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Hydrogen and P_b defects at the (111)Si-SiO$_2$ interface: An *ab initio* cluster study

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Employing *ab initio* density functional methods and atomistic cluster models, we investigate the properties of P_b defects and their interactions with hydrogen at the (111)Si-SiO$_2$ interface. Our calculated hyperfine parameters agree quantitatively with experiments indicating that the P_b defect is a silicon dangling bond at the silicon side of the interface. We calculate the local minimum energy structures for one and two hydrogen atoms interacting with the P_b defect. From these calculations, we derive reaction energies for H_2 adsorption and H desorption. Comparing our results to experimentally derived activation barriers, we suggest different atomistic mechanisms for the observed reactions. [S0163-1829(99)05228-5]

I. INTRODUCTION

Point defects at the Si-SiO$_2$ interface and their interactions with hydrogen has garnered much attention in the literature.[1–9] At the (111)Si-SiO$_2$ interface, one type of electrically active defect has been clearly identified via electron spin resonance (ESR) and is labeled the P_b defect.[1,2] Analysis of the data indicates that the dominant P_b defect is consistent with an isolated silicon dangling bond (Si$_{db}$) on the silicon side of the interface. Semiempirical atomistic calculations agree qualitatively with this analysis.[3,4] At the (100)Si-SiO$_2$ interface, two ESR active P_b-like defects have been identified but their structural properties are not well characterized, in part because of the disordered nature of the Si(100) interface. The interaction of hydrogen with P_b defects has been studied for both the (111)Si and the (100)Si interfaces with SiO$_2$.[5–9] Hydrogen is understood to passivate the electrical activity of P_b and other defects but can also be associated with the creation of defects. For instance, recent experiments using deuterium instead of hydrogen in the processing of silicon transistors indicate that hot electrons cause device degradation indirectly by removing hydrogen (or deuterium) which were passivating electrically active defects.[10] Although the (100)Si-SiO$_2$ interface is more important for device applications, understanding defect-hydrogen interactions at the (111)Si-SiO$_2$ is important both from a fundamental standpoint and also as a model for understanding similar interactions at the (100)Si interface.

Hydrogen is observed to passivate P_b defects, for instance, by annealing in an H_2 rich environment.[5] This passivation can be reversed by thermal vacuum annealing[1] or by hot electron excitation.[10] Our understanding of the interactions of H and P_b defects is based primarily on the analysis of two sets of experiments.[5–7] Analysis of the data suggests that the reactions can be characterized by a single barrier, as shown in Fig. 1. The reaction goes from an initial state to the final state by way of a transition state with energies of E_i, E_f, and E_t, respectively. The reaction barrier is given by $E_B = E_t - E_i$ and the reaction energy is $E_R = E_f - E_i$ (note: E_R less than zero corresponds to an exothermic reaction). The experiments involve measuring the kinetics of P_b passivation and depassivation. In the first experiment, the ESR signal of the P_b defect is measured as a function of the time, pressure, and temperature during H_2 annealing. Analysis of the data indicates that the rate-limiting step can be described by the following equation:

$$H_2 + P_b \rightarrow P_b - H + H. \tag{1}$$

Brower found the kinetics to be thermally activated with a single reaction barrier (E_B) of 1.66 eV. More recent experiments over larger temperature and time ranges indicate a Gaussian distribution of barriers is needed to fit the data with $E_B^{ave} = 1.51$ eV and $\sigma = 0.06$ eV.[8] Also, the desorption of H from P_b defects has been measured by vacuum annealing experiments. The P_b defect's ESR signal is measured as a function of time and temperature. Analysis of the data indicate, the observed data can be described by the following equation:

$$P_b - H \rightarrow P_b + H. \tag{2}$$

The measured thermal activation barrier (E_b) is 2.56 eV. In both reaction (1) and (2), the P_b defect is proposed to be a Si$_{db}$ and both H and H_2 are assumed to reside in bulk SiO$_2$.

Reactions (1) and (2) form the basic model for understanding the physical chemistry of P_b and hydrogen at the Si-SiO$_2$ interface. An attractive feature of this model is that combining Eqs. (1) and (2) leads to

$$H_2 \rightarrow H + H, \tag{3}$$

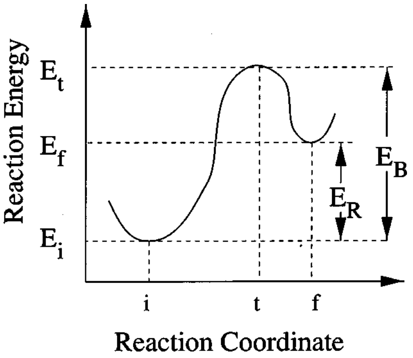

FIG. 1. Reaction diagram: The energy versus reaction coordinate is shown for a simple single barrier two-state reaction.

the equation describing the dissociation of H_2 molecules in SiO_2. Brower and Myers have[7] assumed that the reverse of reactions (1) and (2) are barrierless. In which case, the binding energy in SiO_2 is (2.56 + 1.66) eV = 4.22 eV, which compares favorably with the experimental H_2 binding energy in a vacuum (4.56 eV). Semi-empirical atomistic total energy calculations performed by Edwards[11] considered both Si-H and Si-H-H interactions. Theoretical results were in agreement with the reaction mechanisms proposed by Brower and Myers.[7] However, the theoretical studies were based on semi-empirical calculations so the agreement may be spurious. Recent advances in electronic structure calculations allow for the investigation of large defect models without any empirical fitting. With *ab initio* calculations, we have revisited the properties of P_b defects and their interactions with hydrogen.

Here we present *ab initio* density functional calculations of the interactions of hydrogen with an isolated dangling bond in a cluster model of the (111)Si-SiO_2 interface. First, we have calculated the isotropic hyperfine parameters for dangling bond defects. The quantitative agreement found by comparing directly with experimental ESR values confirms the simple dangling bond model proposed for the P_b defect. In addition, we have calculated the locally minimum energy configurations for one and two hydrogen atoms interacting with an interfacial Si_{db}. From these calculations, we derive reaction energies (E_R) for H_2 adsorption and H desorption. Comparing our results to experimentally derived activation barriers, we determine atomistic mechanisms for the observed reactions. In terms of reaction Eqs. (1) and (2), we find the final state for each reaction is more likely to involve atomic H in bulk Si rather than in SiO_2 as previously assumed.

The rest of this paper is organized as follows. In Sec. II, we discuss details of the theoretical approach used. We discuss our results in Sec. III and, in Sec. IV, we draw our conclusions.

II. CALCULATIONAL DETAILS

For our *ab initio* calculations, we employ the DMol commercial package[12] which is based on density funtional theory (DFT).[13] For the exchange-correlation functional, we employ the local density approximation (LDA) using the results of Ceperly and Alder[14] as parametrized by Vosko, Wilk, and Nusair.[15] To test the LDA calculations, we have employed the generalized gradient approximation (GGA) as developed by Becke, Lee, Yang, and Parr.[16] The basis functions are numerical atomic orbitals and include two orbitals and one polarization function per electron. Spin polarization, core electrons, and relaxations are included when necessary. Other options were set to default values.

We have performed dozens of test calculations on molecules such as H_2, SiH_4, SiH_3, Si_2H_6, and $^{+}(HO)Si_2H_6$. Our results are consistent with previous tests of LDA methods.[17,18] Compared with experiment or higher level quantum chemistry calculations,[19] we found the root mean squared (RMS) deviation in bond lengths was approximately 1%, whereas the bond strength RMS deviation was 7.1%. We found that GGA results for bond strengths were statistically better with an RMS deviation of 4.1%. Below, we report LDA results only. However, we have performed GGA calculations in selected cases to ensure our reported results are not greatly sensitive to our use of the LDA.

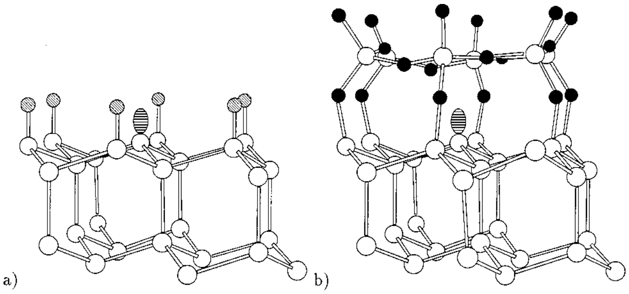

FIG. 2. Cluster models: Two atomistic cluster models depict a silcon dangling bond at (a) the Si(111) surface, and (b) the (111)Si-SiO_2 interface. In both figures, the solid, open and line-shaded circles represent oxygen, silicon, and hydrogen atoms, respectively. In (b), the central oval filled with horizontal lines designates the silicon dangling bond orbital.

We use two cluster models for a Si_{db} as shown in Fig. 2. Model I in Fig. 2(a) simulates the Si(111) surface and includes 22 Si and 27 H atoms. The Si(111) surface includes one Si_{db} and six Si-H bonds. Model II in Fig. 2(b) simulates the Si(111)-SiO_2 interface and includes 87 atoms in total [29 Si and 22 H for the Si(111) surface; and 6 Si, 18 O, and 6 H for the SiO_2 surface]. Note that H atoms used only to passivate the cluster surface are not shown in Fig. 2. The clusters used here are similar to those reported by Cook and White.[3] Our cluster models are not large enough to reproduce bulk properties such as gap energies. For instance, the HOMO-LUMO gap[20] for model I is 3.1 eV, whereas the DFT-LDA gap for bulk Si is ~0.5 eV.[21] However, in many cases, H energetics are more sensitive to the local chemistry. Employing model I, we estimate the bond strength (E_B) of H bound to the central Si_{db}.[22] We find $E_B = 3.6$ eV, which is in good agreement (<0.1eV difference) with DFT-LDA pseudopotential results using periodic models of the Si(111) surface.[18] We conclude that the cluster models employed in our present study are a reasonable compromise between accuracy and efficiency. Although quantitative aspects of our reported reaction energies may vary by 10%, the main conclusions are not sensitive to this uncertainty. Presently, we are involved in a project to employ accurate quantum Monte Carlo methods to estimate H formation energies in Si and SiO_2.[23]

III. RESULTS AND DISCUSSION

A. Structure of P_b defects

Hyperfine parameters determined by ESR experiments can be related to a defect's atomic structure only by modeling of the spin density of the system. Recent developments in electronic structure methods has made it possible to predict spin densities accurately for large atomistic defect models without any empirical inputs.[24,25] By employing *ab initio* DFT-LDA methods and cluster models, we can quantitatively compare theoretical and experimental hyperfine parameters. From such comparisons, one can accurately determine the atomistic structure of P_b defects at the (111)Si-SiO_2 interface.

TABLE I. Hyperfine parameters: theory versus experiment. The isotropic interaction is reported (in units of Gauss) for Si_{db} defects. In brackets we report the percent deviation between theory and experiment.

Structure	Experiment	Present work	Cook and White [c]	Edwards [d]
SiH_3	190	173 (−9%)		
Si_{db} at (111)Si-SiO$_2$	112, [a] 110 [b]	99 (−11%)	129 (+15%)	142 (+27%)

[a] Reference 1.
[b] Reference 2.
[c] Reference 3.
[d] Reference 4.

Analysis of the ESR data indicates that, for the (111)Si-SiO$_2$ interface, the one paramagnetic defect, labeled P_b, is consistent with a silicon dangling bond on the silicon side of the interface pointing in the (111) direction.[1,2,8] These results are corroborated by the fact that the number density of Si atoms in SiO$_2$ is much lower than in bulk Si; thus, at the interface, there will naturally be a number of under-coordinated Si atoms. Analysis of the data was initially in terms of empirical models based on s,p^3 valence orbital hybrids.[1] Semi-empirical electronic structure calculations have subsequently been performed employing cluster models similar to models I and II.[3,4] These calculations were in qualitative agreement with the original empirical analysis of the data. However, the calculated hyperfine parameters were between 15–30% higher than the experimental value (see Table I). No arguments were given to explain the quantitative discrepancy. One explanation for the discrepancy is that the isolated Si_{db} model itself is in some way deficient. Recently, from theoretical studies of oxygen thermal donors in bulk *c*-Si, it has been suggested that the Si-SiO$_2$ interfacial defects involve silicon atoms which participate in ''frustrated'' bonds, i.e., silicon-oxygen bonds where the oxygen atom is over coordinated.[26] Similar frustrated bonds have also been proposed as the intrinsic paramagnetic defect in amorphous silicon.[26,27] The proposed ''frustrated'' bond model would naturally produce lower hyperfine parameters because the defect wave function is less localized than in the isolated dangling bond model. Given the current unsettled situation, we have decided to revisit the calculation of hyperfine parameters for the P_b defect models.

The goal of our calculation is to test the accuracy of the dangling bond model for the P_b defect observed at the Si(111)-SiO$_2$ interface. To do this, we calculate the hyperfine interactions which can be obtained directly from ESR experiments. Several hyperfine parameters have been measured for Si(111)-SiO$_2$ interface. These interactions include the contact (or isotropic) interaction, the dipolar interaction, and nearest neighbor (or super-hyperfine) interactions. Each of these interactions can be calculated theoretically for a given structural model. For more details regarding the theoretical calculation of hyperfine interactions see Refs. 3, 4, and 24. We limit ourselves to the isotropic interaction since it is the strongest and most localized of the interactions. Also, only the isotropic interaction has been measured for the SiH$_3$ molecule which provides a nice benchmark. For silicon, the isotropic interaction can be calculated with the equation: a_{iso} (Gauss)$=285.522\, g_{\mathrm{Si}^{29}}\, \rho_{spin}(R_{\mathrm{Si}})$, where $g_{\mathrm{Si}^{29}}=-1.11052$ (Ref. 28) is the nuclear magnetogyric ratio, and $\rho_{spin}(R_{\mathrm{Si}})$ is the spin density at the position of the defect silicon atom in atomic units. Thus, to accurately calculate hyperfine interactions, one needs an accurate method for calculating the spin densities.

Theoretically, we determine the value of $\rho_{spin}(R_{\mathrm{Si}})$ using *ab initio* density functional cluster calculations as described in Sec. II. To calculate $\rho_{spin}(R_{\mathrm{Si}})$, we perform spin-polarized, all-electron calculations. Using the fixed-core approximation significantly alters our results. The spin density $\rho_{spin}(R_{\mathrm{Si}})$ is very sensitive to the relaxation of the Si_{db} and nearest neighbors. We allow all atoms to fully relax until the force on each atom is less than 0.1 eV/Å . We have calculated a_{iso} for SiH$_3$ and for the Si_{db} in cluster model I. In Refs. 3 and 4 the geometry and electronic structure of the Si_{db} are found to be well converged for cluster model I. Thus, we have not examined larger clusters such as model II.

In Table I, we compare our present results to previous theoretical calculations and also to experiment. Our value of a_{iso} for SiH$_3$ is 173 G which is 9% lower than experiment. Since the structure of SiH$_3$ is not in question, our error is due entirely to the DFT-LDA implementation used. Thus, for an accurate model of the P_b defect, we expect our calculated value for a_{iso} to be lower than the experimental value by roughly 10%. References 3 and 4 did not report hyperfine parameters for SiH$_3$, so it is difficult to gauge the accuracy of the methods they used. Our value of a_{iso} for cluster I is 99.1 G which is $\sim$11% lower than experiment suggesting the isolated Si_{db} is a good model for the P_b defect. The results from Refs. 3 and 4 for cluster model I are found to be higher than experiment by 15 and 27%, respectively. Differences in theoretical estimates of a_{iso} are due to the different approximations used in each calculation. Although we have not performed an extensive analysis of the approximations used in Refs. 3 and 4, we did examine the effect of using a minimal basis. If we use a minimal basis within our DFT-LDA framework, then, for SiH$_3$, the value for a_{iso} is 43% higher than experiment. Thus, the use of minimal basis sets in Refs. 3 and 4 may in part explain their overestimation of a_{iso}.

Our results indicate that the isolated dangling bond is a good model for the P_b defect at Si(111)-SiO$_2$ interface. We do not have an atomistic structural model for the competing frustrated bond defect so we cannot definitively rule it out. The frustrated bond model is essentially a three-fold silicon atom which is frustrated in its effort to bond to a nearby oxygen because the oxygen already has two bonds. The defect wave function should be less localized on the silicon atom than in the case of the isolated dangling bond model. Therefore, the defect's spin density and a_{iso} may be too low to agree with experiment. As a crude test, we place an H$_2$O

TABLE II. Relative energies for several local minima related to the passivation of a Si_{db} by an H_2 molecule.

Site	E (eV)
a. $Si_{db}+H_2^{\parallel}(SiO_2)$	0.0
b. $Si_{db}+H_2^{\perp}(SiO_2)$	0.0
c. Si–H + H (SiO_2)	1.1
d. $\equiv SiH_2$	0.2

molecule above the dangling bond in cluster I. Relaxing all coordinates led to a Si-O distance of 2.1 Å compared to 1.6 Å in quartz. The O-H bond lengths were 1.0 Å , the same as isolated H_2O. The calculated value for a_{iso} for the Si defect is 22 G which is ~80% lower than the experimental value. This result does not lend support to the frustrated bond model.

Our results indicate that the simple dangling bond model is entirely sufficient to explain the hyperfine data for the (111)Si-SiO_2 interface. It remains to be seen whether a variant on the isolated Si_{db} will also be sufficient to explain ESR active defects in more complicated systems, e.g., in bulk amorphous silicon or at the (100)Si-SiO_2 interface.

B. H_2 passivation of P_b defects

In Sec. III A, we have identified the electrically active P_b defect as an isolated Si_{db} at the (111)Si-SiO_2 interface. Below, we report calculations used to determine the reaction energies involved in the passivation of P_b defects by H_2. The reactions involve dissociating an H_2 molecule in the presence of a Si_{db} as indicated in Eq. (1). The process proposed by Brower and Myers[7] involves an H_2 molecule initially above the Si_{db} in an open SiO_2 interstice. Then, the H_2 dissociates such that one H passivates the Si_{db} and one remains in the open SiO_2 interstice. From their analysis, the H_2 binding energy in SiO_2 is estimated to be $\leqslant 4.2$ eV. Semiempirical calculations by Edwards[11] support this model reaction. Since these initial calculations were performed, advances in electronic structure methods and computer hardware make it possible to study this system with *ab initio* total energy calculations to test the proposed reaction model.

Our goal is to examine likely mechanisms for H_2 passivation of P_b defects at the (111)Si-SiO_2 interface. There are an unlimited number of pathways by which H_2 can dissociate in the presence of a Si_{db}. In order to make progress, we have limited ourselves to the calculation of the various locally stable configurations for two hydrogen atoms and a Si_{db}. We consider four configurations which have been previously identified as important.[11,29] We employ the DFT-LDA local orbital method described in Sec. I and cluster model II to examine the local minimum energy configurations for two hydrogen atoms interacting with a Si_{db} at the (111)Si-SiO_2 interface. In these specific calculations, we apply the fixed-inner-core approximation which is applied only to the Si$(1s,2s)$ atomic orbitals. Also, spin polarization is included since there is an odd number of electrons. For each local minima found, we allow all the coordinates to relax until the forces on each atom are less than 0.2 eV/Å . Our total energy results are summarized in Table II. These results will be discussed in the context of the reaction equation (1) and Fig. 1.

In reaction equation (1), the initial state involves an H_2 molecule in SiO_2 and a P_b defect at the interface. We consider two initial configurations with an H_2 molecule (a) parallel ($\parallel$) and (b) perpendicular ($\perp$) to an isolated Si_{db} at the (111)Si-SiO_2 interface. In both cases, the molecule's center of mass is 4.3 Å above the Si_{db} and is at the height of the outer oxygen atoms shown at the top of Fig. 2(a). The nearest atoms to the central H_2 are oxygen atoms at a distance of 4.0 Å . The electronic structure of both configurations include a localized gap level localized on the Si_{db}. The energy of these two configurations are identical and are set to zero in Table II. We find the H_2 molecules compare well to H_2 in free space. The bond lengths are (a) 0.80 Å and (b) 0.77 Å compared to 0.77 Å calculated for H_2 in free space. Also, the binding energies[22] are within 0.1 eV of the calculated free space value.

In reaction equation (1), the final state involves one H atom passivating the P_b defect and one atomic hydrogen. We consider two possibilities for the final configuration of the atomic hydrogen. First, the H atom is placed above the Si-H bond at 4.3 Å from the Si atom. There is little interaction between the H atom with either the Si-H or the SiO_2 ring. We find less than 0.1 eV is needed to move the H atom from its SiO_2 position to free space. The electronic structure includes a gap level localized on the atomic H atom and the energy of the final state is 1.1 eV.

Another possible final state is with the free H entering the silicon side of the interface. An intermediate configuration ($\equiv SiH_2$), involving an over-coordinated silicon atom, has been previously identified with DFT-LDA pseudopotential methods.[29] We find the $\equiv SiH_2$ complex involves a long Si-Si and two Si-H bonds which all share one plane. The three Si-Si bond lengths are 2.36, 2.37, and 2.49 Å , and both Si-H bond lengths are 1.55 Å . The electronic structure includes a gap level localized primarily on the central silicon atoms and both hydrogen atoms. These results agree with the results reported in Ref. 29. We find the final energy of the $\equiv SiH_2$ complex is 0.2 eV greater than the configuration with H_2 above the Si_{db}. In Ref. 29, it was determined that less than 0.2 eV is needed to dissociate the $\equiv SiH_2$ complex into a final configuration with one H passivating the P_b center and one H atom in bulk silicon far from any defect.

Combining the results reported above and in Table II, we are able to reevaluate the reaction model proposed by Brower and Myers.[7] From our calculations, we provide estimates for the reaction energy (E_R in Fig. 1) for reaction Eq. (1). To fully understand the mechanisms by which H_2 passivates Si_{db} defects at the Si-SiO_2, one would have to calculate the full total energy hypersurface to determine the relevant transition state energies (E_t in Fig. 1). Such a calculation is beyond the scope of the present study and will be the subject of future work. Nevertheless, our estimates of E_R provide interesting insight into the mechanisms for the observed reactions. We find E_R is 1.1 eV or ~0.2 eV depending on whether the atomic hydrogen enters bulk SiO_2 or bulk silicon, respectively. Therefore, the H atom will strongly favor the silicon side of the interface. Indeed, in simulations where the atomic hydrogen is placed in an arbitrary site above the Si-H bond, we find the system relaxes to the $\equiv SiH_2$ configuration. These results suggest an H_2 dissociation mechanism with the $\equiv$SiH$_2$ complex as an intermediate state. One aspect of this mechanism is that the reaction energy is much lower than the measured activation energies. Our preliminary calculations of the reaction barrier, within the adiabatic approximation, indicate that E_B is larger than 1.0 eV and so may be consistent with experiment.

In addition, we estimate H_2 in SiO$_2$ will have a binding energy[22] equivalent to H_2 in free space, which theoretically is 4.7 eV and experimentally is 4.5 eV. This result is higher than the upper bound of 4.2 eV proposed in the analysis of experiments by Brower and Myers.[7] However, the value determined by Brower and Myers[7] assumed hydrogen would only occupy SiO$_2$ interstices, which appears unlikely given that bulk silicon provides a lower energy bonding environment.

C. Desorption of H from P_b defects

In Sec. III B, we reported calculations of the reaction energies for H_2 atoms passivating P_b defects at the Si(111)-SiO$_2$ interface as described in reaction equation (1). Here we present results for the reaction energies for H desorption from P_b defects as described by reaction equation (2). Thermally activated desorption of hydrogen from P_b centers at the Si(111)-SiO$_2$ interface have been examined in great detail by Brower.[5] Analysis of the data indicate that the activation barrier for reaction (2) is 2.56 eV. The assumption of Brower and Myers[7] that the H desorbs into bulk SiO$_2$ is also supported by the semi-empirical calculations of Edwards.[11] However, based on DFT-LDA pseudopotential calculations of H in bulk Si, it has recently been suggested that the H desorption is more likely to occur via the silicon bulk and not through the vacuumlike region above a Si$_{db}$ at the (111)Si-SiO$_2$ interface. Our results from Sec. II B support this suggestion. To clarify the situation, we have studied hydrogen desorption from a dangling bond at the Si(111)-SiO$_2$ interface with DFT-LDA cluster caclulations. As in Sec. III B, here we confine ourselves to the calculation of local minimum energy configurations which allows us to estimate the reaction energy for Eq. (2) assuming various dissociation paths. By comparing our calculated energetics with the experimentally derived activation barriers, we conclude that reaction (2) is most likely to involve a final state with atomic hydrogen desorbing in a bulk silicon environment rather than into bulk SiO$_2$.

Our goal is to determine the most likely pathways for the desorption of hydrogen from the strong Si-H bond. As in the case of H_2 adsorption, there are an unlimited number of pathways by which the Si-H bond can dissociate. In order to make progress, we have limited ourselves to the calculation of the various locally stable configuration for H as it dissociates from the Si$_{db}$. With DFT-LDA methods within a supercell framework, local minima have been determined for hydrogen in bulk crystalline Si,[18,30] near a Si$_{db}$ in c-Si,[31] and in bulk crystalline silicon-dioxide.[32] In Refs. 30 and 31, the barriers between local minima were also determined for H in Si. However, the relative energy of hydrogen in silicon versus silicon-dioxide has not yet been examined. We place H near previously identified[30–32] local minima and allow neighboring atoms to fully relax until the force on each atom is less then 0.2 eV/Å . As in Sec. III B, we employ cluster model II and the fixed-inner-core approximation.

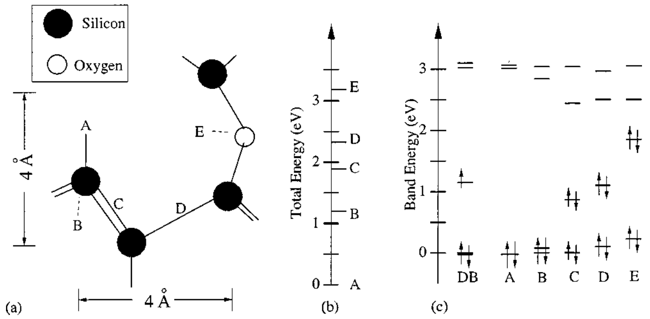

FIG. 3. H desorption: Presented is (a) a ball and stick sketch of the unrelaxed positions of five local minima (**a**–**e**) for H near a silicon dangling bond at the (111)Si-SiO$_2$ interface, (b) the total energy, and (c) the eigenlevels for each configuration. For (c), we also include the eigenlevels for the dangling bond (DB) to aid in comparison.

We have examined the relaxed geometries, the relative total energy and the electronic structure of H at five local minima. Our main results are reported in Fig. 3. In Fig. 3(a), we show the position (with the atoms in their unrelaxed positions) of each local minima found, sites **a**–**e**. The final relaxed configurations for each local minima reasonably agree with previously published results for similar systems. The total energies including zero point energies are reported in Fig. 3(b). The eigenlevels near the Fermi energy are reported in Fig. 3(c). These results will be discussed in the context of the reaction equations (2) and Fig. 1.

First consider H at site **a**, fully passivating the Si$_{db}$. The total energy for the model with H at site **a** sets the zero of energy in Fig. 3(b). We find the binding energy to be 3.6 eV, identical to Si-H at the Si(111) surface reported above in Sec. II. Thus, to remove the neutral H from site **a** and place it in free space costs 3.6 eV, assuming no intermediate barrier (i.e., $E_R = E_B$). The band gap for this model is given by the HOMO-LUMO (Ref. 20) gap with H at site **a**. The gap is found to be 3.1 eV, as indicated in Fig. 3(c).

Sites **b** and **c** were determined to be local minima for H interacting with an isolated Si$_{db}$ in bulk c-Si.[31] We find H at the antibonding site **b** has an energy of 1.3 eV and electrically active localized eigenlevels appear near the gap. We find H at the nearest bond center site **c** has an energy of 1.9 eV. As demonstrated in Fig. 3(c), with H at site **c**, the HOMO and LUMO (Ref. 20) eigenlevels move significantly deeper into the gap. The HOMO level is associated with the silicon dangling bond and is lower than the isolated dangling bond (DB) level due to displacements and interactions caused by the interstitial H at site **c**. The LUMO level is associated with a silicon-silicon antibonding state and is lowered into the gap due to the presence of the H atom. These results compare favorably with DFT-LDA pseudopotential plane-wave calculations of Si-H interactions in c-Si.[18,31] One discrepancy is that Refs. 18 and 31 find H at sites **c** has a relative energy of 1.5 and 1.75 eV, respectively. It should be noted that the H atom at sites **b** and **c** is still strongly bound to the Si$_{db}$.

In bulk silicon, atomic hydrogen favors the bond center (BC) site for both the neutral and positive charge state.[30] The next nearest bond center site **d** is found to be a local minimum for H with a relative energy of 2.2 eV. This energy is 0.3 eV lower than the 2.5 eV reported by Ref. 18 to move a neutral H from site **a** into a BC site in bulk Si far from any defects. In our case, there is some charge transferred from the H site to the Si_{db}, leaving the H atom positively charged. Such charge transfer is reasonable since the H related defect level is higher in energy than the Si_{db} defect level, as indicated in Fig. 3(c). Therefore, the system lowers its energy by transferring negative charge from the H site to the Si_{db}. A Mullikin analysis confirms that the H atom at site **d** is positively charged. The activation barrier experienced by atomic hydrogen moving from the Si_{db} site to the silicon side of the interface should not be much larger than 2.5 eV since the activation barriers for atomic hydrogen in bulk Si are found to be 0.5 eV or less.[18,30] Our results reasonably agree with the experimentally derived activation barrier of 2.56 eV.[7]

Since the H atom at site **c** is positively charged, we expect the H will move into SiO_2 as a positively charged species. In bulk SiO_2, positively charged atomic H forms strong bonds with oxygen.[32] Therefore, we place H in the vicinity of the nearest neighboring oxygen atom. As suggested in Fig. 3(a), a strong bond forms between the oxygen and positively charged H atom at site **e**. The O-H bond length is 1.0 Å, similar to bond lengths in H_2O, while the Si-O bonds lengthen from 1.6 Å each to 1.8 and 1.9 Å . This structure is close to the configuration reported in Ref. 32 for H^+ in bulk SiO_2. A Mullikin analysis indicates that with H at site **e**, charge transfer occurs, leaving the H positively and the Si_{db} negatively charged. Indeed, the Si_{db} atom moves out of the plane of its three neighbors, consistent with it being negatively charged. The energy of H at site **e** is 3.3 eV. In Sec. III B, we estimated the energy of a neutral H in SiO_2 to be the same as in free space, which is +3.6 eV on the scale in Fig. 3(b). Thus, it appears that only ~0.3 eV is gained by the charge transfer between H and the Si_{db}. These results indicate that over 3.0 eV is needed to move atomic hydrogen from the Si_{db} site to a local minima in bulk SiO_2. It appears the barrier to enter SiO_2 is over 3.0 eV which is too large to agree with the experimentally derived activation energy of 2.56 eV.[7]

As indicated in Fig. 3(c), the Si_{db} related HOMO level rises significantly for H at site **d** in silicon to site **e** in SiO_2. Thus, the gain in energy could be due primarily to the charging of the Si_{db} during dissociation. To examine this possibility, we passivated the Si_{db} with one H atom, then considered both H^0 and H^{+1} at sites **d** and **e**. In both cases, over 0.5 eV is needed to move H from site **d** to site **e**. The main conclusion drawn here is that, for atomic hydrogen, bulk silicon provides a lower energy bonding environment than bulk SiO_2. Thus, as proposed in Sec. III B for reaction (1), our results indicate that it is more likely for atomic H to desorb into bulk Si rather than into bulk SiO_2.

IV. CONCLUSION

With *ab initio* DFT-LDA calculations employing cluster models of the (111)Si-SiO_2 interface, we examine atomistic models for P_b defects and their interactions with hydrogen atoms. First, we have calculated the isotropic hyperfine parameters for dangling bond defects. The quantitative agreement found by comparing directly with experimental ESR values supports the simple dangling bond model proposed for the P_b defect. In addition, we have calculated the locally minimum energy configurations for one and two hydrogen atoms interacting with an interfacial Si_{db}. Thus, we have calculated values for the reaction energy E_R for various reaction paths. From these calculations, we derive reaction energies (E_R) for H_2 adsorption and H desorption. Comparing our results to experimentally derived thermal activation barriers, we propose atomistic mechanisms for the observed reactions. In terms of reaction Eqs. (1) and (2), we find the final state for each reaction is more likely to involve atomic hydrogen in bulk Si than in bulk SiO_2.

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[1] K. L. Brower, Appl. Phys. Lett. **43**, 1111 (1983).

[2] M. Stutzmann and D. K. Biegelsen, Phys. Rev. Lett. **60**, 1682 (1988).

[3] M. Cook and C. T. White, Phys. Rev. Lett. **59**, 1741 (1987).

[4] A. H. Edwards, Phys. Rev. B **36**, 9638 (1987).

[5] K. L. Brower, Phys. Rev. B **38**, 9657 (1988); K. L. Brower, Appl. Phys. Lett. **53**, 508 (1988).

[6] K. L. Brower, Phys. Rev. B **42**, 3444 (1990).

[7] K. L. Brower and S. M. Myers, Appl. Phys. Lett. **57**, 162 (1990).

[8] A. Stesman, Appl. Phys. Lett. **68**, 2723 (1996).

[9] E. Cartier, J. H. Stathis, and D. A. Buchanan, Appl. Phys. Lett. **63**, 1510 (1993); J. H. Stathis and E. Cartier, Phys. Rev. Lett. **72**, 2745 (1994).

[10] J. W. Lyding, K. Hess, and I. C. Kizilyalli, Appl. Phys. Lett. **68**, 2526 (1996).

[11] A. H. Edwards, Phys. Rev. B **44**, 1832 (1991).

[12] The DMol simulation package, licensed through Molecular Simulations Inc., is based on work of B. Delley. See, for example, B. Delley, J. Chem. Phys. **92**, 508 (1990).

[13] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B869 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[14] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[15] S. J. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[16] A. D. Becke, J. Chem. Phys. **88**, 2547 (1988); C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[17] B. Tuttle, Ph.D. thesis, University of Illinois at Urbana-Champaign, 1997.

[18] C. G. Van de Walle, Phys. Rev. B **49**, 4579 (1994); C. G. Van de Walle and R. A. Street, *ibid.* **49**, 14 766 (1994).

[19] The H^+ binding energy in $^+(HO)Si_2H_6$ and $H^+_{BC}Si_2H_6$ is not available experimentally. For these structures, we used a method based on Hartree-Fock called G2 which is an option in the G94 commercial simulation package. The method is described and evaluated in the following reference: L. Curtiss, K. Raghavachari, J. A. Pople, Chem. Phys. **98**, 1293 (1993).

[20] The HOMO and LUMO eigenlevels stand for the highest occupied molecular orbital and the lowest unoccupied molecular orbital.

[21] C. Filippi, D. J. Singh, and C. J. Umrigar, Phys. Rev. B **50**, 14 947 (1994).

[22] The binding energy is positive for systems that are bound, e.g., the cluster with an Si-H bond is bound relative to a cluster with an H in free space far from the Si_{db}. See Ref. 18 for more details. Note that we have also taken care to include zero point energies which we derive from our cluster calculations and Ref. 18.

[23] B. Tuttle and C. Filippi (unpublished).

[24] C. G. Van de Walle and P. E. Blochl, Phys. Rev. B **47**, 4244 (1993).

[25] A. H. Edwards, Phys. Rev. Lett. **71**, 3190 (1993).

[26] S. T. Pantelides and M. Ramamoorthy, *Proceedings of the 8th International Symposium on the Silicon-on-Insulator Technology and Devices* (Electrochemical Society, NY, 1997).

[27] B. Tuttle and J. B. Adams, Phys. Rev. B **57**, 12 859 (1998).

[28] G. H. Fuller, J. Phys. Chem. Ref. Data **5**, 835 (1976).

[29] B. Tuttle, C. G. Van de Walle, and J. B. Adams, Phys. Rev. B **59**, 5493 (1999).

[30] C. G. Van de Walle, P. J. H. Denteneer, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. B **39**, 10 791 (1989).

[31] B. Tuttle and C. G. Van de Walle, Phys. Rev. B **59**, 12 884 (1999).

[32] A. Yokozawa and Y. Miyamoto, Phys. Rev. B **55**, 13 783 (1998).