Defect Generation by Hydrogen at the Si-SiO_2 Interface

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Hydrogen is known to passivate Si dangling bonds at the Si-SiO_2 interface, but the subsequent arrival of H^+ at the interface causes depassivation of Si-H bonds. Here we report first-principles density functional calculations, showing that, contrary to conventional assumptions, depassivation is not a two-step process, namely, neutralization of H^+ by a Si electron and subsequent formation of an H_2 molecule. Instead, we establish that H^+ is the only stable charge state at the interface and that H^+ reacts directly with Si-H, forming an H_2 molecule and a positively charged dangling bond (P_b center). As a result, H-induced interface-trap formation does not depend on the availability of Si electrons.

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Hydrogen plays a major role in controlling several properties of Si-SiO_2 interfaces, a key ingredient in microelectronics. H is essential to produce high-quality interfaces by passivating dangling bonds, known by their characteristic electron-paramagnetic-resonance (EPR) signal as P_b centers [1]. However, the interfaces are known to degrade under a variety of experimental conditions. In many cases, e.g., in the presence of hot electrons or ionizing radiation, the degradation has been traced to H being released somewhere else in the device (e.g., from defects in the oxide or the polysilicon gate) and arriving at the interface [2–4]. Experiments using electric fields [4,5] and theory [6–8] have established that H migrates as H^+ ("bare" protons) at room temperature. It is believed that these protons are neutralized at the Si-SiO_2 interface by capturing an electron from the Si side, and then the neutral H "depassivates" a dangling bond via the reaction

$$\text{Si-H} + \text{H} \rightarrow \text{D} + \text{H}_2, \quad (1)$$

where D is a dangling bond (threefold-coordinated Si atom) [1,9]. This two-step process implies that the dynamics of depassivation is strongly coupled with the injection dynamics of Si electrons, which is controlled by local electric fields. On the other hand, once H^+ is neutralized, its own dynamics is decoupled from the local electric fields.

In this Letter, we report first-principles calculations in terms of which we establish that H^+ is the only stable charge state at the Si-SiO_2 interface, H^+ diffuses easily in the interfacial plane, and depassivation of Si-H bonds occurs directly through the reaction

$$\text{Si-H} + \text{H}^+ \rightarrow \text{D}^+ + \text{H}_2. \quad (2)$$

Thus, the depassivation process is not coupled to the dynamics of Si electrons and the space charge regions. Once depassivation occurs, however, the positively charged dangling bond can freely interact with Si electrons. The complete dynamics of the H reaction at the interface is, therefore, described by a very different set of coupled equations than is generally assumed. The key result that H remains positively charged at the interface is consistent with the known fact that H is a "negative-U" center (i.e., H^0 is not a stable charge state) in both Si and SiO_2 [6,10,11].

Recently, there has been extensive theoretical interest in the Si-SiO_2 interface. Most of the work has focused on bonding arrangements at "intrinsic interfaces," namely, structures without impurities and all atoms having their preferred coordination (4 for Si; 2 for O) [12–17]. The atomic structure of dangling bonds was recently studied in detail by calculating the components of the hyperfine tensor and comparing with EPR data [18]. In other recent work, migration of H^+ in SiO_2 [6] and interactions of H^+ with intrinsic interfaces [8] were studied. Finally, the inverse of reaction (1) and the spontaneous release of an H atom by a passivated dangling bond (Si-H → D + H) were investigated [19]. The forward form of reaction (1), however, which has been presumed to dominate the degradation of the Si-SiO_2 interface, is generally assumed to be valid without any independent theoretical backing.

The present calculations were based on density functional theory, the local-density approximation for exchange correlation, ultrasoft pseudopotentials, supercells, and plane waves [20]. The pseudopotentials used for the present study have been thoroughly tested in earlier work on a variety of Si-O-H systems [16,21,22]. As in that work, the energy cutoff for the basis set was 24 Ry, and integrations over the Brillouin zone were done using the Monkhorst-Pack scheme with two k-points in the relevant irreducible wedge [23]. For studying charged defects we introduced a homogeneous negative (positive) background when removing (adding) electrons in the supercell.

The calculations were performed for supercells containing a model interface, as recently reported by Buczko *et al.* [16]. Si-SiO_2-Si "superstructures" contain seven to eight planes of Si layers separating the SiO_2 layers. A large

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number of intrinsic superstructures with distinctly different local bonding arrangements [16] were examined, including interfaces with suboxide bonds (Si-Si bonds on the SiO_2 side) and interfaces with SiO_2-like protrusions into the Si side [8]. The structures were relaxed until the total energy was minimized (the force on each atom is smaller than a tolerance, in this work, 0.1 eV/Å).

Consistent with earlier work that probed a limited number of cases [8], the new calculations establish that H^+ is the only stable charge state at intrinsic Si-SiO_2 interfaces. A wide range of sites was examined: in the Si-Si bonds of the first Si layer on the Si side or attached to inequivalent O atoms on the first SiO_2 layer of an abrupt interface, in suboxide bonds (Si-Si bonds on the oxide side), and in various configurations in small SiO_2 protrusions into the Si side. The results were independent of the local bonding (cristobalitelike, quartzlike, or tridymitelike) [16]. The result was established in two complementary ways:

(i) The empty localized energy level associated with H^+ was monitored and found to be always much higher than the Si conduction band edge. This result is consistent with previous calculations by Bloechl who considered similar defects in bulk SiO_2 and extrapolated to the interface [7]. However, this method of investigating charge-state stability is based on the one-electron Hamiltonian in density-functional theory; i.e., it can be considered as only an approximate indication of relative stability.

(ii) The total energies of different charged states were compared using Janak's density functional implementation [24] of Slater's argument (which postulates that the energy difference is equal to the energy of the highest occupied eigenstate of the half-charge state with respect to the vacuum level [25]). We found that the positively charged states of all of these defects are at least 2.5–3 eV more stable than their neutral states if the Fermi energy lies at the top of the Si valence band. Therefore, we conclude that H^+ is the only stable charged state of hydrogen at the Si-SiO_2 interface.

Since two H^+ arriving at the interface would repel each other electrostatically, any complexing between them is very unlikely. Thus, when an H^+ arrives at the interface, it is either immediately trapped at a suboxide bond or SiO_2 protrusion [8] or it migrates laterally with barriers ranging between 0.3–0.5 eV (the energy of the barrier depends on the migration path through interfacial Si-Si bonds). The barriers to escape either to the Si or the SiO_2 side are larger [8]. If Si-H bonds are present at the interface, the next logical step is to enquire about the reaction of H^+ with such a defect.

For studies of an Si-H defect, in order to have a supercell of practical size, we used a model similar to that used in Ref. [18]. One Si atom and its four neighboring atoms were removed from the SiO_2 layer at the interface. The four dangling bonds were passivated by H. Such a configuration has most of the features of a real environment, especially the back bonds and the presence of an interface. Note that two of the Si-H bonds are true interfacial Si-H bonds. In calculations used to probe the depassivation process of one of these two Si-H bonds by an H^+ arriving from the oxide side, the other three Si-H bonds were monitored and indeed were found to remain undisturbed. The calculations were repeated using several distinctly different local environments. In each case, an interstitial H^+ was brought into the vicinity of the target H atom in the Si-H bond and the forces on the two atoms were monitored (Fig. 1a). At a distance of approximately 1.6 Å a mutual attraction between H^+ and the bonded H atom was sensed as nonzero. At that point, we explored several options. We first froze the intruding H^+ and allowed all the other atoms to move. Alternatively, we allowed all atoms to move, including the intruding atom. The electron density was monitored. In all cases, for a wide range of approach directions and local environments, the same basic behavior was observed. The reaction path when H^+ goes through the big-void interstitial is optimal, but the reaction energy and the barrier do not depend strongly on the path.

The entire reaction process happens exclusively between the proton and the Si-H bond and does not involve any other atoms. If the position of the proton is fixed, we observe an increase of the Si-H bond length and a gradual formation of a "bridge" between Si-H and H^+ (Fig. 1b).

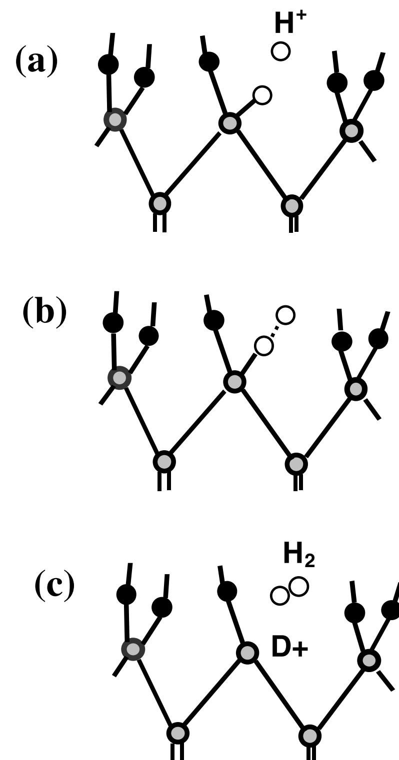

FIG. 1. Reaction between H^+ and an interfacial Si-H bond: (a) a proton approaches an H atom from a Si-H bond; (b) an H^+-H-Si "bridge" is created; (c) an H_2 molecule and a positively charged defect D^+ are formed. Si is shown in gray, O in black, and H in white.

Then both electrons from the Si-H bond leave the bond and make the H_2 molecule neutral. After that, we have a neutral H_2 molecule in the void, and the positively charged D^+ defect at the interface (Fig. 1c). When the position of the proton is not fixed, the motions of the H^+, H, and Si atoms are somewhat more complicated, but the final products of the reaction are the same.

The depassivation process can be traced in detail if we consider electronic density contours in the region around the considered defect (Fig. 2). One can see the originally bare proton approaching the Si-H bond, the formation of the Si-H-H^+ bridge, and the creation of a neutral hydrogen molecule. The absence of electron density near the Si atom at the final stage of the reaction proves that we initially get a positively charged D^+ defect.

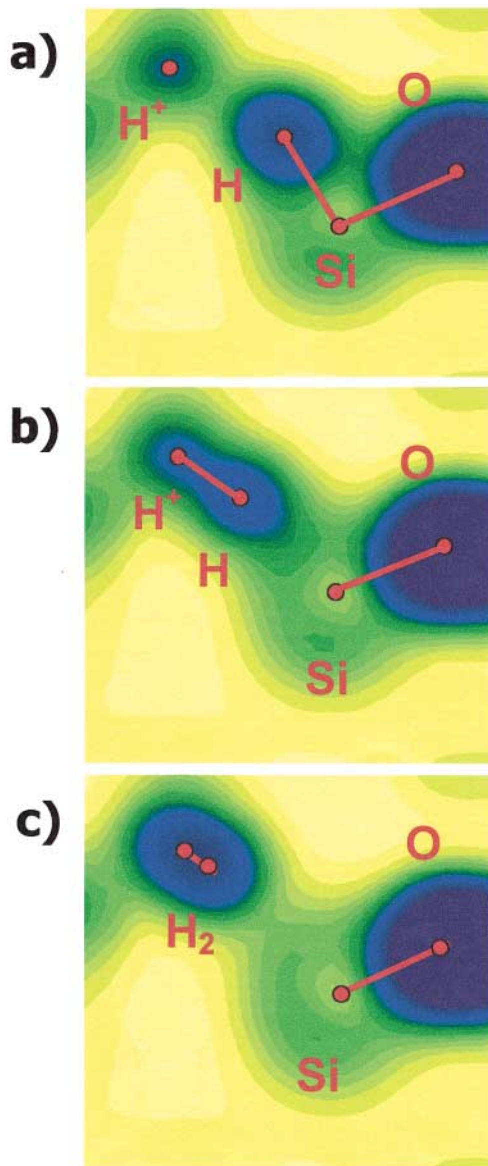

FIG. 2 (color). Electronic density at different stages of the reaction between H^+ and a Si-H bond: (a) a proton approaches a Si-H bond; (b) an Si-H-H^+ bridge is created; (c) an H_2 molecule and a D^+ defect are formed.

As already mentioned, the reaction is initiated when H^+ is approximately 1.6 Å from the H atom in the Si-H bond. Upon completion of the reaction, the total energy release is about 1.3 eV. There is an energy cost, however, to get the H^+ to within 1.6 Å of the other H atom from the nearest O site in SiO_2 or the nearest Si-Si bond on the Si side. This energy, effectively the reaction barrier, depends on the local bonding, but lies in the range 0.2–0.3 eV, roughly the same as the barrier for diffusion in the interface plane. Therefore, the total estimated energy release in the reaction between H^+ and the Si-H bond is about 1.1 eV (Fig. 3).

The barrier for the reverse reaction, namely, passivation of a D^+ defect by an H_2 molecule in an annealing experiment, is 1.3 eV (Fig. 3). If the initial dangling bonds are neutral, the activation energy would be larger by the P_b's ionization energy, which is about half of the Si band gap, i.e., 0.55 eV. Thus the net activation barrier would be 1.85 eV. This value is in excellent agreement with the experimental value reported by Brower [1], namely, 1.66 eV.

The depassivation of the dangling bond and formation of the D^+ defect (positively charged P_b center) occur due to a reaction with a proton that is independent of the availability of electrons at the interface. On the other hand, the subsequent charge state of the defect is independent of possible interactions with hydrogen. Once the defect is formed, it is free to exchange charge with the silicon substrate. The probability of an electron from the Si side getting trapped and neutralizing the dangling bonds depends on the interface electric fields. In particular, under the positive bias conditions that favor H^+ transport to the Si-SiO_2 interface, the Fermi level is located so that the initially charged D^+ defect will capture an electron from the

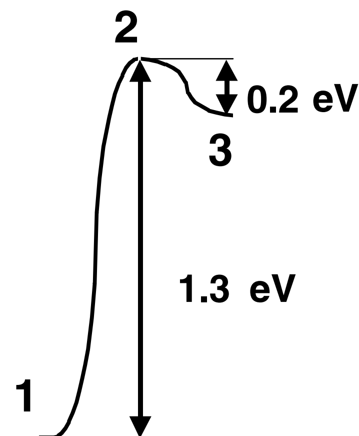

FIG. 3. The energy diagram (reaction energy vs reaction coordinate) for the reaction between H^+ and an interfacial Si-H bond. Point 1 corresponds to the final stage of depassivation (D^+ + H_2); 2: H^+ is in the big void; 3: H^+ is attached to oxygen in the oxide.

Si [1–4], but this transfer is only energetically favorable after the H^+ reaction has been completed.

Combining the present results with earlier results on trapping of H^+ by suboxide bonds [8], we conclude that, when an H^+ arrives at the Si-SiO_2 interface, it can do one of the following: (i) become trapped at a suboxide bond or SiO_2 protrusion [8], (ii) immediately depassivate a Si-H bond, or (iii) migrate laterally until it finds a suboxide bond, a protrusion, or a Si-H bond and react accordingly. Such a behavior confirms the experimental fact that practically all the protons released in an oxide exposed to ionizing radiation eventually react at the interface [26]. In the end, the only defects are H^+ at suboxide bonds that act as "fixed charge" [8,27,28], depassivated dangling bonds that freely trade electrons with the Si substrate, and, of course, free H_2 molecules that can migrate away without breaking up. In the special case of H^+ in a SiO_2 layer (having a high O vacancy concentration) between two Si-SiO_2 interfaces, it is sometimes possible to cycle the protons back and forth by reversing an external electric field [29]. The latter behavior presumably results from H^+ capture at suboxide bonds at a saturation level [8], establishing "walls" that stop a new flux of H^+ until the electric field is reversed.

In summary, we have studied interactions between hydrogen and the (001)Si-SiO_2 interface. We have found that H^+ is the only stable state of hydrogen at an Si-SiO_2 interface. The depassivation of the Si-H bonds at the Si-SiO_2 interface is related to the direct interaction of the proton arriving at the interface with the hydrogen atom in the Si-H bond. This result is contrary to the conventional understanding that H^+ picks up an electron from the Si side first and then depassivates the dangling bond. An important consequence of this result is that interface-trap formation does not depend on the availability or dynamics of electrons from the silicon.

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