Intrinsic and H-induced defects at Si-SiO$_2$ interfaces

D. J. Chadi

NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540

Defect reactions pertaining to Si-SiO$_2$ interfaces are investigated using a first-principles total-energy approach. Interesting results on the atomic structures of interstitial H$^+$ and OH$^-$, H$_2$O, and H$_3$O$^+$ in SiO$_2$ are presented. Three center O–H$^+$–O hydrogen bonding is found to play a significant role in the stabilization of all these molecules. The relative stabilities of H$^+$ and H$^-$ in Si and SiO$_2$, H-induced diffusion of oxygen from SiO$_2$ into Si, oxygen vacancy-interstitial pair formation under electron injection conditions, and Si vacancy and interstitial defects in SiO$_2$ are examined.

I. INTRODUCTION

The reliability of metal-oxide-semiconductor devices as linear dimensions and gate oxide thicknesses approach a few nanometer length scales is a major issue in current silicon technology. Increased gate oxide leakage currents, charging of the oxide layer, and a reduced threshold for dielectric breakdown are among the main problems that need to be addressed. Defects and impurities play an important role in these processes.

Hydrogen is known to play a significant role in defect creation and annihilation at Si-SiO$_2$ interfaces. Beneficial effects of H in passivating Si-dangling bond defects at the interface have been recognized for many years.[1] There is also substantial experimental evidence[1–3] supported by theoretical studies[4–6] that H can create defects at the interface.

In this paper we examine intrinsic and impurity-induced defect reactions pertaining to the Si-SiO$_2$ interface. The most stable states of defects are determined from first-principles total-energy-minimization calculations, and defect reaction energies for various combinations and placements of defects on either side of the interface are calculated.

A major problem in theoretical studies of defects at Si-SiO$_2$ interfaces has been the modeling of the interface between a crystalline and an amorphous material.[7] Despite the lack of periodicity, the interface is nearly ideal in that the vast majority of Si and oxygen atoms retain their preferred fourfold and twofold coordinated configurations. The flexibility for achieving this ideal interface is provided by the Si-O-Si bond angle which can range over a large range of values around the value of 144° in α-quartz.

In this study we avoid the problem of the exact nature of the interface bonding by considering the two sides of the interface as bulk atomic reservoirs that can exchange atoms and impurities between each other. In this way, the change in energy arising, for example, from the transfer of an interstitial H atom from Si to SiO$_2$ or an interstitial oxygen atom from SiO$_2$ to Si can be easily calculated. The defects that can be examined in this way are a subset of the defects that could occur in amorphous silica. Despite this limitation, a great variety of defects and defect reactions can be examined and important information on the properties of Si-SiO$_2$ interfaces can be extracted using this approach.

In our calculations we model SiO$_2$ with α-quartz using a tetragonal unit cell with 72 atoms per cell and Si with 32 and 64 atom cubic cells. A plane-wave cutoff of 25 Ry for the kinetic energy is used in all the calculations but Fourier components up to 100 Ry were included for the calculation of electronic charge densities and potentials. The Kleinman-Bylander-type[8] of separable potentials and Troullier-Martins pseudopotentials[9] were employed in the self-consistent total-energy calculations. All structures were optimized by minimizing the magnitude of Hellmann-Feynman forces acting on the atoms. Several distinct types of structures were examined for each defect to determine the energetically most favorable state.

The band gap of SiO$_2$ is calculated to be about 5.3 eV as compared to an experimental value of approximately 9 eV.[10] Underestimation of the band gap is typical of first-principles calculations based on the local-density approximation. The calculated 2.1 eV valence and 2.6 eV conduction-band offsets between Si and SiO$_2$ are also underestimated as compared to experimental estimates of about 4.6 and 3.2 eV.

In Sec. II we first examine several H-induced defects and defect reactions in SiO$_2$. The structural states for interstitial H$^+$, H$^-$, OH$^-$, H$_2$O, and H$_3$O$^+$ centers as well as the binding of H$^+$ to an oxygen-vacancy in SiO$_2$ are examined. Hydrogen-bonding in which an H$^+$ ion is Coulombically bound to two negatively charged oxygen atoms is found to be an important factor in the stabilization of several of these H-induced defect complexes. Hydrogen interacts strongly with intrinsic point defects in SiO$_2$, in particular, with oxygen vacancy and oxygen interstitial defects in SiO$_2$ and it lowers the barrier for the diffusion of oxygen from SiO$_2$ into Si. The most important intrinsic defects in SiO$_2$ consisting of oxygen-vacancy, oxygen-interstitial, and Si-interstitial and vacancy defects are considered in Sec. III. Oxygen vacancy, interstitial, and vacancy-interstitial pair defects are found to exhibit strong bistability, i.e., they undergo significant changes in structure as their charge states are changed. Optical excitation resulting in electron-hole creation or direct charge injection into SiO$_2$ can alter therefore the structure and electronic properties of these defects. The structure and electronic properties of a variety of hydrogen-induced and intrinsic defects are described below.
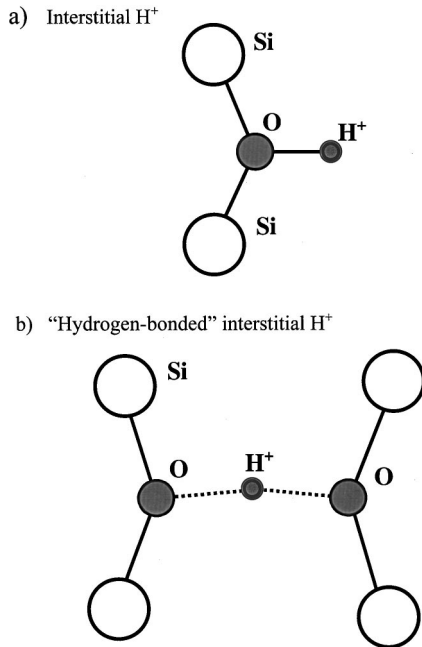
a) Interstitial H$^+$

b) "Hydrogen-bonded" interstitial H$^+$

FIG. 1. Two different configurations for an H$^+$ ion are shown. In (a) H$^+$ is covalently bonded to a bridging oxygen atom whereas in (b) it is in a three-center hydrogen-bonded state where it is stabilized by the Coulombic interaction energy with two negatively charged oxygen atoms. The results of our calculations show that H$^+$ has a lower energy in state (b).

II. HYDROGEN-INDUCED DEFECTS

A. Interstitial H$^+$ in SiO$_2$

It has been well accepted for many years that in SiO$_2$, the bonding of interstitial H to a twofold coordinated bridging oxygen atom [Si=O-H$^+$ configuration shown in Fig. 1(a)] results in an H$^+$ state.[3,4] Surprisingly, we have found another interstitial site for H$^+$ in SiO$_2$ with an even lower energy. In this state [Fig. 1(b)], the H$^+$ ion lies in *between* two nearest-neighbor oxygen atoms (not bonded to the same Si atom) with an O-H-O angle of about 167°. The hydrogen atom lowers its energy by taking advantage of the Coulombic interaction with the negatively charged oxygen atoms. This type of bond is well known in chemistry and has been designated as a "hydrogen bond." The two oxygen atoms are initially about 3.24 Å apart but each one relaxes by nearly 0.35 Å towards the H atom resulting in an O-O separation of about 2.63 Å. This is consistent with Pauling's estimate[11] that "for most hydrogen bonds between oxygen atoms the O–O distance lies between 2.50 Å and 2.80 Å." The calculated O-H$^+$ separations in the hydrogen-bonded state are about 28% larger than in a covalently bonded free O-H molecule with a bond length of 1.03 Å.

From the results of our calculations, interstitial H$^+$ in the hydrogen-bonded state is 0.3±0.2 eV more stable than the Si=O-H$^+$ configuration. The new H$^+$ state in Fig. 1(b) is expected to be even more stable than Si=O-H$^+$ in amorphous silica where the H ion is more likely to find two oxygen atoms at the optimal separation of around 2.63 Å. The binding energy of an H$^+$ ion in the H-bonded state in Fig.

1(b) is calculated to be 3 eV relative to the state where the H$^+$ ion is in an interstitial void. As discussed in Sec. II F, H$^+$ has a larger 3.5-eV binding energy to an oxygen vacancy. No gap states for interstitial H$^+$ were found, independent of whether the H atom is bonded to a bridging oxygen atom or is in a hydrogen-bonded state.

B. Interstitial H$^-$ in SiO$_2$

We find, in agreement with a previous theoretical study,[4] that placing an interstitial H atom near a Si atom along an antibonding Si-O axis leads to an H$^-$ state. The H atom displaces the Si atom and bonds to it, stretching the Si-O bond by 9% and forming an H$^-$ defect. H$^-$ has a localized state in the band gap of SiO$_2$ at about 2.3 eV above the bulk valence-band maximum (VBM).

Negatively charged atomic H is not very stable in SiO$_2$. In the presence of a neutral oxygen interstitial (O$_{int}$) defect, the reaction

$$H^- + O_{int} \rightarrow (OH)^- \qquad (1)$$

is exothermic by 3.4 eV while the competing reaction
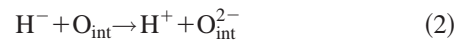
$$H^- + O_{int} \rightarrow H^+ + O_{int}^{2-} \qquad (2)$$

is exothermic by 2 eV. The structures of (OH)$^-$, O$_{int}$ and O$_{int}^{2-}$ defects are discussed in the following sections. H$^-$ is also unstable in the presence of H$^+$. The reaction

$$H^- + H^+ \rightarrow H_2, \qquad (3)$$

where H$_2$ lies in an interstitial void of SiO$_2$, is exothermic by nearly 2 eV.[12]

The presence of H$^-$ in SiO$_2$ can, in principle, also lead to the creation of oxygen vacancy defects through the reaction

$$SiO_2{:}H^- \rightarrow V(O) + OH^- \qquad (4)$$

in which H$^-$ leads to the formation of a neutral oxygen vacancy and an interstitial OH$^-$ molecule. The reaction, however, is found to be *endothermic* by 2.7 eV.

Molecular H$_2$ in SiO$_2$ is found to be inactive as far as creation of defects is concerned. Interstitial H$_2$ is found to have very nearly the same energy in SiO$_2$ as in Si.

C. Relative energies of H$^+$ and H$^-$ in SiO$_2$ and Si

In bulk Si, the most stable position for interstitial H$^+$ is at a bond-centered site.[13] The energetics for the migration of interstitial H$^+$ from bulk Si into SiO$_2$ can be examined by considering the total-energies for the reaction:

$$SiO_2 + Si{:}H^+ \rightarrow SiO_2{:}H^+ + Si, \qquad (5)$$
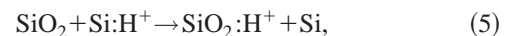
where SiO$_2$ denotes bulk SiO$_2$ (α-quartz), Si:H$^+$ bond-centered H in bulk Si, etc. We find that the reaction is *exothermic* by 0.7 eV.

Negatively charged interstitial H in bulk Si lies close to a tetrahedral interstitial site, along a Si-Si antibonding axis. The motion of H$^-$ from Si into SiO$_2$ represented by the reaction
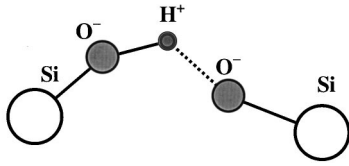
Interstitial OH$^-$ in SiO$_2$

FIG. 2. The most stable state of an OH$^-$ interstitial molecule in SiO$_2$ is shown. This structure is also stabilized by Coulombic interactions between the H atom and its two neighboring oxygen atoms. The two O-H distances are unequal and the long bond which is about 40% larger than a normal O-H bond length of 1.03 Å is shown as a dashed line.

$$SiO_2 + Si{:}H^- \rightarrow SiO_2{:}H^- + Si \qquad (6)$$

is found to be *endothermic* by 1.6 eV. There is a very large difference therefore in the energetics of migration of H from Si into SiO$_2$ depending on the charge state of H. SiO$_2$ clearly prefers H$^+$ to H$^-$.

D. (OH)$^-$ molecule in SiO$_2$

By far the most stable state for OH$^-$ in SiO$_2$ is found to be the "peroxy radical" configuration in which an OH molecule is inserted between a Si-O-Si bond to form a Si-O-H-O-Si type of configuration shown in Fig. 2.[14] This state is about 1.9 eV more stable than OH$^-$ in an interstitial void. The actual charge distribution of Si-O-H-O-Si is: Si-O$^-$⋯H$^+$⋯O$^-$-Si where ⋯ denotes a highly stretched bond, with effectively onefold coordinated and negatively charged oxygen atoms surrounding a positively charged hydrogen atom in a configuration typical of hydrogen bonding stabilized by Coulombic interactions. The two O-H bonds are stretched by 19 and 33% above their normal free molecular bond length of 1.03 Å. The OH$^-$ defect gives rise to highly localized occupied states at $E_v + 0.7$ eV and $E_v + 1$ eV where E_v corresponds to the energy level of the VBM.

Interstitial OH in SiO$_2$ can also exist in a metastable *positively* charged state, binding to a bridging oxygen atom denoted as O=Si to form an O-H$^+$-O=Si type of state. This state is metastable with respect to dissociation into isolated H$^+$ and oxygen interstitial defects. The dissociation lowers the total-energy by 0.5 eV.

E. Interstitial H$_2$O and H$_3$O$^+$ in SiO$_2$

The addition of an H$^+$ atom to the OH$^-$ state described above gives rise to a very stable Si-OH⋯HO-Si state for an interstitial H$_2$O molecule in SiO$_2$. The structure shown in Fig. 3 involves essentially the incorporation first of an OH$^-$ molecule between an Si-O-Si bond and then an additional H$^+$ atom to tie up the resulting "dangling bond" on the original oxygen atom in the Si-O-Si bond.[15] The reaction
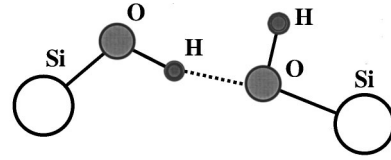
$$OH^- + H^+ \rightarrow H_2O \qquad (7)$$

Interstitial H$_2$O Complex in SiO$_2$

FIG. 3. The atomic structure of an interstitial H$_2$O complex in SiO$_2$ is shown. The H-O separation shown by the dashed line is about 1.6 Å.

in which interstitial OH$^-$ and H$^+$ molecules combine to form an H$_2$O complex lowers the total energy by 0.9 per H$_2$O molecule produced. As can be seen from Fig. 3, the structure of the H$_2$O complex in SiO$_2$ is quite different than that of a water molecule. The interstitial H$_2$O molecule is not found to have any states in the SiO$_2$ band gap.

The creation of H$_2$O from the reaction:

$$H_2 + O_{int} \rightarrow H_2O \qquad (8)$$
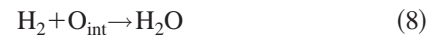
in which interstitial molecular H$_2$ and atomic oxygen combine to form H$_2$O in the configuration shown in Fig. 3 is exothermic by 2.5 eV.

Interstitial H$_2$O in SiO$_2$ can easily accommodate an H$^+$ ion between the two oxygen atoms in Fig. 3 to form an (H$_3$O)$^+$ interstitial complex shown schematically in Fig. 4. The reaction is only slightly (0.2 eV) exothermic.

From the results presented above, it is clear that hydrogen bonding plays an important role in the stability of many H-induced defects in SiO$_2$ including H$^+$, OH$^-$, H$_2$O, and H$_3$O$^+$ interstitial complexes.

F. Hydrogen induced oxygen vacancy formation in SiO$_2$

An interesting and important defect reaction at the Si-SiO$_2$ interface is

$$SiO_2 + Si \rightarrow SiO_2{:}V(O) + Si{:}O_{int} \qquad (9)$$
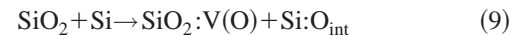
in which an oxygen atom migrates from bulk SiO$_2$ into bulk Si resulting in the formation of an oxygen vacancy V(O) in SiO$_2$ {denoted by SiO$_2$:V(O)} and an oxygen interstitial O$_{int}$ in Si denoted by Si:O$_{int}$. The formation of an oxygen va-
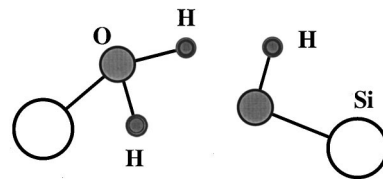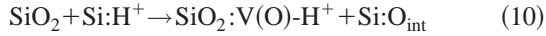
Interstitial H$_3$O$^+$ in SiO$_2$

FIG. 4. The atomic structure of an H$_3$O$^+$ complex in SiO$_2$ is shown.

cancy in SiO_2 breaks two Si-O bonds and creates two three-fold coordinated Si atoms which dimerize to form a Si-Si bond. In contrast, an oxygen interstitial in bulk Si forms two Si-O bonds and breaks a Si-Si bond. The reaction in Eq. (9) therefore leaves the total number of Si-O and Si-Si bonds unchanged. The reaction is found to be *endothermic* by 1.3 eV, largely because of the strains introduced by rebonding in SiO_2 and by the oxygen interstitial defect in Si.

The energy for the reaction in Eq. (9) is reduced significantly in the presence of hydrogen ions in Si, i.e., the reaction

$$SiO_2 + Si:H^+ \rightarrow SiO_2:V(O)\text{-}H^+ + Si:O_{int} \qquad (10)$$

does not cost any energy and may actually be slightly exothermic.[16]

In this reaction, interstitial H^+ in Si moves into SiO_2 and takes a position very close to the missing oxygen atom forming stretched bonds with its two nearby Si atoms. The Si-H-Si angle is found to be 148°. The most stable state for this V(O)-H complex is the single positively charged state. Hydrogen enhancement of oxygen diffusion into Si is consistent with experimental data.[17] For V(O)-H^+ we find a state at nearly 1 eV below the conduction-band minimum that is localized on the central H atom and its two neighboring Si atoms. A similar type of state is found for the nonhydrogenated V(O)$^{2+}$ vacancy. The reaction in Eq. (10) has a higher probability of occurrence at the interface between SiO_2 and Si. This is because the oxygen atom released by vacancy formation in SiO_2 is more likely to become an interstitial atom in Si instead of in SiO_2 thereby making the reaction exothermic. The diffusion of an oxygen interstitial (in its ground "peroxy radical" state discussed in Sec. III) from SiO_2 into Si is

$$SiO_2:O_{int} \rightarrow Si:O_{int} \qquad (11)$$

where it forms two Si-O bonds is found to be highly exothermic, releasing 4.8 eV in energy.

The binding energy of an H^+ ion in SiO_2 to a neutral oxygen vacancy is calculated to be 3.5 eV, about 0.5 eV larger than its binding to oxygen atoms shown in Fig. 1(b). Hydrogen does not therefore have a unique binding energy in SiO_2, consistent with recent experimental data.[18]

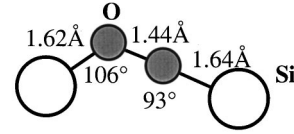### III. INTRINSIC DEFECTS IN SiO_2

A. Interstitial oxygen in SiO_2: Neutral state

The atomic structure of atomic oxygen interstitials in SiO_2 has been investigated by several groups and the present results are consistent with earlier ones.[19,20] The most stable state for interstitial atomic oxygen is the "peroxy radical" configuration shown in Fig. 5 in which an oxygen atom is inserted into a Si-O-Si bond to form a Si-O-O-Si types of bonding state. The Si-O-Si bond is able to accept the interstitial oxygen without much strain. The peroxy radical configuration gives rise to sharply localized occupied electronic states at VBM and unoccupied ones at the conduction-band minimum (CBM). The wave functions for these states are localized on the two central oxygen atoms of the bond.
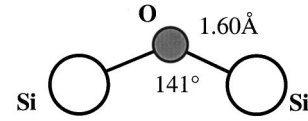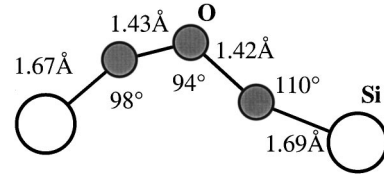

FIG. 5. The peroxy configurations for interstitial atomic oxygen and of O_2 are shown. A Si-O-Si bonds in SiO_2 shown in (a) has sufficient flexibility to absorb atomic (b), or molecular oxygen (c), and even an O_3 complex. The separation between the two Si atoms gets larger as additional oxygen atoms are added.

The peroxy radical state is found to be capable of easily accepting an additional interstitial oxygen atom to form the interstitial O_2 configuration shown in Fig. 5(c). This structure is energetically not as favorable as an O_2 molecule in an interstitial void.[20] The peroxy structure can even accommodate an Si-O-O-O-O-Si type of O_3 interstitial molecular state. Experimentally there is some evidence for interstitial ozone molecules in SiO_2.[21] The O_2 and O_3 peroxy states give rise to highly localized occupied states at about 1.5 eV above the VBM. We find that in going from normal Si-O-Si bonding to Si-O-O-O-O-Si the Si-Si distance increases gradually from nearly 3.0 to 3.6 Å, 3.8 Å, and finally to 4.1 Å as extra oxygen atoms are added.

B. Negatively charged interstitial oxygen

Interstitial oxygen in SiO_2 can occur in a negatively charged 2- state in a configuration very different from that of the peroxy state shown in Fig. 5(b). In the 2- state, the interstitial oxygen forms bridging bonds with two nearest-neighbor Si atoms,[22] forming a Si-O-Si angle of 140° and Si-O bonds that are about 7% longer than normal bonds in SiO_2. Each of the two Si atoms bonding to the interstitial oxygen is displaced towards it, significantly stretching an existing Si-O bond. This effectively leads to the creation of two distant singly coordinated oxygen atoms 6.86 Å apart which act as acceptors, giving rise to the 2- state for the oxygen interstitial. The defect has highly localized occupied states in the band gap extending from the VBM at E_v to $E_v + 1.2$ eV. At the Si-SiO_2 interface where the Fermi level is set by the doping in Si, the 2- state is not stable with respect to the neutral state. However, as discussed in Sec.

III D, the 2-state of the oxygen interstitial defect is expected to play an important role in degradation phenomena under electron injection conditions.

C. Oxygen vacancy and divacancy

There is great interest in oxygen-deficiency-centers in SiO$_2$ consisting of either oxygen monovacancies or divacancies.[23–26] The oxygen vacancy defect V(O) in SiO$_2$ has been extensively studied. In the most stable state the two Si atoms surrounding the vacancy form a dimer bond. This state is the most stable for all Fermi levels at the Si-SiO$_2$ interface where the Fermi level is determined by p or n doping in Si. The dimerized state has no levels in the SiO$_2$ band gap.

If free holes are injected into SiO$_2$, the vacancy undergoes a structural transformation which breaks the dimer bond and which pushes the two Si atoms into planar sp^2 bonded configurations.[26] The $+2$ charged vacancy has unoccupied levels about 1 eV below the CBM of SiO$_2$. This state can capture electrons and transform the defect into the dimerized neutral state.

As discussed earlier in Sec. III, ionized hydrogen (H$^+$) binds very strongly to V(O) to form a V(O)-H$^+$ complex. The hydrogen atom takes the place of the missing oxygen and forms two stretched Si-H bonds with its nearest-neighbor Si atoms.

The oxygen divacancy defect was also examined. In the divacancy, a given Si atom loses two of its nearest-neighbor oxygen atoms. In α-quartz, such a divacancy affects three Si atoms. Two of these Si atoms are threefold coordinated and the third one is twofold coordinated. The crystalline α-quartz structure has sufficient structural flexibility to allow Si-Si bond formation and the elimination of all four dangling bonds on the Si atoms. The resulting neutral defect has no electronic states in the band gap. The stability of a fully relaxed neutral divacancy (with two Si-Si bonds) with respect to two neutral monovacancies (each with one Si-Si bond) was examined. The divacancy is found to be 0.5 eV less stable than two monovacancies in α-quartz. The energy difference is small and represents mostly the extra strain energy required to achieve the two Si-Si bondings for the divacancy. For the neutral divacancy with Si-Si dimer bonds, we do not find any states in the band gap.

We have also examined the electronic properties of just the divalent (twofold coordinated) Si atom resulting from the removal of two oxygen atoms around that atom. The dangling bonds on the two threefold coordinated Si atoms resulting from the divacancy were saturated with hydrogen in order to study the remaining divalent Si atom. This defect is found to give rise to a strongly localized state at about midgap. Results form cluster calculations suggest that divalent Si atoms are responsible for several defect related absorption and luminescence lines seen in SiO$_2$.[27]

D. Electron injection and oxygen vacancy-interstitial pair formation

The negatively charged O^{2-} state of interstitial oxygen is important under electron injection or UV irradiation condi-

tions in SiO$_2$. Under prolonged electron injection into the conduction band of SiO$_2$, the formation energy of the extended defect consisting of an oxygen-vacancy and an oxygen-interstitial defect is found to be very low. In particular, the energetics of formation of an oxygen-vacancy oxygen-interstitial pair in SiO$_2$ via the reaction

$$SiO_2 \rightarrow SiO_2:\{V(O)+O_{int}\} \tag{12}$$
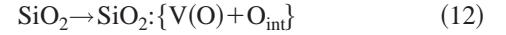
is about 6 eV. However, under electron injection conditions, the reaction

$$SiO_2 + 2e_{CBM} \rightarrow SiO_2:\{V(O)+O_{int}^{2-}\} \tag{13}$$

in which the interstitial oxygen atom captures two electrons from the conduction-band minimum of SiO$_2$ is endothermic by only 0.5 eV. If the interstitial is near the Si-SiO$_2$ interface, its motion from SiO$_2$ into Si to form an oxygen interstitial, leaving behind an oxygen vacancy in SiO$_2$, should result in a large drop of the total energy, making the defect formation at the interface an exothermic process.

E. Silicon interstitial defects in SiO$_2$

Because of the difference in molecular volume between Si and SiO$_2$, oxide growth on a Si substrate is accompanied by a flow of Si atoms away from the interface into Si and SiO$_2$. The primary out-diffusion is believed to be into the more open SiO$_2$ side of the interface.[28] We have examined the Si interstitial defect in both Si and SiO$_2$ in various atomic configurations and charge states. From the results of our calculations we find that the relative stability of an interstitial Si atom in bulk Si versus bulk SiO$_2$ is strongly charge state dependent. A neutral Si interstitial is far more stable in Si (by more 2.5 eV) than in SiO$_2$. However, in $2+$ and $4+$ charge states a Si interstitial in SiO$_2$ near a Si-SiO$_2$ interface is as stable as a corresponding interstitial in Si, i.e., a comparison of the energies for the following two states:

$$SiO_2:Si_{int}^{4+} + 4e_{CBM}(Si) \leftrightarrow Si:Si_{int}, \tag{14}$$
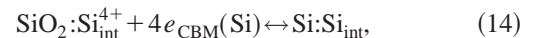
in which a Si interstitial in SiO$_2$ transfers four electrons to the CBM of Si to go to a $4+$ charge state versus a neutral Si interstitial in bulk Si, shows them nearly equal in energy. As might be expected, a $4+$ state defect is a highly polarizing one in SiO$_2$. The Si interstitial in this charge state pulls four distant oxygen atoms towards itself to maximize the Coulombic interaction energy. *Ab initio* calculations using supercells, as is in here, generally tend to overestimate the binding energy of highly charged states. It is likely therefore that the Si interstitial in SiO$_2$ has a higher energy than a corresponding defect in Si, independent of charge state.

F. Silicon vacancy defect in SiO$_2$

The Si vacancy in SiO$_2$ is an important defect that has not received as much attention as the oxygen vacancy. There is some evidence that Si vacancy defects occur in SiO$_2$ and may give rise to *EX* centers in thermal oxides grown on Si.[29]

In its simplest state the vacancy gives rise to four singly coordinated oxygen atoms with deep acceptor states. In the neutral charge state, the four oxygen atoms surrounding the vacancy undergo a Jahn-Teller distortion resulting in two weakly coupled O-O pairs that lowers the energy by nearly 1 eV. The paired state has localized occupied states close to the VBM and empty states at about 3 eV above the VBM. The paired state can undergo additional reconstructions which further lower its energy. For example, one of the four oxygen atoms surrounding the vacancy can move away from its site (breaking its bond with a Si atom) to form an interstitial peroxy-type configuration [as in Fig. 5(b)] with two of the other oxygen atoms. In this process the total energy decreases by 0.5 eV. The peroxy state for the vacancy also has highly localized occupied and empty states in the SiO_2 band gap.

The Si vacancy has 1- to 4- negatively charged states. Electron injection into the CBM of SiO_2 would greatly reduce the energy of the Si vacancy, however, even under this condition the formation of a Si-vacancy Si-interstitial pair defects in SiO_2 costs a large energy of nearly 6 eV. At the Si-SiO_2 interface where the Si-interstitial atom from SiO_2 can be injected and incorporated into bulk Si as an interstitial the formation energy of the vacancy interstitial would still be about 3 eV. The energetics of Si defect formation in SiO_2 is expected to be very sensitive to the presence of hydrogen and possibly other impurities. The large binding energy of H with oxygen can significantly lower the formation energy of Si vacancy formation in SiO_2.

IV. SUMMARY

Intrinsic and hydrogen-induced defects in SiO_2 and defect reactions at Si-SiO_2 interfaces mediated by hydrogen were examined via first-principles total-energy calculations. Three-center $O^- - H^+ - O^-$ hydrogen bonding is found to stabilize a number of hydrogen containing defects in SiO_2. At a Si-SiO_2 interface, hydrogen significantly lowers the energy barrier for the migration of oxygen from SiO_2 into Si resulting in a hydrogenated oxygen vacancy in SiO_2 and an interstitial oxygen in Si. At a Si-SiO_2 interface, positively charged hydrogen ions are found to have a lower energy in SiO_2 than in Si whereas H^- has a significantly lower energy in Si. The formation energy of oxygen vacancy-interstitial complexes in SiO_2 is found to be drastically reduced from 6 to 0.5 eV under electron injection into the conduction bands of SiO_2. Near a Si-SiO_2 interface, the diffusion of oxygen interstitials from SiO_2 into Si would further lower the total energy and lead to a degradation of the interface.

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