordinated carbon has a level in the gap that varies in position with the nature of the defect, which also determines the geometry of the defect. The level contains a single electron (amphoteric) and can be passivated by a single H. We also studied a variety of defects involving two C atoms and found that, in general, pairs of threefold-coordinated C atoms behave as if they were isolated threefold-coordinated carbons. In contrast, fourfold-coordinated C atoms do not have states in the gap. Finally, threefold-coordinated Si atoms (dangling bonds) can have Si, C, or O neighbors, yielding defects with varying positions in the gap. They can also be passivated by monatomic H.

We also studied graphitic rings. They give levels in the gap that can be passivated by H, but topologically it would be very difficult to form such rings.

The overall conclusion for the most likely scenario is that large amounts of excess C at the interface form a bonded Si-C-O interlayer, as described earlier, in accord with the experimental data

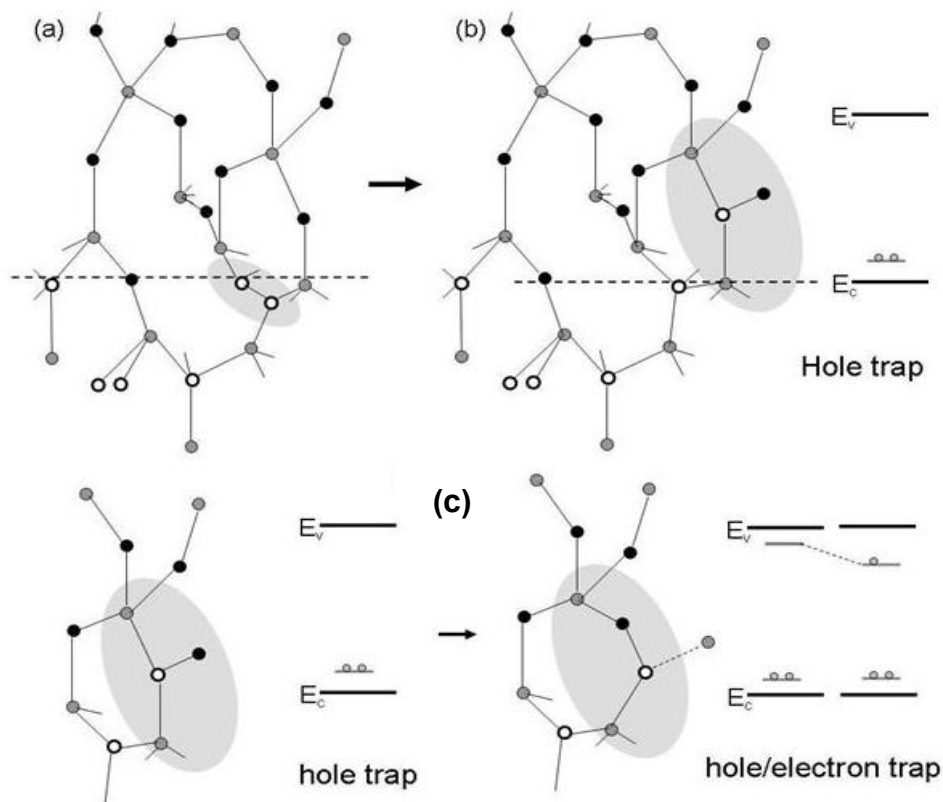


Fig. 11. Schematic configurations of single C atom at an otherwise abrupt SiC/SiO<sub>2</sub> interface (open circles are C atoms, black dots are O atoms and gray dots are Si atoms). Upper part: a) configuration in which the extra C atom shares a site with an interface C atom b) lowest-energy configuration of the extra C atom on the oxide side of the interface. Lower part: c) transformation of configuration b to a slightly-higher-energy configuration, which can capture an electron (as shown in the level schematic) and become energetically favored. In (c), note that the C atom is now weakly bonded to a Si atom from an adjoining ring.

of Fig. 3. As in amorphous diamond, in this bonded network, C has both fourfold and threefold configurations. The latter, which may be called C dangling bonds, have localized levels that span most of the energy gap of SiC and give rise to the observed density of interface traps. Threefold-coordinated Si (Si dangling bonds) are also present, but they have a variety of backbonds and a spread of energy levels. *This spread of energy levels and orientations of both Si and C dangling bonds is the most likely reason that electron-paramagnetic-resonance (EPR) signals are difficult to detect* (they are broadened by disorder as in the case of dangling bonds in amorphous Si, where the signal is much broader than that at the Si/SiO<sub>2</sub> interface [28]). At the SiC/SiO<sub>2</sub> interface, in addition to a spread of orientations, we also have a spread of energy levels because of different backbonds and geometries that affect the localization of the wave function. Nevertheless, detection of C dangling bonds by EPR has been reported [39,40]. There also exists a report of an EPR signal that has been interpreted as a Si vacancy on the SiC side of the interface [41].

### Passivation of the Si-C-O Interlayer by H and by N

We already discussed how H passivates threefold-coordinated C and Si atoms (dangling bonds) in the bonded Si-C-O interlayer. H<sub>2</sub> molecules must first be broken and then monatomic H does the passivation. The result is fully consistent with the experimental data that show H passivation only when molecular hydrogen is passed through a metal such as Pt, where it breaks up (Fig. 2).

Passivation by nitrogen is an altogether different process. Calculations show that N can replace threefold-coordinated C and remove the gap states. Nitrogen can also replace a threefold-coordinated Si and again remove the gap state. Thus, N is an effective passivator of both C and Si dangling bonds in the bonded network. The EELS profiles of Fig. 10 indeed show that nitridation

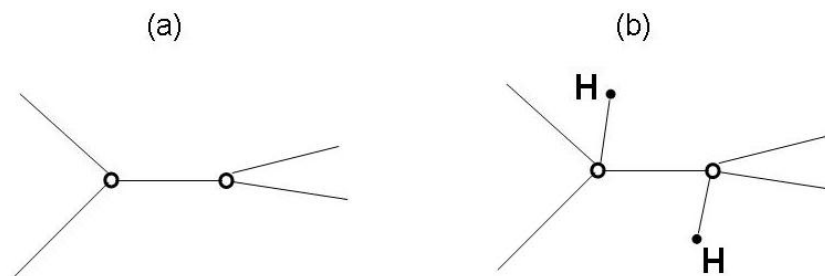


Fig. 12. a) Schematic of two C atoms at the SiC/SiO<sub>2</sub> interface. The nearest neighbors could be any combination of Si, C, and O atoms. b) The same defect passivated by two H atoms.

leads to a reduction of C at the interface, corroborating the theoretical result. The net result is a bonded Si-C-N-O interlayer.

Thermodynamics and entropy of course always conspire to thwart complete passivation. The NO treatment clearly leads to partial passivation by C or Si replacement. The Si-C-N-O interlayer still has residual threefold-coordinated C and Si. 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 of course a bonded Si-C-N-O-H interlayer, which, inevitably, has residual defects with levels in the midgap region.

### Si-Si Bonds at the SiC/SiO<sub>2</sub> Interface

So far we discussed only the consequences of excess C at the interface. In this Section we make the case that, even if all C were to be successfully removed from the SiC/SiO<sub>2</sub> interface, the interface trap density would still be significantly worse than that at the Si/SiO<sub>2</sub> interface. The problem is Si-Si bonds. In the case of the Si/SiO<sub>2</sub> interface, we only have suboxide bonds, i.e., Si-Si bonds on the oxide side of the interface. The bonding-antibonding splitting of these defects is very large compared with the Si band gap if the Si-Si bond is normal length. Only unusually long Si-Si bonds have small enough bonding-antibonding splittings to result in “tail states” at the Si band edges as in amorphous Si. These very long bonds are effectively passivated by two H atoms.

In contrast, at the SiC/SiO<sub>2</sub> interface, all Si-Si bonds are defects. Even those with normal bond length (2.35 Å) have bonding-antibonding splittings that are comparable to the SiC energy gap! Calculations show that the Si-Si bonding level is near the top of the 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. The problem is that normal-length or slightly-long Si-Si bonds are not passivated by hydrogen! Only the very long ones are. This theoretical result is in agreement with the experimental data of Fig. 2.

Nitrogen passivation of Si-Si bonds is an intriguing process. We found that a single N atom can be inserted in a Si-Si bond to form a Si-N-Si bridge, with a localized state at the valence band edge. This localized level contains only one electron, whereby every such defect would become negatively charged in n-type SiC. If indeed a large density of Si-Si bonds exists prior to N passivation, the data rule out such a process because a large density of negatively-charged defects is not observed. Indeed, something else goes on. Even for normal-length Si-Si bonds, a N atom can replace a Si atom resulting in a threefold-coordinated N (no levels in the gap) and a dangling Si bond. Even more likely, two N atoms can replace both Si atoms and form two threefold-coordinated N defects that have no states in the gap. This process is analogous to something that has already been observed: two As atoms in a Si grain boundary, where all Si atoms are fourfold-coordinated, go substitutional at specific neighboring sites where the back bonds allow enough relaxation for both As atoms to become truly threefold-coordinated. Thus, an As dimer forms via As-As *repulsion*, which lowers the energy by achieving threefold coordination. The same effect is even more likely for N, for which even the normal Si-Si bond length provides enough room to achieve threefold coordination for two N atoms. Again these results, namely that N is more effective than H at passivating the

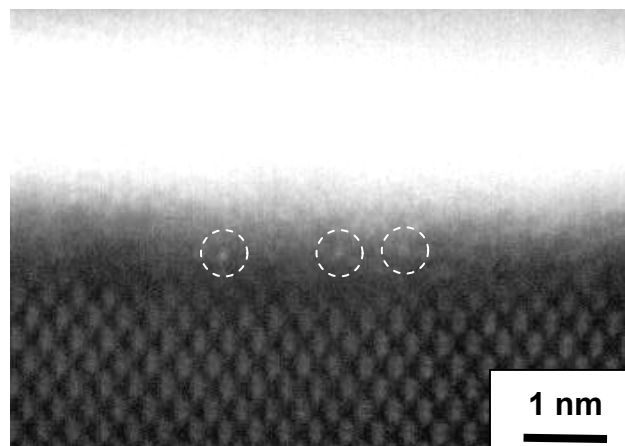


Fig. 13. Z-contrast image of a Si/SiO<sub>2</sub>/HfO<sub>2</sub> structure. Individual Hf atoms in the SiO<sub>2</sub> interlayer are circled. From Ref. 45.

Si-Si interface states near the band edges, is in accord with the experimental data of Fig. 2. Inevitably, however, thermodynamics dictates a residual density of unpassivated Si-Si defects that is higher than that at the Si-SiO<sub>2</sub> interface.

Finally, we note that Si-Si bonds that are somewhat farther from the nominal interface may behave more like O vacancies and contribute to so-called slow interface traps. Traps in the near-interface region of the oxide (outside the bonded interlayer) are discussed in Ref. 21.

### The Future

Looking into the future for Si MOSFETs, we note that the future is here. After several decades of reducing the dimensions of MOSFETs without changes in materials, changes are finally happening. Strained Si has already been introduced for the channel region because of higher mobilities [42]. SiO<sub>2</sub> is scheduled to be replaced by “alternate dielectrics”. In Fig. 13 we show a Z-contrast image of one candidate, a Si/SiO<sub>2</sub>/HfO<sub>2</sub> gate stack. The picture shows stray Hf atoms in the SiO<sub>2</sub> interlayer, which cause mobility degradation. Theory and modeling are also breaking new ground. We recently developed a first-principles atomic-scale approach to calculating mobilities [43] and accounted for the enhanced mobility of strained Si and the degradation of mobilities by stray Hf atoms [44]. The prospects for successfully modeling Si devices in the realm of new materials are very good.

The future of SiC is also bright. It is intriguing to note that with C being the key element for living matter and Si being the key element for electronics, SiC may prove to be the most effective material for high-power, high-temperature electronics. It certainly looks that way. In the last five years, with nitridation and hydrogenation, electron mobilities have gone from single digits to ~55 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for the (0001) Si-face of 4H-SiC [14]. A surprising result is that mobilities of order 100 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> have been achieved for the a-face of 4H-SiC, even though the interface trap density is higher than that on the Si-face [14]. Recent reports of mobilities exceeding 100 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> when oxidation is catalyzed by metals such as Al [46] offer even more promise. The origin of the mobility enhancement in these structures remains elusive.

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