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Defects in SiO₂ as the possible origin of near interface traps in the SiC/SiO₂ system: A systematic theoretical study

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A systematic study of the level positions of intrinsic and carbon defects in SiO₂ is presented, based on density functional calculations with a hybrid functional in an α -quartz supercell. The results are analyzed from the point of view of the near interface traps (NIT), observed in both SiC/SiO₂ and Si/SiO₂ systems, and assumed to have their origins in the oxide. It is shown that the vacancies and the oxygen interstitial can be excluded as the origin of such NIT, while the silicon interstitial and carbon dimers give rise to gap levels in the energy range inferred from experiments. The properties of these defects are discussed in light of the knowledge about the SiC/SiO₂ interface.

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I. INTRODUCTION

SiC, a wide band gap semiconductor with SiO₂ as its thermal oxide, is a natural candidate for the material of power metal-oxide-semiconductor (MOS) devices. Still, its use has been so far hindered by a high density of interface traps, D_{it} (see, e.g., Refs. 1–3, and references therein). A particular feature of this $D_{it}(E)$ is, that it rises toward the conduction band (CB) of SiC, reaching ever higher values near the band edge, as the band gap increases from one polytype to another.^{1,4} In 4H-SiC (which has a band gap of $E_g=3.3$ eV, the highest among the technologically important polytypes), the D_{it} exceeds 10^{13} cm⁻² eV⁻¹ in the vicinity of the CB. Using special techniques, peaks of slow acceptor states could be revealed in this distribution, which appear to be fixed with respect to the CB of SiO₂, independent of the polytype and orientation of the SiC substrate, and—to a certain extent—even of the oxidation conditions.^{5–8} These states are assumed to have their origin in the oxide and are usually called near interface traps (NIT).^{2,3}

Photon stimulated tunneling (PST) measurements on SiC-based MOS structures resulted in a mean barrier energy of 2.8 eV, indicating that the electron energy levels of the negatively charged NIT are at $E_C(\text{SiO}_2)-2.8$ eV, where $E_C(\text{SiO}_2)$ is the position of the CB edge in silica.^{5,6} Similar experiments on Si-based MOS structures⁵ showed that such NIT can also be found there at the same energy position (in fact, above the CB edge of Si) and with a density comparable to the one found in the case of SiC. This seems to give further support to the idea that these traps are defects of the oxide. Based on cases where similar traps have been observed in the oxide, it was suggested that they are connected to oxygen deficiency (or Si excess) in SiO₂.

NIT peaks have also been found in TDRC (thermal dielectric relaxation current) measurements on oxidized SiC.^{8,9} In the case of 4H-SiC, a sharp peak at $E_C(4\text{H-SiC})-0.11$ eV, and, with different charging characteristics, also a broad hump between -0.1 and -0.7 eV were found. Considering the conduction band offset between SiO₂ and 4H-SiC [2.7 eV (Refs. 10 and 11)], the sharp peak coincides with the barrier observed in PST. It should be noted, though, that PST measures the energy position of the negatively charged acceptor level with respect to the CB edge, while TDRC measures the thermal activation energy of the negative to neutral charge transition. The results of the two measurements can only be interpreted in terms of the same defect as origin, if the atomic relaxation of that defect upon change in charge state is small. Since it has been observed¹² that injected electrons, trapped in the oxide (on silicon), could be optically released by a photon energy of ~ 3.0 eV, but the thermal reactivation energy was only 1.7 eV, the lattice relaxation of acceptor traps in the oxide is not always small. Considering also the second set of states observed by TDRC,^{5,7} it is likely that several acceptor defects of the oxide may contribute to the NIT—at least in the case of the SiC/SiO₂ system, where trapping of injected electrons in the oxide leads to the generation of new interface states, the density of which has shown correlation with the presence of carbon.^{2,13}

Nevertheless, the NIT peak itself, as observed by PST, could not be correlated with the carbon contamination of the interface prior to oxidation,^{2,5} and a recently published microanalysis⁸ specifically ruled out graphitic particles or larger carbon clusters at the interface as the origin of the NIT observed by TDRC. Individual carbon atoms or pairs can, of course, not be excluded,⁸ but theoretical studies have

shown¹⁴ that such defects in connection with the SiC phase at the interface may explain deep traps in the gap, but cannot give rise to acceptor states near the CB edge of 4H-SiC either. It seems fair to conclude that some of the NIT are connected to intrinsic defects of SiO₂, while others may be specific to SiO₂ on SiC, but those, too, are formed in the oxide phase. As outlined above, the situation is quite complicated in MOS structures, and only data regarding the electronic structure is available. In bulk silica many optical absorption centers are known, but apparently there is no evidence to link them to these acceptor states. (Additional information could be obtained if such an optical absorption was correlated with other spectroscopic observables, like paramagnetic resonance.) Therefore, a systematic theoretical study of defects of SiO₂, with acceptor levels in the upper part of its band gap, could be helpful. In a previous study¹⁴ we have calculated defects at the interface in search for the origin of fast interface states. Here we present calculations on defects in the bulk oxide to shed light on the origin of slow NITs. Both intrinsic defects (relevant also for the Si/SiO₂ system) and carbon defects (specific to (SiC/SiO₂)) will be considered.

Intrinsic defects of silica have received ample attention from theorists in the past decades, and reviewing them is beyond the scope of this paper. Most of the studies concentrated either on the optical absorption centers of silica, which are mostly connected with oxygen vacancies without hydrogen (see, most recently, e.g., Refs. 15–17 and references therein), or on oxygen diffusion, i.e., various forms of interstitial oxygen (see, most recently, e.g., Ref. 18 and references therein). Both molecular^{19,20} and atomic²⁰ oxygen interstitials were found to exhibit acceptor behavior. The former is a fast diffuser, but the latter could be relevant for NIT. However, the calculated (0/2–) charge transition level of this negative-U, bistable system was predicted to be below mid-gap in SiO₂. The oxygen vacancy is usually considered as a bistable deep donor in SiO₂,^{15,21} though it has recently been shown that, in amorphous material, the majority of oxygen vacancies are relatively shallow hole traps, and are not bistable.^{17,22} Still it has been suggested²³ that the bistable oxygen vacancy can act as an acceptor as well, and explain the NIT. Interstitial silicon is usually dismissed because of its large formation energy,²⁴ even though its presence has been postulated in the near interface region during oxidation of silicon,^{25,26} and is expected in the case of SiC as well.¹⁴ To our knowledge, no electronic structure has yet been reported. An important intrinsic absorption center of amorphous silica is the nonbridging oxygen hole center (NBOHC),²⁷ however, recent calculations on the position of its levels relative to the band edges predict them in the lower half of the band gap.²⁸ It is also important to note that, according to recent calculations,²⁹ the electronic levels of oxygen-deficiency defects in amorphous SiO₂ have an energy distribution of ~2 eV in width, due to the variation of the environment.

In contrast to the intrinsic defects, very few theoretical papers were published on carbon in silica. An investigation of interstitial carbon and CO molecules has shown³⁰ that both are mobile (with activation energies below 2.7 and 0.4 eV, respectively). It was also shown³¹ that on occasional encounter of CO molecules, oxygen deficient carbon clusters

(up to four atoms) can be formed. To our knowledge, no atomistic calculation of carbon related levels in the band gap of bulk silica has yet been reported.

It should also be noted that a rather common feature of the theoretical work described above is the use of density functional theory (DFT) with one of the “standard” implementations: LDA or GGA (local density or generalized gradient approximation, respectively). These functionals are burdened by the well-known underestimation of the band gap,³² and the resulting uncertainty in the positions of defect levels. Therefore, we present here a systematic study of the electronic structure of both intrinsic and carbon related defects in SiO₂, based on a hybrid functional which gives a proper gap. We have calculated the electronic structure of all four basic intrinsic and of many carbon-related point defects in α quartz, for both the neutral and the negative charge state. (Some preliminary results on the optical excitation energies in the neutral charge state have been published³³ in the *Proceedings of the European Conference on SiC and Related Materials, Bologna, Italy, 2004.*) In Sec. II, the method will be described, while Sec. III summarizes the results, which are discussed in Sec. IV from the viewpoint of the NIT in SiC based MOS structures.

II. METHODS

Since the costs of a comprehensive study of all possible defect types and configurations in amorphous silica would be prohibitive, we have considered defects in α quartz. Since the observed electronic properties of SiO₂ (e.g., density of states in the valence band, band gap) are well known to be mainly determined by the short-range order, this is an acceptable first approximation, used quite generally. It should be noted though, that the crystalline structure imposes stronger restraints on the relaxation of atoms, influencing the electronic energy levels of a defect type. (Obviously, there are also more defect configurations in the amorphous system). We are modeling defects of α quartz with a $3 \times 3 \times 3$ supercell (243 atoms). Since the cell size is big and the dispersion of the SiO₂ bands is small, we use the Γ -point approximation.

In order to elucidate the correct level position of defects in the band gap, the latter should be reproduced adequately. It was shown recently that the application of hybrid functionals within DFT allows a consistently good description of the band gap of many solids, while at the same time reproducing the ground state properties.^{34–37} It has also been shown that defect levels can be reproduced by such methods on par with GW calculations.³⁸ For the present study we have selected the one-parameter hybrid suggested by Becke³⁹ with a mixing factor of 0.28. Using norm-conserving Barthelat-Durand pseudopotentials⁴⁰ and a 21G* valence basis optimized to them⁴¹ (as incorporated into the CRYSTAL program package⁴²), this method gives a SiO₂ band gap of 9.2 eV, in reasonable agreement with experiment (9.0 eV for amorphous silica⁴³ and 9.6 eV for α quartz⁴⁴).

Because of the use of Hartree-Fock type exact exchange, calculations with a hybrid functional scale by the fourth power of the number of basis functions. Therefore, in order

to economize on resources, the geometry of the investigated systems was relaxed by using a standard LDA functional.^{45,46} For that purpose, the SIESTA code⁴⁷ was applied with Troullier-Martins pseudopotentials⁴⁸ (core radii: $r_C=1.14$, $r_O=1.25$, and $r_{Si}=1.89$ bohr) and a numerical atomic orbital basis of double- ζ quality (21G*). (Note that these calculations were performed using a matrix diagonalization solver for the Kohn-Sham equations, i.e., not the order-N option of the SIESTA code.) Conjugate gradient (CG) relaxation was performed until the forces fell below 0.016 eV/Å. A completely unrestricted relaxation of the perfect lattice gives a 1.5% underestimation of the lattice constants as is usual for LDA. Since interstitial defects may have a large number of metastable configurations even in crystalline SiO₂, a preliminary screening among the possibilities was performed by the density-functional based tight binding (DFTB) method.⁴⁹ (Slater-Koster files tested previously in Ref. 30 were applied.) The configurations of lowest energy were then relaxed with *ab initio* DFT in the SIESTA code. The maximum forces calculated by the hybrid functional are about twice as large as obtained by the LDA calculations. Our experience in SiC has shown that this does not produce a considerable change in the geometry anymore.

For comparison with the available experimental data, the following information is required from the calculations. Thermally stimulated current methods like TDRC sweep the Fermi level across the gap and detect the discharge of traps through the change in the current of the carriers. The relevant theoretical quantity is the charge transition level (also called occupation level), which is the Fermi level position with respect to the VB edge, where the equilibrium charge state of a defect changes. Considering our system to be composed of the explicitly treated part of the crystal (containing the defect) and of a reservoir of carriers with an average energy E_F (representing the rest of the doped solid), the charge transition occurs where

$$E(q_2) + (q_2 - q_1)E_F^{q_2/q_1} = E(q_1).$$

Here $E(q)$ is the total energy in the equilibrium configuration of the charge state q . Therefore, geometry optimization was carried out for the neutral and typically the (2−) charge state of the defects.⁵⁸ The resulting geometry was then fixed and a hybrid functional calculation was executed to obtain the electronic structure. The LDA total energies were corrected for the error in occupied defect level positions with respect to the hybrid functional result. In principle, the total energy of the charged state should have been corrected for the artificial interaction between charges in the repeated supercells. Since it has been shown that the only available scheme for such a correction, strictly valid for periodically repeated point charges, gives a gross overestimation and sometimes even the wrong sign for delocalized charges, we did not apply any correction at all, anticipating errors in the (0/2−) charge transition levels smaller than 0.5 eV, cf. Ref. 50. As it turns out, even such an inaccuracy allows an unambiguous disqualification of many defects as the origin of the NIT. In PST the acceptor traps are populated by photoexcitation, and the barrier is measured for their tunneling out of the acceptor state through the oxide. The relevant theoretical quantity is

TABLE I. Electronic structure of basic deep acceptor defects in α quartz. All data relate to the valence band edge of SiO₂ in electron volts. The position of the highest occupied level in the (2−) charge state is to be compared to the value deduced from the PST experiment (the barrier height of 2.8 eV subtracted from ~ 9 eV, the band gap of silica). The (0/2−) charge transition level should be compared to the values deduced from the TDRC experiments by using the band off-sets.

Defect	Highest occupied defect level in the (2−) charge state	(0/2−) transition level
O _i	2.50	2.91
V _O	4.30	6.35
Si _i	4.83	5.67
C _i	4.74	5.36
C _i =C _i	2.91	3.47
C _O =C _O	6.08	6.20
TDRC		5.5-6.2
Broad hump		
TDRC		~ 6.2
Sharp peak		
PST	~ 6.2	

the position of the one-electron energy of the filled acceptor level with respect to the CB edge. This has been obtained from the hybrid functional calculation at the equilibrium geometry of the (2−) charge state. The one electron energy level of the filled acceptor states and the (0/2−) charge transition level calculated from total energy differences between the equilibrium configuration of the two charge states will be given in Table I with respect to the VB edge. Finally it has to be determined whether or not a defect in the oxide, near to the interface, can exchange charge with the SiC. Since the band offsets between SiO₂ and SiC are known, the relevant quantities are the internal ionization energies of the defect in SiO₂, i.e., the energy required to promote a hole from the VB edge to an occupied defect level (positive ionization of the defect) or an electron from the conduction band to an unoccupied defect level (negative ionization). The best candidates for the NIT all have a doubly occupied and an empty state in the lower and upper half of the SiO₂ band gap, respectively. An estimate of the internal ionization energies can be obtained from the level positions (with respect to the band edges), calculated with one electron promoted from the occupied state to the unoccupied one at the equilibrium geometry of the neutral defect.⁵¹ These will be given in Fig. 4.

III. RESULTS

Although the NIT were associated with oxygen deficiency,⁵ we start our study with the oxygen interstitial O_i, partly for the sake of completeness, but also since it was predicted to be an acceptor²⁰ and can be used as a test case. In agreement with earlier work, we obtain the peroxy-linkage (Si-O-O-Si) as the most stable configuration in the neutral

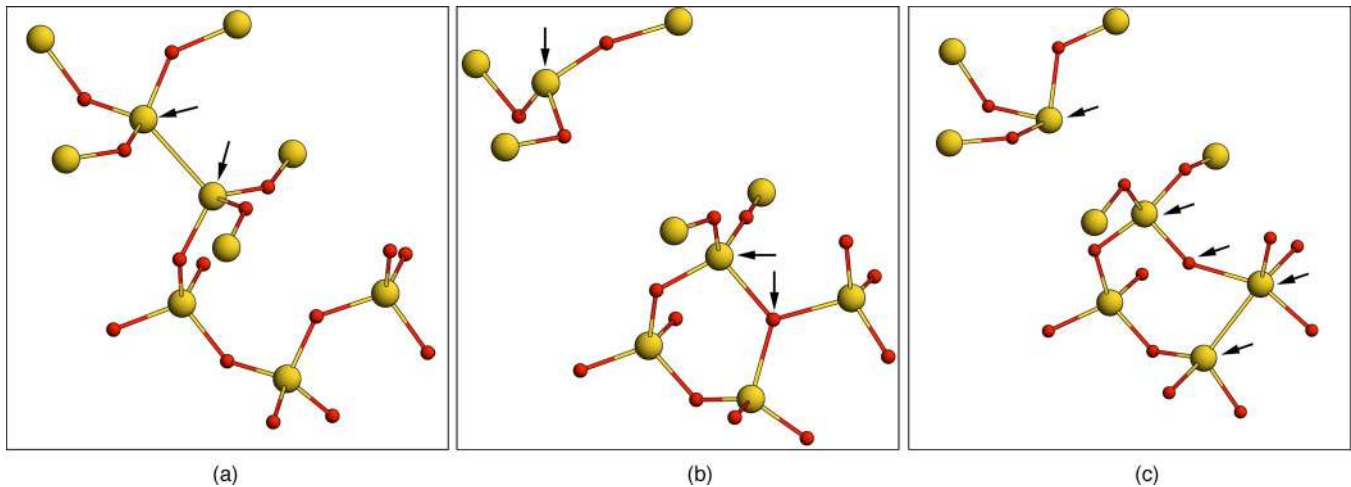


FIG. 1. (Color online) Oxygen vacancy in the neutral (a), the (2+) (b), and in the (2-) charge states (c). Silicon larger yellow and oxygen smaller red spheres. The figures have been extracted from the network cutting Si-O bonds. Atoms, which have changed their bonding configuration with respect to the perfect α -quartz lattice, have been marked with black arrows. All other atoms have “normal” coordination, even if not all ligands are shown.

charge state. The LDA calculation gives an occupied gap level at $E_V(\text{SiO}_2)+0.93$ eV and an unoccupied one at $E_V(\text{SiO}_2)+5.50$ eV, in good agreement with the results of Ref. 20: 0.95 and 5.44 eV, respectively. Upon occupation of the empty state by two electrons, we also observe the spontaneous change of the configuration into a “double bridge,” where both oxygen atoms form a Si-O-Si linkage between the same two silicon atoms. The uncorrected (0/2-) charge transition level is calculated to be at $E_V(\text{SiO}_2)+2.27$ eV, while the correction shifts that to $E_V(\text{SiO}_2)+2.91$ eV. As can be seen, even with the correction included, the charge transition level is far deeper than the range of the NIT (considering the 3 eV offset between the VB of 4H-SiC and SiO_2 , it actually falls below the VB edge of SiC).

We have also checked out the silicon vacancy (V_{Si}), and found that in the neutral charge state the oxygen neighbors rebond pairwise into two peroxy linkages, very similar to the case of O_i . The peroxy bridge in the negative charge states is unstable, so charging causes one of the oxygen neighbors to go to an interstitial position, leaving a NBOHC behind. This rearrangement allows the accommodation of up to three excess electrons: one for the NBOHC and two for the double-bridge oxygen interstitial. Since the corresponding charge transition levels are in the lower half of the SiO_2 band gap, we can discount both oxygen excess defects, O_i and V_{Si} , as the source of the NIT.

Next, we investigate the simple oxygen deficiency defects. For the oxygen vacancy V_O , we obtain the well-known bistability between the Si-Si bond [Fig. 1(a)], in the neutral charge state, and the Si···Si-O backbond [Fig. 1(b)], in the positive ones.²¹ As in Ref. 23, we find negative-U behavior with an uncorrected (2+/0) charge transition level at $E_V(\text{SiO}_2)+2.02$ eV (compared to 2.2 eV in Ref. 23). The correction moves this to $E_V(\text{SiO}_2)+2.32$ eV. Based on results obtained in a 72-atom unit cell, Oshiyama has suggested,²³ that the Si···Si-O back-bonded configuration remains metastable in the neutral charge state, and survives negative charging with two more electrons. In our 243-atom

calculation, the (2-) charge state [started from the Si···Si-O backbond configuration of Fig. 1(b)] undergoes strong reconstruction, as shown in Fig. 1(c). The excess electrons are accommodated by the dangling bond of the other Si neighbor of the vacancy (which is the highest occupied orbital), and by a newly formed strong Si-Si bond (2.34 Å), which makes one of the background Si atoms fivefold coordinated. (The Si-O distances around this Si increase by ~ 0.6 Å.) Oshiyama reported the double negative state of the Si···Si-O configuration to be 2 eV lower in energy, than the Si-Si configuration [Fig. 1(a)] with two additional electrons on the CB edge. In our case, LDA gives an advantage of 2.7 eV for the configuration in Fig. 1(c), which increases to 5.1 eV after correction. So, it seems that V_O has a stable (2-) charge state, indeed. Still, after removal of the two extra electrons, the configuration shown in Fig. 1(c) relaxes spontaneously back to the neutral ground state of Fig. 1(a), through the configuration shown in Fig. 1(b). That means that our CG relaxation does not find the Si···Si-O configuration metastable in the neutral charge state, i.e., we have not found the barrier of 0.1 eV reported in Ref. 23. (It should be noted though, that this might be the consequence of using a localized basis set, instead of plane waves.) The corrected (0/2-) charge transition level, is at $E_V(\text{SiO}_2)+6.35$ eV, while the highest occupied level in the (2-) configuration, corresponding to the Si dangling bond, is at $E_V(\text{SiO}_2)+4.30$ eV (see also Table I).

Silicon interstitials (Si_i) have a high equilibrium formation energy in SiO_2 (Ref. 52), but during oxidation of Si or SiC they are necessarily created.^{14,25,26} They also have a high energy in SiC, therefore, unlike in the Si/ SiO_2 system,²⁴ in the case of SiC/ SiO_2 they are more stable in the oxide (by more than 5 eV in the neutral charge state⁵⁹). Si_i has several metastable states in the α -quartz structure. The most stable one in the neutral charge state is shown in Fig. 2(a). The structure is somewhat similar to that of the carboxyl defect,³⁰ [see also Fig. 2(b)], in the sense that the interstitial silicon atom pushes an oxygen out of its place, making a Si-Si-Si bridge (instead of a Si-O-Si bridge), with a nonbonding oxy-

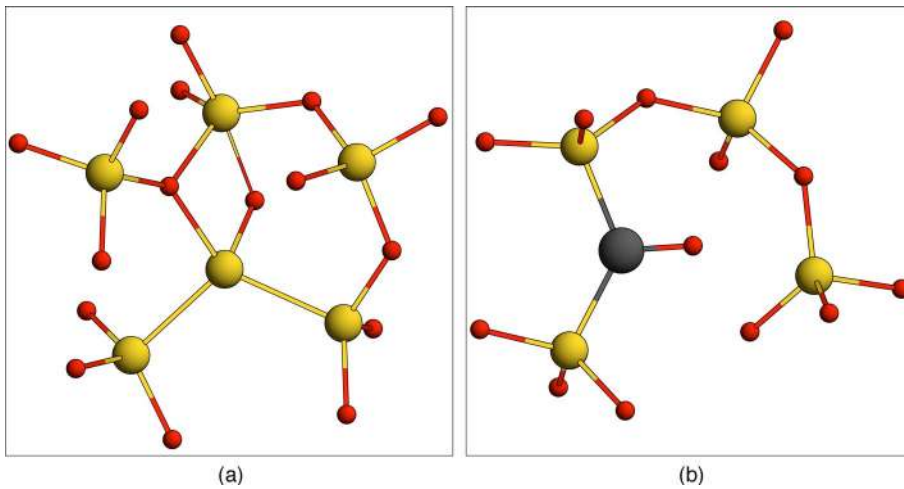


FIG. 2. (Color online) The geometry of cationic interstitials in SiO₂: (a) silicon, Si_i, and (b) carbon, C_i. Silicon: larger yellow; oxygen: smaller red; and carbon large black spheres. The figures have been extracted from the network cutting the Si-O bonds of the oxygen atoms on the perimeter of the displayed structure.

gen (NBO, similar to the NBOHC) attached to the middle. The difference to carbon is that the larger silicon interstitial atom, with preference for fourfold coordination, also binds to another nearby oxygen atom of the network, making that threefold coordinated. The trivalent oxygen is a donor, supplying an electron to the acceptor NBO. Therefore, the latter is negatively charged and has a strong electrostatic interaction also with the silicon neighbor of the former, as indicated by the thin line in Fig. 2(a). The system has a doubly occupied gap level due to the charged NBO, and an empty one corresponding to an antibonding state between the Si_i and the trivalent oxygen. Giving one or two negative charges to the system, this antibonding state becomes occupied and breaks up the third bond of the oxygen. As a result, the latter relaxes away (rotating outward, around the axis of its two original Si neighbors), and the Si_i remains threefold coordinated with the NBO still attached. Besides the NBO, the dangling bond of the now threefold coordinated Si_i also becomes doubly occupied. Despite the qualitative difference between the configurations in the neutral and the negative charge states, the defect cannot be considered truly bistable because, upon removal of the excess electrons, it relaxes spontaneously back into the neutral configuration shown in Fig. 2(a). The corrected (0/2-) charge transition level, is at $E_V(\text{SiO}_2) + 5.67$ eV, while the highest occupied level in the (2-) configuration is at $E_V(\text{SiO}_2) + 4.83$ eV (see also Table I). Accordingly, Si_i is an acceptor with levels somewhat above midgap. We note that a recent study⁵² using plane-wave LDA on a 72-atom α -quartz supercell has resulted in a structure for Si_i where the interstitial appears to be twofold coordinated in both the neutral and the negative charge state. Our geometry optimization starting from a similar Si-Si_i-O-Si bridge resulted in the structure described above. The difference in the two calculations is probably mainly in the relaxational freedom. A more recent calculation by the same group⁵³ in a 108-atom model of amorphous SiO₂ has found that Si_i structures similar to ours are more stable than the twofold coordinated ones by ~ 1 eV.

Turning to carbon related defects, our *ab initio* LDA calculations confirm the carboxyl defect³⁰ as the most stable configuration of the neutral carbon interstitial C_i [Fig. 2(b)]. The dangling *p* orbital of the threefold coordinated C_i, as

well as the oxygen atom attached to it, make this defect a double acceptor (see Table I). Charging this complex negatively causes a strong electrostatic attraction between the NBO and the nearest Si atom [lower right in Fig. 2(b)], causing considerable but not qualitative change in the atomic positions. After removal of the extra electrons, the system relaxes back to its original geometry. Still, both C_i undergoes pronounced relaxation upon charging, as reflected by the difference between the electronic and the charge transition levels $E_V(\text{SiO}_2) + 4.74$ eV and $+5.36$ eV, respectively.

The encounter of two C_i may lead to a strong double bond between them, as shown in Fig. 3(a). (The double bond between the C atoms offsets the energy advantage of the carboxyl configuration over a peroxylike configuration for C_i.) It was shown that the dry oxidation process of SiC emits not only CO molecules into the oxide but produces C-C pairs at the interface.¹⁴ While complex formation between C_i atoms (or interstitial CO molecules, as described in Ref. 31) should be a relatively rare event, the strongly bonded C-C pairs of the interface can “grow into” the oxide, as the oxidation proceeds. One possible form is such an interstitial pair C_i=C_i. In the neutral charge state the occupied *pp* π and the unoccupied *pp* π^* states of the C=C double bond appear in the band gap of SiO₂. The former is in the gap, while the latter is above the CB of 4H-SiC (see also Fig. 4). Such a defect can trap holes but not electrons from SiC. However, hot electrons injected into the oxide can be captured by the high lying *pp* π^* state. After adding two more electrons to the system, one of the oxygen neighbors of the C=C dimer carries most of the charge and is pushed out into an interstitial position (halfway between Si atoms which are not linked by an oxygen), while a direct C-Si bond is established. This change is reversible after removing the electrons, giving the charge transition level in Table I. The low value is explained by the fact that the highest occupied orbital in the (2-) charge state is on the interstitial oxygen. Moving the interstitial oxygen a bit away from its (metastable) position, it forms a double-bridge configuration out of a nearby Si-O-Si bridge, with an energy gain of 0.99 eV. We have not calculated the barrier, but can safely assume that it is low (the oxygen interacts only electrostatically with its neighborhood in the metastable state). In this sense, the C_i=C_i defect is not

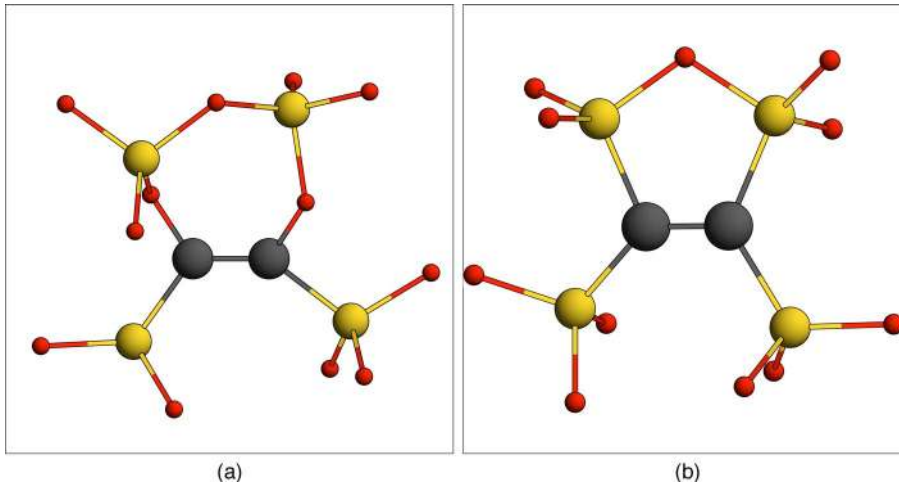
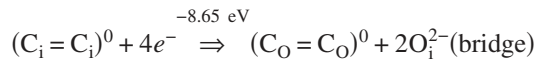
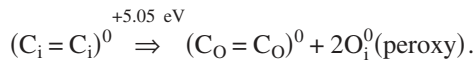


FIG. 3. (Color online) The geometry of carbon pairs in SiO_2 : (a) carbon di-interstitial $\text{C}_i=\text{C}_i$ in the neutral charge state, and (b) pair of carbon atoms substituting for oxygen $\text{C}_O=\text{C}_O$. Silicon: larger yellow; oxygen: smaller red; and carbon: large black spheres. The figures have been extracted from the network cutting the Si-O bonds of the oxygen atoms on the perimeter of the displayed structure.

stable against charging: upon capture of electrons it will transform into a $(\text{C}_O=\text{C}_i)^0$ defect, while O_i^{2-} may diffuse away. Charging the $\text{C}_O=\text{C}_i$ defect, we observe the same emission of a charged oxygen interstitial, resulting in the stable $\text{C}_O=\text{C}_O$ defect [see Fig. 3(b)]. In end effect, the transformation process



releases 8.65 eV. In contrast, $\text{C}_i=\text{C}_i$ in the neutral charge state is 5.05 eV more stable than $\text{C}_O=\text{C}_O$ plus two neutral interstitial oxygen atoms



Single carbon substitutionals are energetically very unfavorable at both sites.³⁰ In case of substitution at a silicon site, this is due to the fact that the “natural” length of the C-O bond is shorter than that of Si-O. In principle, a carbon pair, produced at the interface, could also be incorporated at a Si site in the oxide. We find, however, that such a defect is 4.6 eV less stable, than a $\text{C}_i=\text{C}_i$ pair and a silicon self-interstitial, Si_i . [The double bond between the carbon pair is not maintained in a $(\text{C}-\text{C})_{\text{Si}}$ defect.] Since Si_i defects should be abundant in the near-interface region during oxidation,^{14,25,26} such $(\text{C}-\text{C})_{\text{Si}}$ defects are unlikely to survive in the oxide.

The $\text{C}_O=\text{C}_O$ defect [Fig. 3(b)] has a double bond, with the other four bonds of the two sp^2 -hybridized carbon atoms being nearly (but not entirely) coplanar. It remains stable—with only little relaxation—even if the antibonding $pp\pi^*$ state becomes doubly charged. This is reflected in the small difference between the electronic and charge transition level positions in Table I. The energy position of the strongly localized antibonding $pp\pi^*$ state of $\text{C}_O=\text{C}_O$ (at 6.28 eV) is much lower than that of $\text{C}=\text{C}$ dimer at the interface,¹⁴ or that of the $\text{C}_i=\text{C}_i$ pair in the oxide (7.46 eV, c.f. Fig. 4). The reason is that all four Si ligands of $\text{C}_O=\text{C}_O$ have a net positive charge, while the other two dimers have two negatively charged neighbors (carbon or oxygen, respectively).

IV. DISCUSSION

With the knowledge about the structure, stability and electronic structure of possible intrinsic and carbon related defects in silica, we can discuss them in the context of the experimental observations on NIT. Table I shows those electronic structure characteristics of the investigated defects, by which they could be identified with the NIT. The level position in the $(2-)$ charge state can be related to PST, the $(0/2-)$ charge transition levels to TDRC results, as shown in the last rows of Table I. The position of the highest occupied and lowest unoccupied levels in the neutral charge state indicate the possibilities for carrier trapping from the semiconductor or the insulator, as shown in Fig. 4.

The NIT peak positions observed by PST and TDRC (sharp peak) correspond to an electronic level in the $(2-)$ charge state, and to a $(0/2-)$ charge transition level, respectively, at around $E_V(\text{SiO}_2) + 6.2$ eV. Regarding the uncertainties in the calculation (usage of an α -quartz model, various error sources in the calculation), we may consider a some-

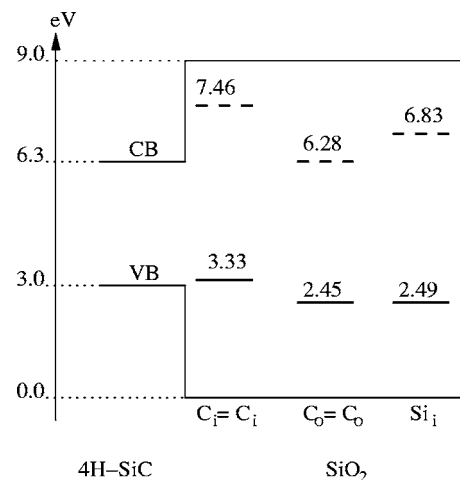


FIG. 4. Schematic representation of the band lineup between 4H-SiC and SiO_2 . The positions of highest occupied (thick solid line) and the lowest unoccupied (thick dotted line) defect levels in the neutral state are also shown, as calculated by the half-electron method.

what wider range (about ± 0.5 eV) around this value. The broad hump observed by TDRC requires (0/2⁻) charge transition levels between $E_V(\text{SiO}_2) + 5.5$ and 6.2 eV. Still, as already mentioned, the intrinsic defects, amounting to a relative oxygen-excess O_i and V_{Si} , can safely be ruled out based on their level positions alone.

The oxygen deficiency defects need closer examination. Our calculations confirm the suggestion of Oshiyama,²³ that a stable V_{O}^{2-} defect complex is possible—arising from the back-bonded (Si $\cdot\cdot$ Si-O) configuration, which is stable in the (2⁺) charge state—although we did not find the latter to be metastable in the neutral charge state. Even if we accept the existence of a barrier of ~ 0.1 eV, between the back-bonded (Si $\cdot\cdot$ Si-O) and the Si-Si bonded dimer configurations in the neutral charge state, as reported in Ref. 23, the equilibrium population of the former will be very low since the reported energy difference was 3 eV. It should also be added that recent calculations in amorphous SiO₂ (Refs. 17 and 22) find the back-bonded configuration to be rare even in the positive charge state. Therefore, it is unlikely that V_{O} contributes significantly to the NIT. The calculated low electronic level position in the (2⁻) charge state rules it out as the origin of the PST signal, anyhow. The (0/2⁻) charge transition level is close to the sharp peak observed by TDRC, but a much wider energy distribution is expected for intrinsic oxygen-deficiency defects in the thermal oxide.²⁹ Therefore, we feel, that the contribution of oxygen vacancies in silica to the NIT could only be marginal, at best. We also note, that if the NIT originated from oxygen vacancies or strained Si-Si bonds, the reoxidation treatment would be much more effective.

The silicon interstitial is strongly bonded to its environment: Besides the two Si-Si bonds, also due to the charge transfer between the two oxygen atoms attached to it. Therefore it may very well survive during oxidation and subsequent annealing, since the reaction barrier to remove it could be quite high. The bonding situation—described in the previous section—gives rise to an empty state (antibonding between the trivalent oxygen and Si_i) in the appropriate range. However, capture of electrons on this state leads to breaking the bond between the trivalent oxygen and the Si_i, and the highest occupied state will just be a dangling bond on Si_i with a level around midgap. (Since this state exists only in a doubly occupied state, it is not observable by paramagnetic resonance techniques). Therefore, Si_i can also be excluded as the origin of the PST signal. Nevertheless, Si_i should be abundant in the near interface region of the oxide, since the required change in specific volume during oxidation makes their emission necessary and they are more stable in SiO₂ than in SiC. (Regarding the stabilization mechanism described above, simple reoxidation at low temperature is not likely to remove them easily either.) The calculated charge transition level at $E_V(\text{SiO}_2) + 5.67$ eV makes Si_i a good candidate for the origin of the broad hump observed by TDRC, especially, since the electronic structure can be expected to be sensitive to the local environment in amorphous material, giving rise to a broad distribution. The acceptor level of the neutral Si_i in α quartz is calculated to be 0.5 eV above the CB edge of 4H-SiC (see Fig. 4), but considering the expected spread of level positions in the amorphous material,

this would still allow electron capture from the CB of 4H-SiC.

All in all, the calculated level positions of the intrinsic point defects in the negative charge state are all too low to explain the tunneling barrier observed in PST. The same is true for the single carbon interstitial. Even though the calculated charge transition level is close to the lower end of the broad hump in TDRC, C_i is relatively mobile in SiO₂ at the temperature of oxidation,³⁰ and should be removable in reoxidation. In addition, carbon is emitted during oxidation in the form of mobile CO molecules from the interface into the oxide, rather than C_i , or is built in as C-C pairs at the interface.¹⁴ Therefore, the carbon dimers should be inspected, instead, as possible sources of NIT. The environment of the investigated substitutional and interstitial dimers are representative of the possible ligand fields of a carbon dimer in the amorphous material. Based on our results, they can very well explain the observed generation of new interface states upon electron injection, in correlation with the carbon content of the interface,¹³ and give a model for the NIT as well.

The carbon dimers, with one or more oxygen neighbors in SiO₂, have donor levels somewhat above the VB edge, and they are all electron traps, with acceptor levels well above the CB edge of 4H-SiC (as shown for $C_i=C_i$ in Fig. 4). These defects can capture holes from the VB of SiC, but electrons only from the CB of SiO₂. Upon capture of injected electrons, they undergo partial decomposition, and eventually a C=C dimer with no oxygen neighbor, i.e., $C_{\text{O}}=C_{\text{O}}$ becomes the stable final product, with no donor level in the gap of 4H-SiC. The captured negative charge is stored in the emitted oxygen interstitials (which have a (0/2⁻) charge transition level below the VB of SiC). Remarkably, the $C_{\text{O}}=C_{\text{O}}$ defect has its charge transition level close to its electronic level position in the (2⁻) charge state (due to the relatively small atomic relaxation upon charging), and both levels are very near to the NIT peak in PST and to the sharp peak in TDRC. Due to the very localized nature of the acceptor state, and the very rigid C=C and Si-C bonds, the levels of this defect should not be affected by the local variation of the amorphous SiO₂ network, so a narrow energy distribution is expected. Therefore, the $C_{\text{O}}=C_{\text{O}}$ defect could explain both the TDRC and the PST observations, providing a common origin for the dominant part of the NIT. In addition, the electron injection induced removal of the deep carbon related donors is in line with the results of the internal photoemission (IPE) experiments in Ref. 13. The observed decrease of carbon related deep states and the simultaneous increase of the density of states near the CB edge⁵⁴ might also be connected to the transformation of variously coordinated carbon pairs, into the more stable $C_{\text{O}}=C_{\text{O}}$ defects at the temperature of the “reoxidation” annealing.

Although the presence of $C_{\text{O}}=C_{\text{O}}$ in SiO₂ on SiC appears to be logical, and is supported by theoretical modeling, the assignment of the main component of the NIT to them is problematic. PST measurements did not show correlation between varying surface carbon contamination (prior to oxidation) and the NIT (which have also been observed in the Si/SiO₂ system).⁵ It has to be pointed out, however, that *in situ* x-ray photoemission spectroscopy (XPS) studies on SiC

have found that the initial surface carbon is largely removed,⁵⁵ while our C=C dimers are produced¹⁴ by the oxidation. High resolution analytics on reoxidized SiC/SiO₂ samples excluded interface carbon enrichment as the origin of NIT observed by TDRC, but of course, it was “impossible to rule out that the near-interface traps are due to one or two carbon atoms or carbon interstitials.” In fact, the presence of carbon near the detection limit throughout the oxide can be inferred from both EELS (electron energy loss spectroscopy) and EFTEM (energy filtered transmission electron microscopy) measurements.⁸ The postulated transformation of carbon dimer related donors into acceptor-type NIT could be checked by correlated IPE and PST measurements after electron injection.

In case of the thermal oxidation of SiC, carbon is introduced into the oxide by the oxidation itself, while deposited SiO₂ layers typically have some carbon contamination, too. Even the thermal oxides on silicon have carbon impurities in them, but only around the SIMS (secondary ion mass spectrometry) detection limit, allowing for a carbon content of $<10^{12}$ cm⁻² at the interface.⁵⁶ So, even if the C_O=C_O defects might be a good candidate for the NIT in the SiC/SiO₂ system, such a model is harder to defend for an equally high density of NIT in the Si/SiO₂ system. We can only say that our present results seem to exclude any simple intrinsic defect of the oxide, as the origin of the NIT at around $E_C(\text{SiO}_2)$ -2.8 eV. Unless one intrinsic defect can be found, which is at the same time insensitive to local variations of the amorphous network, and shows very small relaxation upon charging, the TDRC and PST observations cannot be explained with a common intrinsic origin.

V. SUMMARY

In search of near interface traps (NIT) of the SiC/SiO₂ system, i.e., acceptor states near the conduction band of the

oxide, we have investigated the electronic structure of basic intrinsic and carbon related defects in silica, both in the neutral and in the (2-) charge state. The results make it definite that, among the simple intrinsic point defects, only silicon self-interstitials may act as NIT, and the calculated properties make them a good candidate for the broad hump of states observed by TDRC. The only defect which could explain the observed barrier in PST experiments is a pair of carbon atoms substituting for oxygen at nearby sites, and doubly bonded to each other. This defect can give rise to the sharp peak in TDRC, which nearly coincides with the PST barrier. The C_O=C_O defects in the oxide arise from the transformation of carbon pairs formed at the interface during oxidation. Upon trapping of injected electrons, C=C pairs built into the oxide in another form than C_O=C_O (with varying number of oxygen ligands) are transformed into neutral C_O=C_O and charged, deep, interstitial oxygen acceptors. At the same time the donor activity of the C=C pair disappears. This explains the observed generation of interface charge and the decrease of carbon related occupied states upon injection. Although the experimental confirmation of carbon pairs, diluted in the oxide, as origin of the NIT may be difficult, their presence in the near-interface region of the SiC/SiO₂ system is rather logical. Although such defects may occur in the Si/SiO₂ system as well (due to the interface enrichment of the background carbon contamination), a similar density as in SiC, cannot be expected.

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- ⁵⁷The two sets of states in TDRC were interpreted (Ref. 9) as the fingerprints of the same defect right at the interface (sharp peak), and in a continuous distribution from the interface toward the bulk (broad hump). This explanation is difficult to maintain if we have to assume that the immediate neighborhood of this defect is bulk oxidelike. On the other hand, it should be noted, that the energy levels of various intrinsic point defects in the oxide are sensitive to the local environment in the amorphous silica network, showing energy distributions with widths depending on the defect type. This points toward a different origin of the broad and sharp TDRC peaks.
- ⁵⁸Note that (0/−) and (−/2−) transition levels have not been calculated for economic reasons, and no claim is being made about the negative/positive-U behavior of these defects. The (0/2−) transition level is by any means midway between the single charge transition levels, and gives an indication of the characteristic energy range in the band gap within the desired accuracy.
- ⁵⁹The energy of the Si interstitial has been calculated in a 96 atom 4H-SiC supercell using the same technique as described in Sec. II. The total energies for the bulk SiC and SiO₂ were compared with the interstitial in either the SiC or the SiO₂.