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Spontaneous ionization of hydrogen atoms at the Si-SiO_2 interface

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We present a series of electronic structure calculations that demonstrate a mechanism for spontaneous ionization of hydrogen at the Si-SiO_2 interface. Specifically, we show that an isolated neutral hydrogen atom will spontaneously give up its charge and bond to a threefold coordinated oxygen atom. We refer to this entity as a proton. We have calculated the potential surface and found it to be entirely attractive. In contrast, hydrogen molecules will not undergo an analogous reaction. We relate these calculations both to proton generation experiments and to hydrogen plasma experiments.

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I. INTRODUCTION

It is well recognized that hydrogen plays a series of important roles in semiconductors generally and in the metal-oxide-semiconductor (MOS) system, in particular. Starting with the pioneering work of Balk,[1] wherein he showed that a forming gas anneal reduces the number of interface traps, there have been many studies showing that hydrogen participates in the creation and annihilation of electrically active defects in the bulk silicon dioxide and at the silicon-silicon dioxide interface.[2] Furthermore, there is indirect evidence that hydrogen itself forms charged species in the MOS system.[3–7] In irradiated oxides, hydrogen interacts with preexisting, positively charged defects.[3,4] However, in buried oxides, such as layers formed by wafer bonding or by oxygen implantation followed by a high temperature anneal, positive charge can be introduced into the oxide layer during an anneal at ≈600°C in forming gas.[5] Several groups have shown conclusively that this positive charge is mobile in both irradiated thermal oxide and in buried oxides.[3,6] Accordingly, we refer to this positive charge as protons. However, we point out that the nature of the positively charged hydrogen in silicon dioxide has not been conclusively demonstrated experimentally. While there are reports in the literature of an isotope effect on the transport in both types of oxides,[3,6] other groups have tried and failed to see a consistent effect in buried oxides.[8] However, all groups agree that protons are remarkably stable in buried oxides; they can be cycled back and forth between the two silicon-silicon dioxide interfaces without any observed loss of charge.[6,8] This is not the case in irradiated oxides, where protons are annihilated at the same interfaces.[3] We will amplify this point in Sec. V.

The positive charge state of hydrogen has been studied theoretically by several groups.[9–12] There is broad consensus that in the presence of a positive charge, a hydrogen bonds to a network oxygen forming a threefold-coordinated moiety as shown in Fig. 1.

Furthermore, several groups have studied the transport in a variety of approximations.[9–11,14] In these studies the transport is modeled as hopping between oxygen atoms. They found activation energies that are within several tenths of an eV of the experimental estimate obtained by using dispersive transport ideas to analyzing experiments.[3,7] It has also been shown by Kurtz and Karna[14] and by Rashkeev and coworkers[15] that hopping across rings is much more efficient (by ≈0.5 eV) than hopping between nearest-neighbor oxygen atoms. Finally, we note that Pantelides and co-workers have offered an explanation for the greater stability of protons in buried oxides.[15]

While there is now at least theoretical consensus on the nature and transport of protons, there is not yet a cogent discussion of the creation mechanism in neutral, buried oxides. It has long been thought that the silicon substrate must play a role. In this paper, we show theoretical evidence for a simple mechanism through which isolated, neutral hydrogen atoms can become positively charged. This has been studied using clusters in the past.[16] However, their conclusions were significantly different. The rest of the paper is organized as follows. In Sec. II, we present a simple picture of the electronic structure of the interface based on ideas of Reilly[17] that were later adopted by Pantelides and Harrison.[18] As we show, this can be extended naturally to predict protons and even the mechanism for their creation. In Sec. III, we discuss briefly the method used for calculating the electronic structure of this system. In Sec. IV we present our results and we conclude in Sec. V.

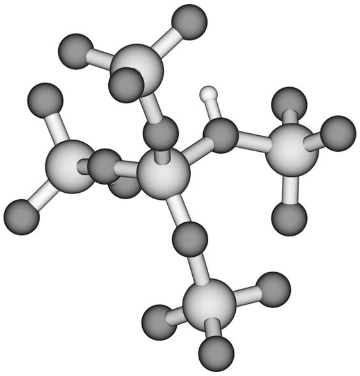

FIG. 1. Equilibrium configuration for proton in silicon dioxide from Ref. 13. Large atoms silicon, smallest atom hydrogen, others oxygen.

II. MODEL FOR PROTON CREATION

As mentioned in Sec. I, Reilly developed a very simple but useful picture of the electronic structure of SiO_2[17] that can be easily generalized for the inclusion of a hydrogen atom. To give context, we review briefly in Fig. 2(a) the original Reilly picture.

The fundamental bonding unit for SiO_2 is actually the Si_2O unit (two silicon atoms facing a central oxygen atom), which exhibits C_{2v} symmetry. To build a picture of the electronic structure, we need consider only the $2p$ orbitals on the oxygen and a pair of sp^α hybrids on the silicon atoms. The symmetric and antisymmetric linear combinations of these hybrids, shown in the upper right-hand corner of Fig. 2(a), are symmetry adapted for C_{2v}. Using the simple rule that only orbitals with the same symmetry character can admix, and using strength of overlap interaction to scale the bonding/antibonding splitting, we can construct qualitative electronic structure for this bonding unit that is seen in the center of Fig. 2(a). We see immediately that the top of the valence band is predicted exclusively to have oxygen lone-pair character. Furthermore, because the isolated oxygen $2p$ manifold is lower in energy than the isolated silicon hybrid manifold, the valence band (the occupied bonding and nonbonding states) will have more oxygen character and the conduction band (the unoccupied antibonding states) will have more silicon character.

We can extend this simple model by placing a hydrogen atom directly above the central oxygen atom while retaining the C_{2v} symmetry, as shown in Fig. 2(b). In this case, the hydrogen $1s$ state has a_1 symmetry and can admix with a valence-band state that is predominantly oxygen $2p_y$-like to form a bonding-antibonding pair. (Note that we are ignoring the interaction with the a_1^* antibonding state because it has primarily silicon character.) The bonding state is hyperdeep and always fully occupied. The antibonding state is half filled in the neutral charge state and empty in the positive charge state. The occupation of the antibonding state leads to two destabilizing effects. First, antibonding states are intrinsically destabilizing as the associated one-electron energy decreases monotonically with interatomic distance, thus favoring dissociation. While it is true that the one-electron energy associated with bonding member of the bonding/antibonding behaves inversely, any occupation of the antibonding state will weaken the bonding interaction. Second, because the one-electron energy level for the hydrogen atom is higher than the a_1 bonding state with which it admixes,[19] the resulting OH bonding state is predominantly oxygen-like, while the antibonding state is predominantly hydrogen-like. If the OH antibonding state is unoccupied, there will be significant ionicity leading to significant Coulombic attraction between the positively charged hydrogen and the negatively charged oxygen. Occupying the antibonding state decreases the net positive charge on the hydrogen atom and this in turn leads to a decrease in Coulombic attraction between the oxygen and hydrogen ions. This difference in occupation of the antibonding state leads to the important consequence that in bulk silicon dioxide in the positively charged state the hydrogen bonds to the oxygen atom, while in the neutral charge state it is repelled.[20]

If the Si_2O-H moiety is *at* the silicon-silicon dioxide interface, the situation can change dramatically. We know from a variety of experimental measurements that, for the Si-SiO_2 system, the conduction band offset is 3.2 eV, the valence-band offset if 4.5 eV, and the electron affinity of silicon dioxide is 0.9 eV. As a first approximation, we superimpose the modified Reilly electronic structure of the Si_2O-H moiety onto the bands of bulk silicon, as shown in Fig. 2(c). We have placed the skeletal levels of Reilly's model such that the non-bonding b_2 state lines up with the experimental silicon dioxide valence-band edge. As the hydrogen atom approaches the interface, the OH separation R_{OH} decreases, pushing the antibonding state upward (indicated by two schematic positions of this level in gray lines) until it is degenerate with the silicon conduction-band edge. At that point the electron in the OH antibonding state can make a transition to a delocalized conduction state and the local electronic structure for the neutral charge state for the O-H unit will again resemble that of the positive charge state. Thus, we can expect the formation of a protonlike species through electron capture into the bulk silicon.

III. METHOD OF CALCULATION

To explore this simple model, we used density-functional theory applied to a supercell of 67–69 atoms with two-dimensional periodicity, shown in Fig. 3(a). Note that we used hydrogen atoms to terminate the upper and lower surfaces of the slab, and that both slab surfaces are, to some degree, oxidized. We will discuss only the more heavily oxidized surface. There are two oxygen atoms on this surface that are bonded directly to the silicon substrate. Throughout this paper we will refer to these as O* and O_{int}. O* is always the oxygen that interacts more strongly with the hydrogen atom(s), while O_{int} is relatively unperturbed. The slabs are separated by 18.5 Å.

The code we used, SEQQUEST, is a gaussian-based solid-state code that incorporates both the local density[21] and the generalized gradient approximation (GGA).[22] We used norm-conserving pseudopotentials to approximate the core electrons. Specifically, we used the Troullier-Martins form[23] for oxygen and the Hamann form for silicon and hydrogen.[24] For most calculations, we used the local-density approximation (LDA), with the Perdew-Zunger parametrization[25] of the Ceperly-Alder free-electron exchange-correlation potential.[26] For selected cases we used the generalized gradient approximation but found no substantial differences. The electronic basis is a split double-ζ basis that includes polarization functions. Finally, for the charged calculations we have used the constant background charge-density approximation for the compensating charge. The equilibrium geometries have been obtained by relaxing all atoms while holding the two-dimensional lattice constant at the experimental value for silicon. We also present some results for the potential surfaces for hydrogen motion. In these cases, all atoms except one (one of the excess hydrogen atoms) were fixed.

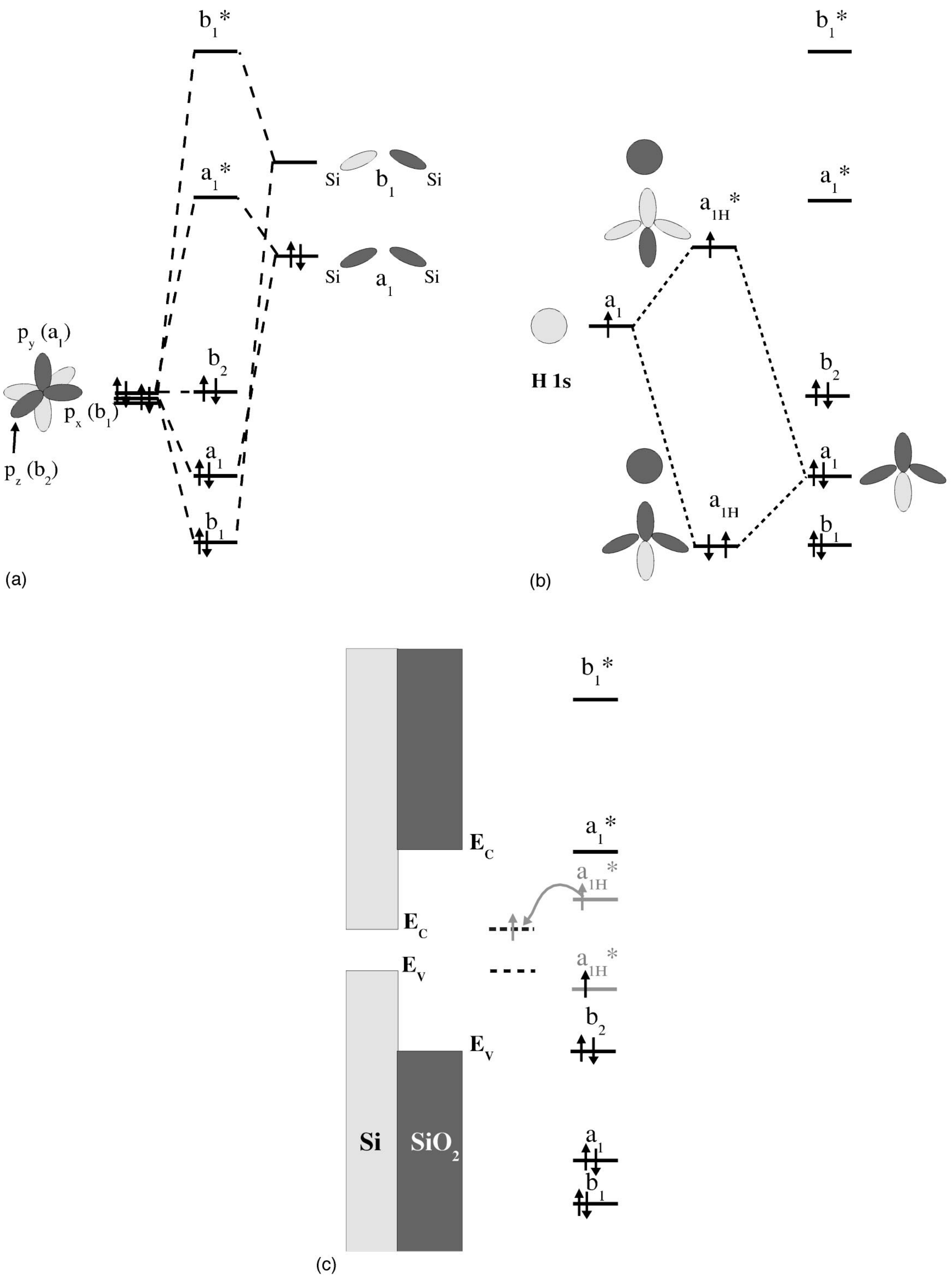

FIG. 2. (a) Simple model for electronic structure of SiO_2. For the orbital cartoons, the shaded area signifies negative (positive) phase. We include the standard labels for the irreducible representations of C_{2v} after Ref. 17(b). Modification of Reilly picture to include hydrogen atom atop Si-O-Si bridge. (c) Same electronic structure superimposed on the band structure of the Si-SiO_2 interface. Upward motion of the antibonding orbital with approach of the H atom toward the interfacial oxygen atom indicated by two gray levels. Silicon band edges represented by two blue lines.

IV. RESULTS

To assure that we have a reasonable model interface, we performed energy minimizations in the absence of any interstitial hydrogen species. Others have used a variety of strategies, including performing molecular dynamics growth[27] and comparing of a variety of periodic models,[28,29] to obtain an *ideal* interface. However, any calculated system is a model system and we need only demonstrate that our structure shares general features with others. The results are

TABLE I. Equilibrium geometrical parameters for proton at the Si-SiO$_2$ interface as a function of total electronic charge on the supercell. All lengths are in Å and all angles are in deg. O* is the interface oxygen to which the hydrogen bonds. O$_{int}$ is the other oxygen atom bonded directly to the silicon interface.

	0	+1
$R_{\text{O*-H}}$	0.99808	1.001
$R_{\text{O*-Si}}$	1.816	1.799
$\angle$Si-O*-Si	137.49	141.09
$R_{\text{O}_{int}\text{-Si}}$	1.659	1.652
$\angle$Si-O$_{int}$-Si	138.77	142.96

shown in Fig. 3(b). As seen by other groups,[18,28] the strain in the SiO$_2$ network is relieved within the first two monolayers. Also, the silicon-oxygen distance on the surface dimer is larger than in bulk SiO$_2$, as expected from simple ionicity arguments.

In Fig. 3(a) we show the equilibrium geometry for a neutral hydrogen atom at the Si-SiO$_2$ interface. Note that it has formed a threefold moiety, very similar to the proton in bulk SiO$_2$. To reinforce our identification as a proton, we performed the same calculation removing one electron and compensating it with a uniform background charge. A quantitative comparison is shown in Table I.

The geometrical differences between these two charge states are small indeed. Thus, our simple model passed the first test. There is a local minimum energy configuration for the neutral species that is nearly identical to the proton in bulk SiO$_2$. For this to be important, the activation energy for the bond formation needs to be small. We have calculated a two-dimensional potential surface in the plane containing both surface oxygen atoms and the proton. This is shown in Fig. 4.

The most remarkable feature is the lack of barrier to formation of the proton by attachment of a neutral hydrogen atom. This attraction, while surprising, can be understood through a delocalization and concomitant lowering of kinetic energy of the antibonding electron as it enters the silicon conduction band. We note, however, that the LDA and GGA have predicted unphysical delocalization in certain systems.[30]

To probe the electronic structure, we show in Fig. 5 the atom-projected density of states for an isolated hydrogen atom and for the proton.

For both Figs. 5(a) and 5(b), the expected behavior for silicon atoms in the bulk of the substrate and for oxygen atoms far from the interface are almost identical to the behavior in bulk silicon and a-SiO$_2$, respectively. In the former case, we see a single valence-band that is ~18 eV wide and a band gap of ~0.6 eV, while in the latter case there are three separate sets of valence-bands with a total width of ~20 eV and a band gap of ~6.5 eV. In order of lowest to highest energy, the three sets of valence-bands correspond to the O-$2s$ semi-core bands, O-$2p$ bonding bands, and O-$2p$ nonbonding bands. Finally, the valence-bands for the bulk O and bulk Si atoms are offset by ~3 eV. These results are similar to those reported by Kaneta,[31] and by others later.[15] Note that, as is usual with the Kohn-Sham eigenvalues, the band gap for both materials is underestimated, as are the band offsets in both the valence and conduction bands. For these reasons, the one-electron results reported here should only be used for qualitative insight. In Fig. 5(a), we show our results for the isolated hydrogen atom. Qualitatively, the density of states meets our expectations; there is one predominant peak associated with the H-1s state. Interestingly, this is predicted to be near the bottom of the Si conduction band, and in the lower half of the silicon dioxide band gap. In Fig. 5(b), we see that there are three strongly localized states with significant H 1s content. The lowest, clearly an O2s-H1s combination, is outside our simple model, but is obviously symmetry allowed. The state at ~-15.6 eV is the Op_z-H1s admixture anticipated in our model. Finally, the antibonding orbital is at -0.6 eV, well above the silicon conduction-band edge, as predicted. There is one electron in the state at the bottom of the silicon conduction band. Note that there is significant contribution from both the surface dimer oxygen and the bulk silicon atom. The relative O-H content in the bonding-antibonding pair is consistent with the level positions in Fig. 5(a) and with our initial assumptions. That is, the bonding (antibonding) state has a preponderance of oxygen (hydrogen) character. This lends support for calling this moiety a proton.

To explore the effects of large hydrogen densities, we have studied H$_2$ and 2 H° (two neutral hydrogen atoms) in our unit cell. In Fig. 3(c) and in Table II we show the calculated equilibrium geometry of H$_2$ at the interface. It sits at the center of a large cavity. Note that one interface oxygen, which we label O*, is noticeably perturbed by the presence of the hydrogen molecule. The associated Si-O*-Si angle is larger by 18° in the presence of H$_2$.

Population analysis reveals that the molecule loses either 0.14 e or 0.03 e, depending on the method of calculation (Löwdin or Mulliken, respectively). Either result would lead one to conclude that the hydrogen molecule is little perturbed by the presence of the rest of the solid. The projected density of states , Fig. 5(c), exhibits a broad, double-peaked distribution of states deep in the oxide valence-bands. From inspection of eigenfunction coefficients, we have confirmed that the two peaks are derived from the $1s\sigma$ bonding state. In fact, calculation of the density of states for isolated H$_2$ place the bonding state at -10.1 eV, between the two hydrogen peaks in Fig. 5(c). The eigenfunctions corresponding to the peak energies have the largest amplitudes on the oxygen sublattice.

We have also calculated a dissociation potential surface

TABLE II. Relevant geometrical parameters for H$_2$ near Si-SiO$_2$ interface. Isolated refers to gas-phase H$_2$ and to the model interface shown in Fig. 3(b). Interacting refers to the system shown in Fig. 3 (c). All distances are in Å. All angles in degrees.

	Isolated	Interacting
$R_{\text{H-H}}$	0.766	0.768
$R_{\text{Si-O*}}$	1.65	1.64
$\angle$Si-O*-Si	141	159

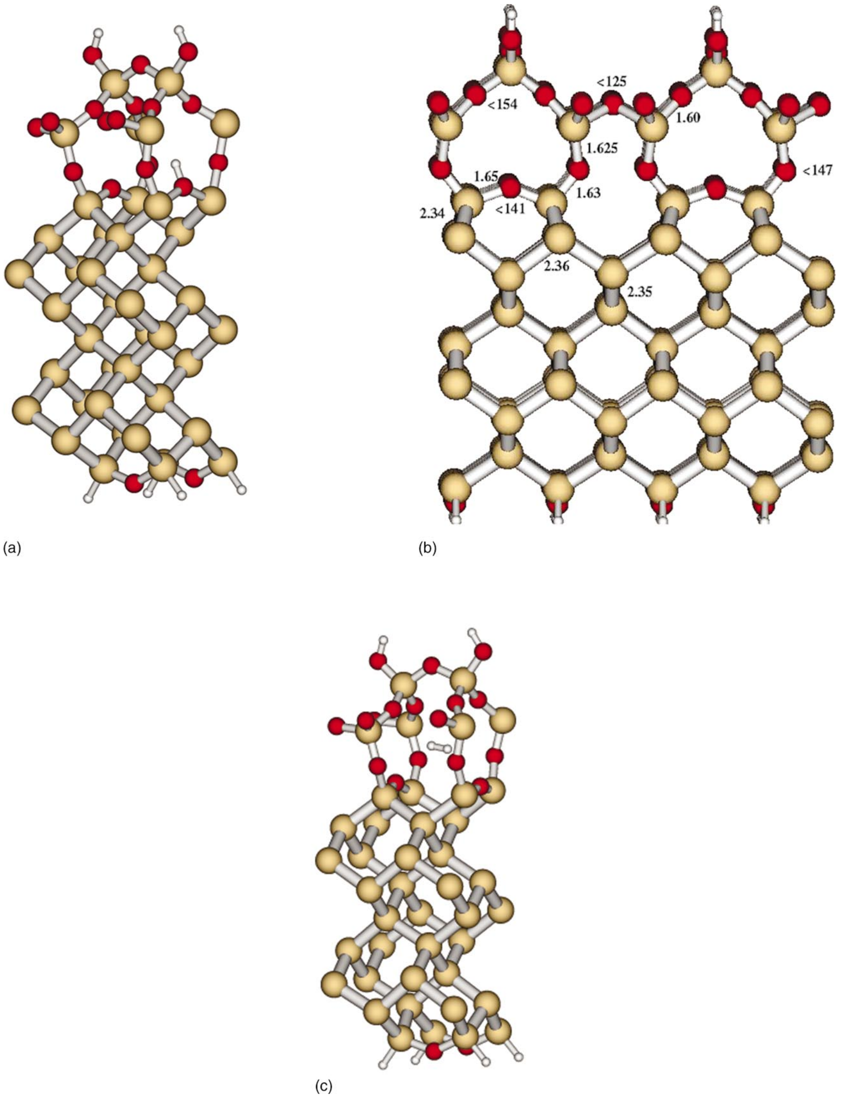

FIG. 3. (Color) (a) Supercell used for current study. Also the equilibrium geometry for neutral hydrogen at the interface. (b) Equilibrium geometry or model interface. Four unit cells shown. (c) Equilibrium geometry for H_2 at the interface. Gold atoms are silicon, red atoms are oxygen, and white atoms are hydrogen.

that would lead to proton formation. That is, starting from the H_2 equilibrium geometry, we have held one hydrogen atom fixed and moved the other in the same plane as was done in Fig. 4(a). The results are shown in Fig. 4(b). We see that the there is only a very small metastable minimum at the equilibrium proton geometry, and that this is 2.5 eV higher than the H_2 equilibrium energy. Stated differently, if a neutral hydrogen atom approaches a proton, these calculations indicate that it would pull the proton from the surface and form H_2.

V. DISCUSSION

Before we discuss experiments with H at the interface relative to protons, we would like to point out the strong analogy of this system to H and H_2 interactions with dangling silicon orbitals. The reaction

$$\equiv \mathrm{Si} + \mathrm{H}_2 \rightleftharpoons \equiv \mathrm{Si}-\mathrm{H} + \mathrm{H} \tag{1}$$

is endothermic going left to right, and also displays no barrier to back reaction as in proton formation from H_2. The simple Si-H bond dissociation is endothermic as is proton dissociation at the interface. The difference here is that the activation energy for the forward reaction in Eq. (1) is almost a volt higher for the proton case.

Cartier and co-workers have performed remote-plasma hydrogen anneals in which they were fairly confident that monatomic hydrogen is arriving at the Si-SiO_2 interface.[32] They have observed generation of anomalous positive charge that one might want to identify as protons. However, the bias dependence of anomalous positive charge is opposite to that for protons. That is, under positive gate bias, anomalous positive charge at the substrate-SiO_2 interface decreases, while that for protons increases. We note, however, that the hydrogen density in their experiment was very large, and thus our calculations predict that protons at the surface would readily react with hydrogen atoms to become hydrogen molecules.

Vanheusden *et al.* have performed a careful annealing study to elucidate creation and annihilation kinetics.[33] Their data were consistent with diffusion-limited growth from the edges of the device. Furthermore, the final proton density depended on the rate at which the sample was cooled. Maximum proton densities were observed with the greatest cool-

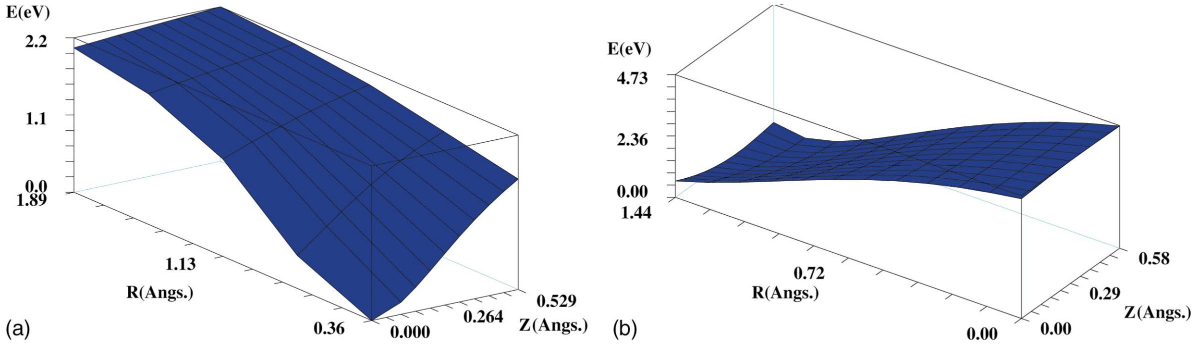

FIG. 4. (Color) Two-dimensional potential-energy surfaces for H (a) and H_2 (b) near the Si-SiO_2 interface. Z is normal to the interface. R is along the O*-O_{int} direction. The orientation of both surfaces is the same; $R,Z=0.0,0.0$ is the equilibrium geometry for the proton bonded to O*

ing rate. To explain this result they assumed that there indeed was a creation mechanism similar to

$$H^0+X \rightleftharpoons H^+ + X + e^- \tag{2}$$

and that the forward and reverse directions dominate at high and low T, respectively. Furthermore, they posited a kinetic equation [Eq. (3)]

$$\frac{d[\mathrm{H}^+]}{dt} = +k_f[\mathrm{H}^0][X] - k_r[\mathrm{H}^+][X]. \tag{3}$$

They assumed that the forward and reverse reaction rate constants, k_f and k_r, are activated. They even mentioned the bridging oxygen at the Si-SiO_2 interface as a possible instance of X in Eqs. (2) and (3). However, this possibility is not supported for the forward reaction by our calculations. Because this center has a huge ideal density, it is likely to be important in the physics of proton formation, but other kinetics equations must apply for this to be true.

When we combine the results for isolated neutral hydrogen atoms and for hydrogen molecules at the Si-SiO_2 interface, we obtain two pictures for high- and low-H concentrations. At low concentrations, hydrogen atoms will spontaneously ionize to form protons. When there is a large concentration of hydrogen molecules, our model requires prior dissociation (presumably at defect) into hydrogen atoms, and this would lead to a low concentration of monatomic species within a very high-H_2 concentration. When the concentration of monatomic hydrogen reaches a critical value, for which neutral hydrogen atoms would encounter

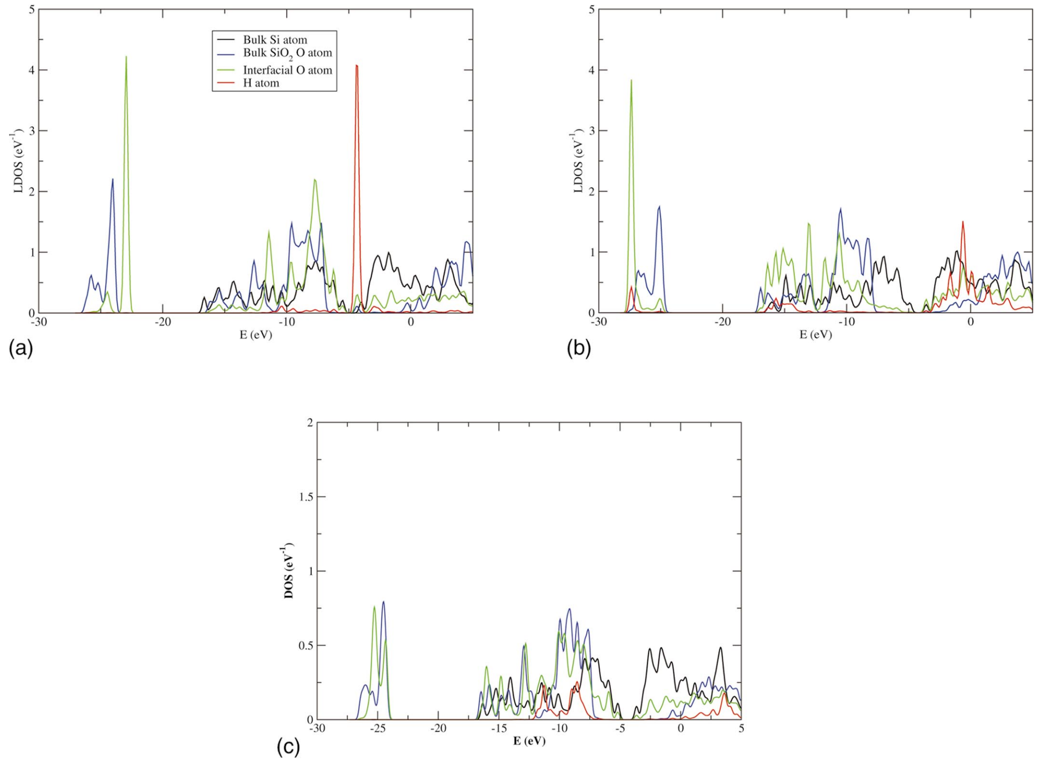

FIG. 5. (Color) Atom-projected density of states for an isolated hydrogen atom (a) , for a hydrogen atom bonded to interface in protonic equilibrium (b), and for a hydrogen molecule near the interface (c). Legends are the same in (a)–(c)

previously formed protons, these would be annihilated with high efficiency. This is consistent with the Cartier experiments and could explain why the maximum density of protons is fairly low.

VI. CONCLUSION

We have performed local-density functional calculations for neutral hydrogen atoms and molecules interacting with bridging oxygen atoms at the Si-SiO_2 interface. These calculations show that a neutral hydrogen atom can participate in threefold coordination of the oxygen atom by donating an electron to the silicon conduction band. Furthermore, it does so without an activation barrier. Neutral hydrogen molecules do not spontaneously dissociate. In fact, a neutral hydrogen near a proton will cause it to dissociate from the bridging oxygen atom without a barrier to form H_2 and gain $\approx$4.7 eV.

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