Theory of oxide defects near the Si-SiO$_2$ interface

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(Received 7 August 1989)

We have analyzed the (100) Si-SiO$_2$ interface based on the crystalline structural model proposed by Ourmazd *et al.* The quantum-mechanical modified intermediate neglect of differential overlap (MINDO/3) technique was employed to investigate the electronic properties and atomic configurations of the interface region with various oxide defects. We find that oxygen vacancies in the near-interface region may explain the existence of several silicon oxidation states which have been observed in core-level photoemission experiments. Our calculations indicate that the properties of the oxygen vacancies are a strong function of their locations. A positively charged vacancy in the first oxygen monolayer is predicted to be unstable against the formation of a neutral Si—Si bond at the vacancy along with the formation of a positively charged P_b-like defect in the silicon substrate. However, a positively charged vacancy in the second oxygen monolayer is predicted to behave very much like an E_1' center in α-quartz. The energy levels associated with these vacancies are predicted to lie close to the Si valence-band edge, probably within the valence band. The positive charge state might therefore be neutralized by tunneling from the Si valence band.

I. INTRODUCTION

The silicon–silicon-dioxide interface has been an active subject of research for many years because of its important role in semiconductor devices.[1] Although a great deal has been learned about the macroscopic properties of this interface, its detailed atomic-scale structures, and therefore its related electronic properties, are still not certain. Several atomic models have been suggested, but some of these lack supporting experimental evidence, and others do not define a sufficiently detailed atomic configuration to allow electronic structure calculations.[2–4]

It has been suggested by Revesz and co-workers that the structure of the oxide will show ordering effects associated with the requirements of bonding to the silicon.[5] A Si-SiO$_2$ interface model of such a type was suggested recently by Ourmazd *et al.* based on their high-resolution transmitted-electron-microscopy (HRTEM) measurements.[6] This model, shown in part in Fig. 1(a), differs from the others in that it proposes that the oxide immediately adjacent to the (100) silicon substrate is tridymite, one of the crystalline forms of silicon dioxide. Attached to these ordered tridymite layers is amorphous silicon dioxide, which in most other Si-SiO$_2$ interface models is assumed to be directly connected to the silicon substrate. The tridymite region, on the average, is only about five silicon and oxygen monolayers thick, barely enough to complete a SiO$_2$ ring. Presumably the electronic properties of such an interface will show many interesting features that are absent in a Si-SiO$_2$ interface model where there is no intermediate crystalline region.

Like any other model of the interface, the Ourmazd model must explain how interfacial bonds between the substrate and the oxide could be arranged so that the coordination number changes from 4 in the silicon substrate to 2 in the oxide. The Ourmazd model assumes that the silicon dangling bonds on the interface are simply dimerized to form silicon-silicon bonds. Under such an assumption the silicon atoms in the interface region will have one oxygen neighbor, commonly denoted as Si^{1+}. However, it has been well established through core-level spectroscopy experiments that silicon atoms near a smooth silicon–silicon-dioxide interface exist in three different oxidation states, namely Si^{1+}, Si^{2+}, and Si^{3+}, and have certain ratios over a narrow range.[7] One of the goals of this paper is to investigate whether, within the framework proposed by the Ourmazd group, it is possible to have not only Si^{1+} but also Si^{2+} and Si^{3+} oxidation states near the interface.

We note that the other two oxidation states may be introduced by considering modifications to the Ourmazd model. One possible variation of the Ourmazd model is that two silicon dangling bonds on the interface are connected to an oxygen to form a Si—O—Si "bridge" bond, instead of simply forming a dimer [Fig. 1(b)]. Simulations show that lattice imaging cannot detect the presence of such bridges, which would impart Si^{2+} oxidation states to the two silicon atoms on the surface.[8]

To generate the other type of silicon oxidation state Si^{3+}, we introduce oxygen vacancies. This possibility is consistent with the early interpretation of Woods and Williams.[9] We may assume that a Si—O—Si bridge exists at the interface and that an oxygen vacancy exists in the first oxygen layer [Fig. 1(c)]. This yields Si^{1+}, Si^{2+}, and Si^{3+} configurations. Alternatively, we may create the oxygen vacancy in the second oxygen layer (an E'-type center), which (with a Si—O—Si bridge at the interface) will generate two Si^{2+} and two Si^{3+} configurations [Fig. 1(d)]. Various combinations of these configurations will produce a range of the ratios of numbers of the different oxidation states.
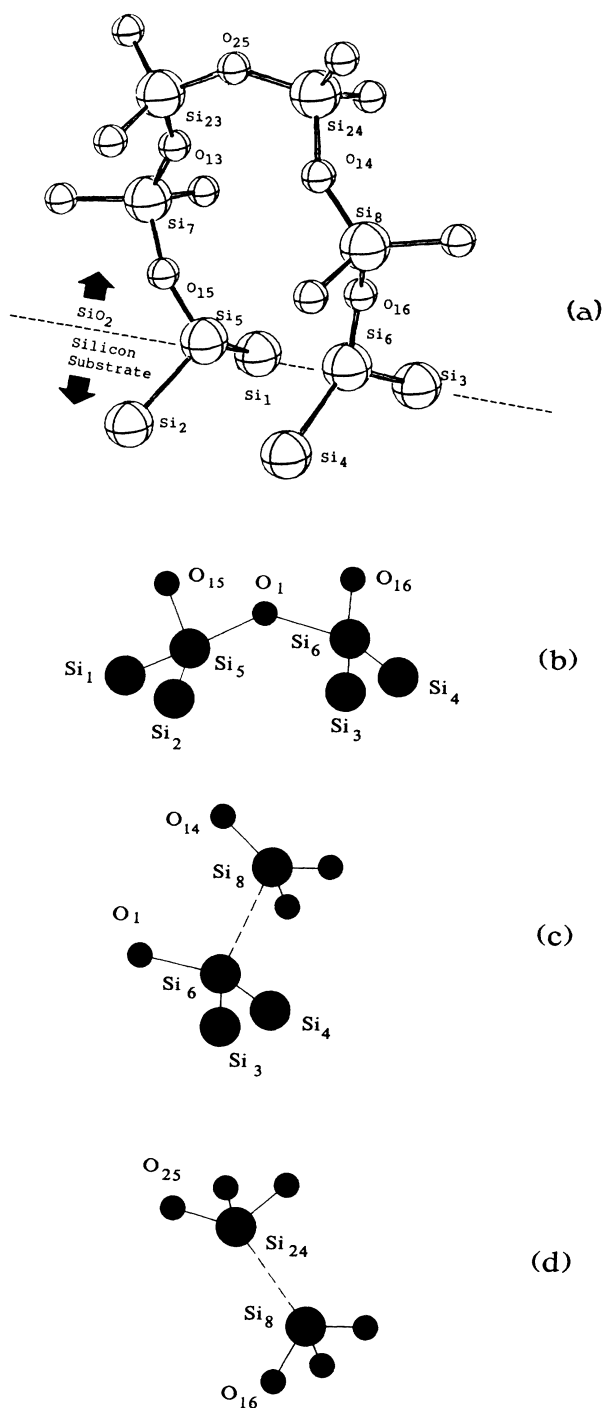
(a)

(b)

(c)

(d)

FIG. 1. (a) A fragment from the original Ourmazd structure of the Si-SiO$_2$ interface. Si(5) and Si(6) on the interface form a dimer (not shown). The labeled atoms are the ones fully relaxed in our subsequent calculations. Hydrogen terminators and one layer of silicon atoms in the substrate are not shown for clarity. Otherwise, the configurations shown are the actual large clusters used in the calculations. Termination at O(13) and O(14) defines the smaller clusters. (b) The bridging model, which yields two Si^{2+} oxidation states. (c) The first-layer oxygen-vacancy cluster, which includes the Si(5)—O(1)—Si(6) bridge and yields Si^{1+}, Si^{2+}, and Si^{3+} (d) The second-layer oxygen-vacancy cluster (E' center), which includes the Si(5)—O(1)—Si(6) bridge and yields two Si^{2+} and two Si^{3+}.

II. CALCULATIONS

The next question is whether these atomic configurations are energetically possible. We have investigated this problem with two approaches. One is the force-field method MM2, a program encoded by Allinger's group,[10] and the other is the quantum-mechanical semiempirical modified intermediate neglect of differential overlap (MINDO/3) technique.

MM2 is a semiclassical method which has rarely been used in the study of solid-state interfaces. In this approach, all short-range interactions among the atoms or ions are simulated by springs whose force constants are derived from experimental results or *ab initio* calculations. Because of its classical characteristics, the only information that it can yield involves the differences of total energies and the corresponding crystal structures. The results from an MM2 calculation need to be carefully calibrated, and more subtle information must be obtained through other more sophisticated methods.

The advantages of the MM2 program are its simplicity and its modest demand for computer resources, as compared with other methods. In a calculation of the interface very large numbers of atoms and electrons are involved, and the required computer resources could be excessive. In such a circumstance MM2 becomes a good tool for a preliminary investigation. MM2 was used here to study the strains on the interfaces due to the interface dimers in the Ourmazd model and to compare with those due to the Si—O—Si bridge in our proposed configuration.

To investigate the electronic properties of the oxygen-vacancy configurations we used MOPN, the open-shell version of MINDO/3, developed by Dewar and co-workers.[11] MINDO/3 and MOPN have been used in the investigations of defects in bulk silicon dioxide for nearly a decade, and have proved to be effective and reliable.[12] In order to take advantage of the Cray supercomputer's parallel processing facility, we have partially rewritten MOPN.

Two groups of clusters of different sizes have been used in these total-energy calculations. Each cluster represents a vertical "slice" taken from a large silicon-tridymite cluster. The larger clusters have the molecular formula Si$_{16}$O$_{13}$H$_{28}$, and the smaller ones Si$_{14}$O$_{11}$H$_{26}$, as shown in Fig. 1(a). Both have three silicon monolayers to simulate the silicon substrate, of which the lowest layer of six silicon atoms is not shown in Fig. 1(a) for the purpose of clarity.

The difference between these two groups is that the larger clusters have two more silicon atoms [Si(23) and Si(24)] and one more oxygen atom [O(25)] to complete the silicon-oxygen ring in the silicon dioxide, and consequently introduce four Si—O—H bonds which do not exist in the other group of clusters of smaller size. All clusters are terminated by hydrogen atoms in order to eliminate the otherwise-existing surface states due to the dangling bonds on the cluster boundary. These hydrogen atoms, and the atoms attached to them, as a whole are called the "cages" and are fixed in the calculations. The bonds in the cages are placed along the directions of the

bonds in an infinitely large crystal with the bond length properly adjusted for OH or SiH. Each cluster has its own cage, which is taken to simulate its environment.

Since the amorphous silicon dioxides attached to the tridymite SiO$_2$ will impose a variety of different environments, it is necessary to see how sensitively the energy is affected as the cage changes shape. We examined this relation by the following sequence of calculations. (a) We attached hydrogen atoms along normal bond directions with values of the bond lengths shown in Table I, and allowed the cage, as well as the inner atoms, to relax. (b) We fixed the cages at the given initial shape and then allowed only the inner atoms to relax.

The comparison of the energies obtained in these two different ways shows that the energy differences range from several tenths to three electron volts, where the clusters with the relaxed cages have lower energies, as could be expected. This reminds us that the cages must be chosen carefully, or the results will be easily obscured by the energy differences due to the cages. We used the structure of ideal crystalline silicon to construct the substrate, ideal tridymite to construct the oxide, and their silicon-oxygen-hydrogen cage. The lattice mismatch between the tridymite and the silicon substrate along the c axis of the tridymite was considered in our calculations by using shorter Si—O bonds (1.491 Å) in that direction, to which the silicon atoms were connected and were then allowed to relax. The mismatch along the direction parallel to the interface and perpendicular to the c axis of the tridymite is about 15%. Full incorporation of this mismatch into the clusters caused distortions and self-consistency problems due to the fixed cluster boundaries. We therefore used normal Si—O bonds in directions other than the c axis. In this situation the tridymite can still be attached to the silicon substrate with ease because of the relativity high flexibility of the silicon-oxygen-silicon bonds. Table I shows the bond lengths and bond angles used as input.

All clusters were fully relaxed in neutral, positively, and negatively charged states. The results from the calculations of these two groups of clusters of different sizes show essentially the same features. It is found for all three charge states that the clusters with an oxygen vacancy in the first layer have the lowest energies of the three configurations (Fig. 2). Furthermore, the positively charged clusters are always the highest in energy, the neutral the next, and the negatively charged clusters are the lowest. This ordering in the energy with charge state is consistent with the Coulomb attraction between an electron and a positive cluster, and with a positive electron affinity for a neutral cluster.

TABLE I. Input values of bond lengths (Å) and angles (deg).

Bonds		Angles	
Si—Si	2.3320	Si—Si—Si	109.5
Si—O[a]	1.6026	Si—O—Si	145.7
Si—H	1.4850	Si—Si—O	109.5
O—H	0.9420	Si—O—H	145.7

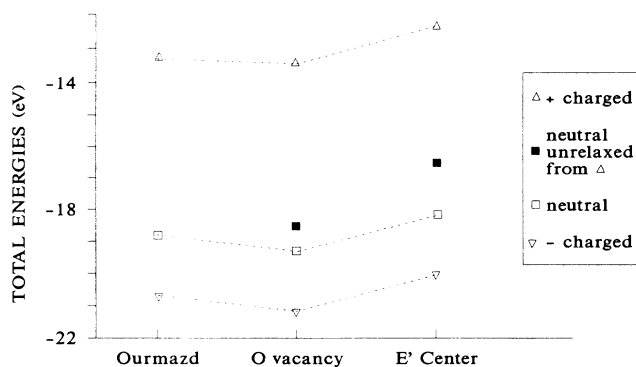[a]$d_{Si-O} = 1.4913$ Å along the c axis of tridymite.

FIG. 2. The total energies of the large clusters in three charge states. The horizontal axis represents three different configurations labeled as Ourmazd, O vacancy, and E' center. "Ourmazd" is the configuration in the Ourmazd model as shown in Fig. 1(a), "O vacancy" is shown in Fig. 1(c), and "E' center" is shown in Fig. 1(d). The solid squares indicate the total energies of the neutral clusters in the configuration of the relaxed positively charged states. (These two energies are used to calculate the level positions in a Franck-Condon-type process, shown as the two upper levels in SiO$_2$ in Fig. 4.)

It is mainly due to the lattice relaxation that the oxygen-vacancy clusters have lower energies than the clusters of the Ourmazd configuration. This is seen from the calculations on the smaller clusters, as shown in Fig. 3. Because of the absence of the Si(23)—O(25)—Si(24) bonds that complete the silicon-oxygen rings in the larger clusters, full relaxation of Si(8) above the first-layer oxygen vacancy is not possible. The stress thus introduced near the vacancy may contribute to the total energy so that the total energy of the oxygen-vacancy clusters becomes higher than that of the clusters of the Ourmazd configuration. However, in a more realistic situation, the lattice will spontaneously relax to reduce the stress. In order to include the effects of this lattice relaxation in our
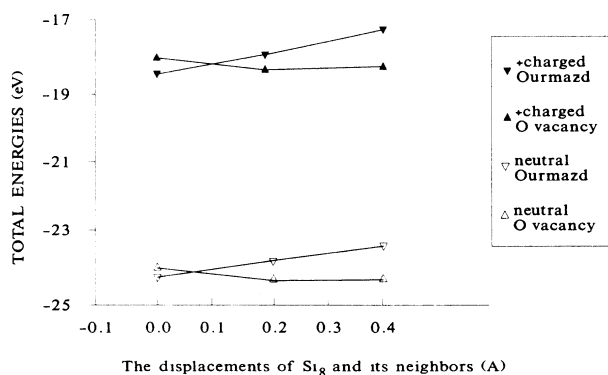

FIG. 3. The total energies of the small clusters in the neutral and positively charged states. It is seen that the energies of the first-layer oxygen-vacancy configuration become lower than the Ourmazd configuration in both states as Si(8) and its oxygen neighbors move towards the interface, simulating the lattice relaxation near an oxygen vacancy.

smaller-cluster calculation, we displaced Si(8) and its surrounding Si—O bonds as a rigid body towards Si(6) in two steps, each being 0.20 Å. After this Si(8) portion had been moved to a new position, we fixed the entire cage and allowed only atoms inside the cage to relax. It is clearly seen in Fig. 3 that as the Si(8) portion approaches the other side of the vacancy, the energies of the oxygen-vacancy cluster first decrease and then increase. At a relaxation of 0.2 Å, the oxygen-vacancy configuration achieves approximately the same energy as that of the Ourmazd configuration.

This result is apparently consistent with the physical picture. When one of the silicon atoms beside the vacancy is approached by the other one, we anticipate the major effect of this lattice relaxation to be the tendency to form a Si—Si bond across the oxygen vacancy, and therefore the total energy is lowered, while for a cluster where there is an oxygen atom between the two silicon atoms, the Si—O—Si bond is squeezed and the total energy increases when the silicon atom is forced to move closer to another silicon atom. It is important here to note that this result does not necessarily mean that the oxygen-vacancy configuration in the real system will be more stable than the Ourmazd configuration, since the energy difference in the real situation can probably be accommodated by energy differences due to the environment. What this result shows is that both oxygen-vacancy and Ourmazd configurations near a silicon–silicon-dioxide interface can be energetically favored according to the local environment.

We had expected that the first-layer oxygen-vacancy cluster [Fig. 1(c)] would show some defect behavior around the vacancy. It is true that from the results of the neutral and negatively charged clusters charges are seen to congregate around the broken bond. However, the vacancy in the positively charged state shows little extra charge or spin density. The upper silicon atom Si(8) is relaxed downward, and a silicon–silicon bond is formed to "heal" the oxygen vacancy. At the same time a Si—Si bond just below the interface is broken, and a positive

hole tends to form on one of the silicon atoms [see Fig. 1(a) and Table II, which shows the relevant parameters]. The remaining electron in the broken Si—Si bond stays on the other silicon, forming a dangling bond. The distance between these two silicon atoms after relaxation is 2.9 Å, closer to the Si-Si distance in silicon dioxide (3.1 Å) than to that in silicon (2.35 Å).

These features suggest two points to us. First, the oxygen vacancy right on the interface might be energetically less favored than the structure with a broken bond beneath the interface, which looks like a P_b center.[13] Second, the unusually long distance of 2.9 Å associated with the broken Si—Si bond might lead to the formation of a Si—O—Si bond in an oxygen-rich ambient. This might imply a mechanism for oxidation.

Experimental evidence has been found that an E' center can exist in the vicinity of a Si-SiO$_2$ interface.[14,15] It is still unknown just how close it can be. The result of our calculations of oxygen vacancies in the second oxygen layer could be part of the answer to this question. The relaxed structure of such an oxygen-vacancy cluster in a positively charged state shows all the known characteristics of an E' center in bulk SiO$_2$. One prominent feature of E' centers is that one of the silicon atoms next to the vacancy will relax into or through the plane of its nearest-neighbor oxygen atoms, leaving the other silicon atom at a position slightly puckered away from the normal tetrahedral position. Another feature of oxygen-vacancy calculations is that in the neutral and negatively charged states both silicon atoms move towards each other and a silicon-silicon bond attempts to form.

Our calculations show similar results, as shown in Table II, where the Si—Si bond lengths and the angles between one oxygen-silicon bond and the plane of three oxygen atoms are displayed. This shows that for the positively charged state, the silicon atom on one side of the vacancy away from the interface is pulled into the plane of its neighboring oxygen atoms, while the other silicon atom is slightly puckered away from its oxygen neighbors. The positive charge is centered on the planar sil-

TABLE II. Calculated parameters in relaxed clusters.

		Spin densities		
	S	P_x	P_y	P_z
	Oxygen vacancy in first oxygen layer (positive charge)			
Si(2)	0.0889	0.0303	0.2603	0.446
Si(5)	−0.0305	−0.0024	−0.0221	0.0003
Si(6)	0.00004	−0.0033	−0.0018	−0.0066
Si(8)	−0.0127	−0.00003	−0.0009	−0.0001
	Si(2)-Si(5) separation: 2.9 Å			
	Si(5)-Si(8) separation: 2.5 Å			
	Oxygen vacancy in second oxygen layer (positive charge) (E' center)			
Si(8)	0.259	−0.0036	0.199	−0.0175
Si(24)	0.0096	0.0019	0.0083	0.00008
	Planar Si(24) angle:[a] 0.73			
	Puckered Si(8) angle:[a] 19.23			
	Si(24)-Si(8) separation: 3.5 Å			

[a]Angular elevation of the silicon atom from the plane of its three oxygen neighbors (deg).

icon, while the puckered silicon contains an electron in the broken bond pointing towards the vacancy. The computed charge on the planar silicon is close to that of Si^{4+}, while the puckered silicon resembles Si^{3+}. Thus core-level experiments on the positively charged vacancy (E' center) might yield results consistent with a Si^{3+} atom and a Si^{4+} atom, while the neutral vacancy might be observed as two Si^{3+} atoms.

It is worthwhile to note that, though energetically the E' configuration is less favored than the other two with their own cages which simulate the ideal tridymite crystal, it still could be stable in some environments that would be simulated by a different cage.

From these total-energy calculations, one can directly obtain the electrical level positions between different charge states for each cluster. The level position is defined as follows:

$$E(0/+)=(E_{v+}-E_+)-(E_{v0}-E_0)$$

$$\text{for a } 0/+ \text{ level}, \qquad (1a)$$

$$E(-/0)=(E_{v0}-E_0)-(E_{v-}-E_-)$$

$$\text{for a } -/0 \text{ level}. \qquad (1b)$$

Here E_-, E_0, and E_+ are the total energies of the fully relaxed negative, neutral, and positive defect clusters, respectively, and E_v is the total energy of the defect-free cluster in a particular charge state. As defined, this would yield the $(0/+)$ level relative to the valence band and $(-/0)$ with respect to the conduction band of silicon. However, we are not confident that we can obtain the E_v's with sufficient accuracy to utilize this expression. As an alternative, we could use the experimental differences[16] between adjacent E_v's which yield the conduction- or valence-band edges. This, however, mixes theory and experiment in a way which is not totally satisfactory. Finally, we must realize the complexity of the physics of a system which has two band structures.

Before proceeding we must consider a further aspect of this problem. If the defect levels are in contact with the silicon bands through a tunneling process, then one should not consider the true level positions (which imply total relaxation for each charge state), but rather one must realize that the tunneling will occur via a Franck-Condon-type process into an *unrelaxed* state.[15] To calculate the proper energy, then, for tunneling from the silicon valence band into a positively charged vacancy, one should obtain the energy of the neutral vacancy in the atomic configuration appropriate to the positively charged vacancy. That energy would then be used in place of E_0 in Eq. (1a).

Using the somewhat unsatisfactory Eq. (1), with experimental Si and SiO$_2$ band alignments to account for the E_v's, yields results for the level positions given in Fig. 4 [which also includes the "tunneling" levels for $(0/+)$, as discussed above]. This shows that for both the first-layer oxygen vacancy and the second-layer E' center, the relaxed $(0/+)$ levels are predicted to lie nearly 1 eV below the top of the Si valence band. For the oxygen vacancy the tunneling $(0/+)$ level is predicted to lie at the top of the valence band, while for the E' center the tunneling
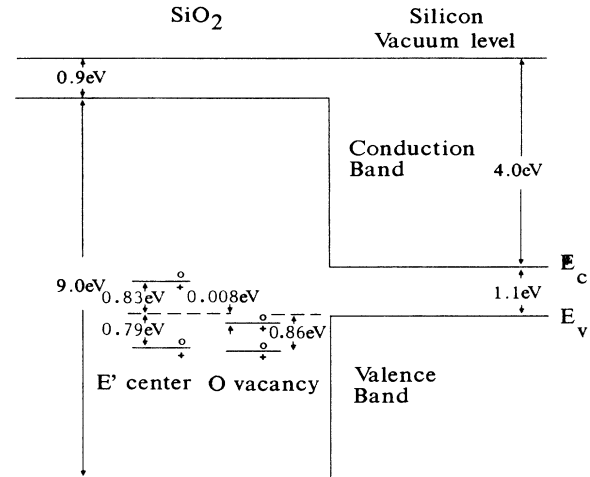

FIG. 4. The energy-band structure of an abrupt Si-SiO$_2$ interface is shown as the juncture of the experimental bulk band structure of each material. The $(0/+)$ levels shown for the oxygen vacancy in the first oxygen layer and for the E' center in the second oxygen layer were obtained as the calculated differences between positively charged and neutral clusters (Fig. 2), plotted relative to the vacuum level. The lower levels are appropriate to fully relaxed clusters (triangles and open squares in Fig. 2), while the upper ones are appropriate to tunneling levels (triangles and solid squares in Fig. 2), as discussed in the text.

$(0/+)$ level is in the upper part of the Si band gap.

An alternative method for obtaining the tunneling level is due to Edwards.[17] First, one looks at the computed spin densities to find where the unpaired electron is concentrated. Then one looks at the "α"-spin wave functions to determine the highest occupied molecular orbital (HOMO). The HOMO is to be identified as the top of the valence band if the corresponding defect orbital has a small spin density. It is to be identified as the defect level if the corresponding defect orbital has a high spin density. If this is the case, then the top of the valence band should be the α-spin level right beneath the defect level.

Using the Edwards method we found that $(0/+)$ tunneling levels for all these clusters of different sizes are several tenths of an electron volt below the top of the silicon valence band. Since the charged defects are only a layer away from the silicon substrate, the levels are actually merged into the subband of the silicon.

It is not surprising that there are differences of the order of 1 eV between these results. The total-energy method involves experimental band positions. Since we cannot claim that the present calculations are capable of predicting level positions in silicon dioxide to within 1 eV, we cannot compare these with confidence to experimental silicon bands. The one-electron Edwards method is more consistent in that it involves only theoretical results, and this method predicts the tunneling $(0/+)$ levels to be within the silicon valence band. Since the tunneling levels will always lie higher than the fully relaxed levels, the Edwards method would imply that the relaxed levels would lie even deeper into the silicon valence bands.

All of the above results, then, are consistent with the

fully relaxed $(0/+)$ levels lying well into the silicon valence bands, for both the first-layer O vacancy and the second-layer E' center. The tunneling levels are predicted with less certainty, but the results in which we have greater confidence predict for both defects that the $(0/+)$ levels also lie within the Si valence bands.

III. SUMMARY

To summarize, we have introduced oxygen bridges and vacancies into the Ourmazd model of the Si-SiO$_2$ interface and note that the resulting model contains Si^{3+}, Si^{2+}, and Si^{1+} oxidation states as found in core-level spectroscopy experiments. The force-field method MM2 and the semiempirical quantum-mechanical approach MINDO/3 have been utilized to explore the stabilities of three proposed configurations. Two groups of clusters of different sizes have been constructed in these total-energy calculations. It is found that a positively charged oxygen vacancy next to the Si-SiO$_2$ interface might not be stable, and that instead a P_b-like center in silicon and a Si—Si bond in silicon dioxide might be formed. It is also found that in a positively charged state an oxygen vacancy in the second oxygen layer would show all the basic charac-

teristics of an E' center. However, these defects may well be unstable in their positive charge state against tunneling from the Si valence band.

While the atomic clusters used in the MINDO/3 calculations are rather large, these calculations should be repeated on still-larger clusters in order to better simulate the three-dimensional tridymite structure. This should be possible, given sufficient supercomputer resources. Of considerable interest as well is the influence of hydrogen on these defects.

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