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Reactions of excess hydrogen at a Si(111) surface with H termination: First-principles calculations

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Hydrogen reactions with silicon substrates is an established technique for the study and control of surface morphology. Here, we report the results of first-principles calculations on the trapping and depassivation reactions involving excess hydrogen (*x*-H) at a fully H-passivated Si(111) surface. We find that *x*-H atoms can depassivate Si-H bonds with a small barrier of 0.8 eV, or they can get trapped in very stable configurations that comprise of a dihydride and a vicinal Si-H bond. Desorption of H_2 molecules from these complexes has an activation energy of 1.68 eV, which can account for pertinent experimental data. We discuss also the effect of strain on the possibility of altering the *x*-H surface profile.

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The interaction of hydrogen with substrates is a topic of fundamental interest in surface physics. In the case of silicon, for example, hydrogen is known to passivate dangling bonds, rendering a generally chemically inert surface. In addition to its technological significance, silicon surface passivation through hydrogenation has been used extensively as a probe of adsorbate-surface interactions. Among the most important issues is the effect of H deposition on surface reconstruction, especially on the 7×7 reconstruction of a Si(111) surface.[1,2] H surface reactions are also important for amorphous thin films[3] and porous[4,5] silicon.

In the ideal case, a full H coverage of one monolayer (ML) can eliminate all dangling bonds and lead to an inert Si(111) surface with monohydride Si-H bonds. H deposition, however, is known to create also higher hydrides[1,2,6–10] on a Si(111) surface with an initial 7×7 reconstruction. The existence of dihydrides and trihydrides has been associated with high Si-H bond stretch frequencies and with experimental results utilizing temperature programmed desorption (TPD).[6] In particular, typical TPD experiments show two peaks, termed β_1 and β_2, which are commonly assigned to H_2 desorption from monohydrides and higher hydrides, respectively.[1,2,6] Calculations[11,12] have largely accounted for the barrier of the β_1 peak. The atomic-scale details of the β_2 desorption process, however, remain elusive. Consistent with the existence of higher hydrides, in certain cases, an oversaturation of a Si(111) surface has been observed with H coverage that ranges between 1.23 ML and 1.5 ML.[1,2] Because of this fact and because complete experimental control on coverage is difficult, it is useful to probe the fate of any excess amount of hydrogen deposited as a passivating agent on a Si surface and investigate its role in the appearance of the β_2 TPD peak.

In this work, we use first-principles calculations to investigate the affect of excess hydrogen (*x*-H) on a Si(111) surface. Specifically, we study the reactions of a single *x*-H atom or a *x*-H pair with Si-H bonds on the so-called Si(111) 1×1:H surface with monohydride termination. 1×1:H domains are known to grow during H deposition on a 7×7 Si(111) surface.[1] 1×1:H surfaces with limited numbers of defects can also be prepared either through HF etching[8] or H deposition on a 7×7 surface at elevated temperatures.[13] For this reason, the use of the 1×1:H surface not only simplifies the calculations, but also facilitates comparison with experimental results obtained through a variety of conditions. In the case of a single *x*-H atom, we find a barrier of 0.8 eV for its reaction with a surface Si-H bond that leads to H_2 desorption and formation of a surface dangling bond. Such depassivation reaction can thus be active even at room temperature. We find, however, that, in addition to depassivation, two excess H atoms can be trapped in a very stable complex with a surface Si-H bond. The corresponding H_2 desorption barrier is 1.68 eV in agreement with observations on the β_2 TPD peak. The Si-H vibrational frequencies of these complexes are also in good agreement with experimental findings for higher hydrides on Si. Finally, we find that strain can have a pronounced effect on the relative stability of different *x*-H surface configurations.

The calculations were performed using density-functional theory, a generalized-gradient corrected exchange-correlation functional,[14] plane waves as a basis set, and ultrasoft pseudopotentials,[15] as implemented in the VASP code.[16] The cutoff for the plane wave basis was set to 300 eV. Use of a 350 eV cutoff for selected cases confirmed convergence of results. We used periodic supercells with 8 Å of vacuum between slabs in the surface (111) direction. Both sides of the slab were passivated with hydrogen and the H atoms were kept fixed on one side. Supercells with a varying size were considered to check convergence of total energy differences associated with trapping. Specifically, we used $6\times6\times8$ (i.e., eight layers of Si with 36 atoms in each layer), $6\times6\times6$, and $4\times4\times4$ slabs. Brillouin zone sampling was performed with two *k* points.[17] Sampling with four *k* points confirms convergence (within 0.02 eV) for the energy differences between studied trapping configurations. Reaction barriers were calculated for the $4\times4\times4$ supercells using the elastic band method[18] with no spatial constraints around the reaction center.

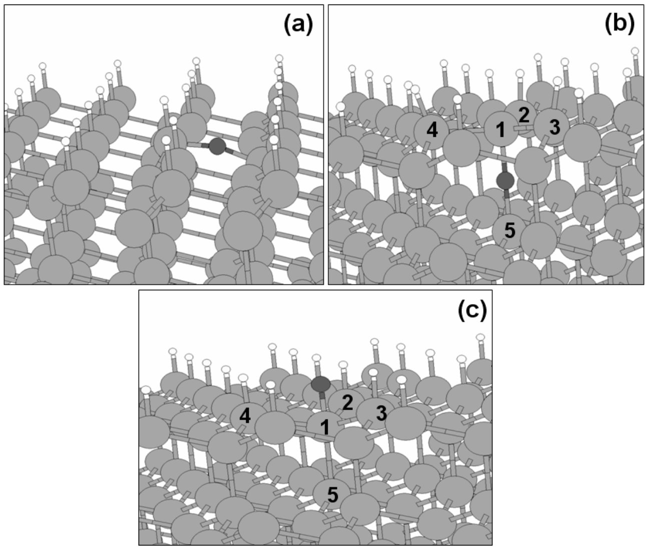

FIG. 1. Bonding configurations for an excess H atom at the H-terminated Si(111) surface: (a) surface, and (b) subsurface Si-H-Si bridge, (c) excess H at a surface antibonding site. (Si, gray; H, white; excess H, dark gray spheres.)

We start by discussing our results for the case of a single excess H atom found at a 1×1:H surface. The configurations we considered as possible trapping sites are shown in Fig. 1. They correspond to (a) an extra H atom in Si-Si bridge configuration next to a surface Si-H bond, (b) an extra H in a subsurface Si-Si bridge, and (c) an extra H at the antibonding site of a surface Si atom. The subsurface bridge of configuration (b) is found to be the most stable among the three studied. In the following we use the numbering of atoms shown in the figures as superscripts for atom labels. The bond length between the excess H atom of Fig. 1(b) and Si^1 (Si^5) is 1.70 Å (1.69 Å). The surface Si atoms 1–4 are almost planar with a 1-2-3-4 torsion of 5.8°. Configurations (a) and (c) have energies higher compared to (b) by 0.22 eV and 0.36 eV, respectively. These results are summarized in Table I. In the former case, the bond lengths between x-H and its neighboring Si atoms are 1.62 Å and 1.67 Å. In configuration (c) the Si^1-Si^5 bond is weakened to 2.53 Å, and the x-H is at a distance of 1.57 Å from Si^1.

We considered the possibility of the x-H atom to interact with a surface Si-H bond and create a dangling bond through a depassivation reaction,

$$\text{Si-H-Si-H} \rightarrow \text{Si-Si}^* + \text{H}_2. \tag{1}$$

In process (1) Si^* is a surface dangling bond and the initial configuration contains a surface Si-H bond and a Si-H-Si bridge in one of its backbonds, as shown in Fig. 1(a). The reaction barrier is only 0.8 eV. Taking into consideration the energy difference between configuration (a) and (b) in Fig. 1, the effective barrier for a depassivation reaction starting from the latter configuration is about 1 eV. This depassivation barrier is close in value to the result found at the Si-SiO_2 interface[19] and room or slightly elevated temperatures can allow its activation and the creation of dangling bonds.

TABLE I. Energies E_t for excess hydrogen at an H-passivated Si(111) surface. Reference energy is for the Si-H-Si bridge configuration of Fig. 1(b). For the 3H complex of Fig. 2(a) E_t is per excess H atom.

Configuration	Figure	E_t (eV)
Surface Si-H-Si bridge	1(a)	0.22
Subsurface Si-H-Si bridge	1(b)	0.00
Antibonding site	1(c)	0.36
3H complex	2(a)	−1.20

The depassivation process (1) competes with another reaction pathway at the surface that releases excess H in a molecular form without disrupting the degree of passivation. The precursor of this pathway is a complex that involves *a pair of excess H atoms* that together with a passivated Si-H bond form a *three-atom H complex* involving a dihydride and a vicinal Si-H bond. This configuration, denoted hereafter as 3H, is shown in Fig. 2(a). A similar atom arrangement was found for small clusters used by Que *et al.*[20] to simulate the adsorption of hydrogen on adatoms and rest atoms of a Si(111) 7×7 surface. We also found configurations reminiscent to the 3H complexes to be present during hydrogen exchange at the Si-SiO_2 interface.[21] The structural details of the 3H complex are as follows: all lengths of H atoms numbered 1 to 3 in Fig. 2(a) to Si atoms 4 and 5 are 1.5 Å. The Si^5-H^2-Si^4 angle is 160° and the Si^4-H^2 distance is 2.1 Å. The H^1-Si^4-H^3 angle is 104° and the four atoms H^1, Si^4, H^3, and Si^5 are coplanar.

The 3H configuration has a trapping energy of 1.2 eV per excess H atom as compared to two isolated configurations (b) described above for single x-H. The 3H complex is, therefore, a very efficient surface trapping site for excess H. Its creation depends on kinetics, and specifically, on the H-deposition rate as well as substrate temperature. Excess H atoms may find themselves in pairs and get trapped in 3H complexes at the surface, they can participate in a depassivation process (1), or they can migrate into the bulk crystal where they can get trapped in other configurations, such as oxygen clusters.[22] Varying the deposition rate and temperature can enhance the possibility of having one of the above processes over the others.

The 3H complex can be thought of as a storage configuration for hydrogen on a Si surface, and we investigated possible release mechanisms from such sites. The transition state of the minimum energy pathway, and the initial (3H) and final (released H_2) configurations, are shown in Fig. 2. The release barrier for this pathway is 1.8 eV and the process is exothermic by 0.9 eV. We obtained also the local vibrational modes of the complex that includes the three H atoms and the Si atom number 4 in Fig. 2. The zero-point energies for the initial and transition state are 0.68 eV and 0.56 eV, respectively, and they modify the 3H desorption barrier to 1.68 eV. The individual stretch modes are found to be (i) 2093 cm^{-1} for the mode dominated by Si^4-H^3 vibrations, (ii) 2154 cm^{-1} for the mode dominated by Si^4-H^1 vibrations, and (iii) 2160 cm^{-1} for the mode dominated by Si^5-H^2 vibrations. The H^3-Si^4-H^1 scissor mode has a frequency of 956 cm^{-1}. In

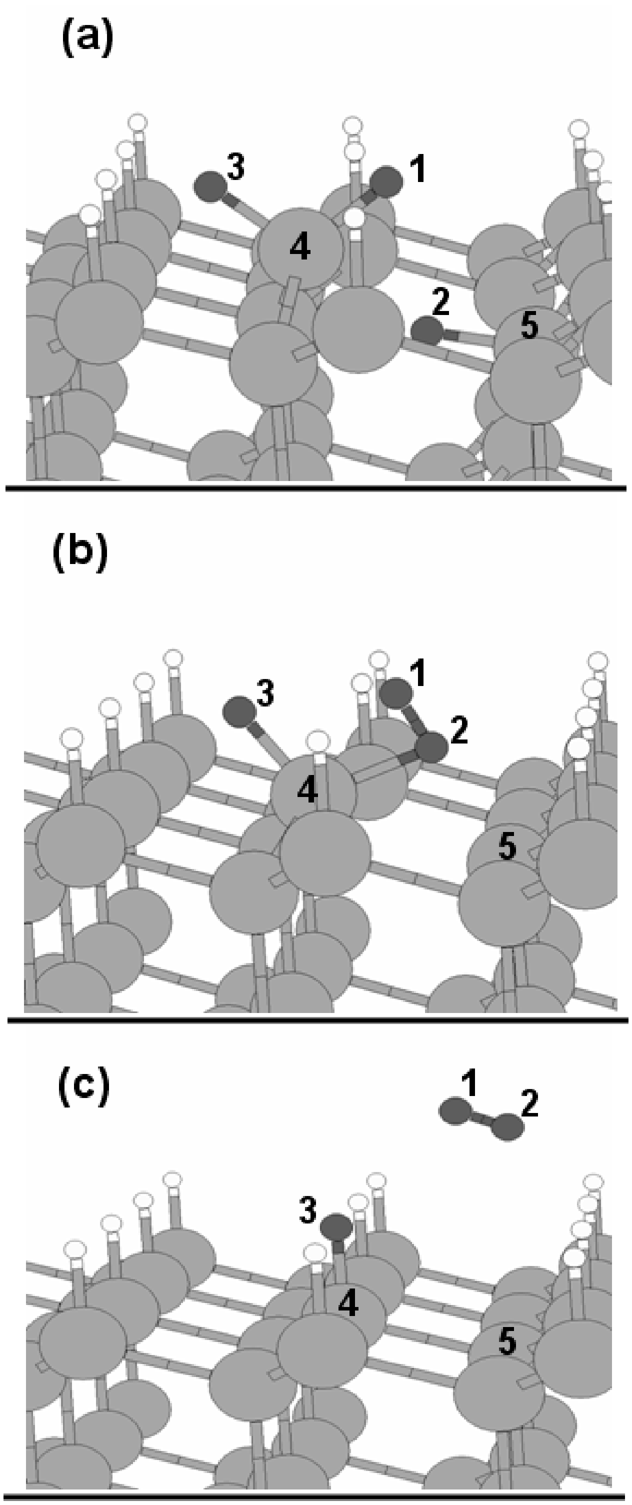

FIG. 2. Release of H_2 from a trapping configuration (termed 3H) for excess H at a Si(111) surface. (b) is the transition state (barrier of 1.68 eV) between (a) initial and (c) final states. (Si, gray; H, white; excess H, dark gray spheres.)

addition to the atoms mentioned, all these modes have small but non-negligible amplitudes on all other atoms of the 3H complex.

We note that, even though the depassivation barrier of process (1) is only 0.8 eV, the effective activation energy including the 3H 1.2 eV trapping energy is much higher than the barrier of the process shown in Fig. 2. Assuming therefore that kinetics favor the creation of 3H complexes, the latter process is the most likely desorption reaction for excess H. Another possible desorption pathway starting from Fig. 2(a) leads to formation of an H_2 molecule out of atoms H^1 and H^3, while H^2 moves to passivate the dangling bond of Si^4. This pathway proceeds through the simultaneous desorption of H^1 and H^3 and the barrier is significantly higher (about 2.6 eV) than the barrier for the process depicted in Fig. 2.

We studied also the effect of strain on the trapping of x-H on a Si(111) surface, in particular, for Si on a Ge substrate and for Si under in-plane compression. We found that for a Si(111) surface grown on Ge, the relative stability of H at the surface changes for the configurations (a) and (b) of Fig. 1. Specifically, configuration (a) has lower energy as compared to (b) by 0.25 eV. The trend naturally reverses if one assumes a compressive strain for the surface. In the case of a large 4% reduction of the in-plane lattice constants, configuration (b) is lower in energy as compared to (a) by 0.67 eV. The most stable trapping site, however, for x-H at the surface under 4% compression is configuration (c) of Fig. 1, for which the energy is 1.43 eV and 0.76 eV lower than configurations (a) and (b), respectively. In this case, the Si^1-Si^5 bond is broken to 3.55 Å, and the x-H forms a regular Si-Hbond of length 1.51 Å with Si^1. The surface Si atoms from 1 to 4 are not planar as is the case in the absence of compression. Trapping of a pair of x-H atoms in a 3H complex results in an extra energy gain of 1.05 eV per x-H atom, as compared to configuration (a). Compression can therefore alter the surface profile of any isolated x-H, whereas the stability of 3H complexes remains largely unchanged for a substrate under strain.

As noted above, experimental evidence for the existence of higher hydrides on a Si(111) surface relate to vibrational frequencies[3,7–9] ($2110\ \mathrm{cm}^{-1}$ to $2154\ \mathrm{cm}^{-1}$) for the Si-H stretch modes that are higher than the value for isolated Si-H bonds. A second major evidence is the appearance of the β_2 TPD peak at about 620 K with corresponding activation energies between 1.5 eV and 2 eV (Refs. 6, 10, and 23 for either crystalline or porous Si. There have been suggestions that the β_2 peak relates to H complexes to be found at defects, such as adatom islands or steps,[1,2] of the 7×7 Si(111) surface. To the best of our knowledge, however, no calculations have identified the atomic-scale details of configurations that are consistent with the β_2 barriers. Our results for the 3H complex are in agreement with the observations, including the value of the calculated barrier (1.68 eV) and the higher vibrational frequencies ($2154–2160\ \mathrm{cm}^{-1}$). Such complexes can be found either in 1×1 domains, or in a similar form[20] on reconstructed parts of a Si(111) 7×7 surface under H exposure.

Recently, the experimental findings of Liu *et al.*[24] on H_2 desorption at room temperature have added to the interest in reactions of H at a Si(111) surface. The technique based on resonant excitation[24] of the Si-H bond stretch mode using intense free electron laser irradiation offers the possibility for new types of investigations on this long-studied system. Since the H_2 desorption in the work of Ref. 24 was observed for a monohydride surface with no β_2 TPD peak, the mechanisms described above for the 3H complex do not apply. However, we should note that resonant excitation can be used to control hydrogen release also in the case that 3H complexes are indeed present at a Si(111) surface. A two-photon resonant excitation of the 3H-complex stretch modes can reduce the effective desorption barrier to a value that is consistent with activation at slightly elevated temperatures. A three-photon excitation can apparently enable the facile release of H_2 molecules even at room temperature. Let us also mention that, depassivation reactions involving excess H can interfere with the creation of templates of dangling bonds[25] on a silicon surface and its possible use for patterned growth of organic thin films.[26]

In summary, we studied possible bonding configurations and reactions of excess hydrogen at a fully H-passivated Si(111) surface. We find that excess hydrogen can react to depassivate surface Si-H bonds with a barrier of 0.8 eV. Alternatively, it can be trapped in very stable complexes involving a pair of atoms and a surface Si-H bond. H_2 desorption from these complexes has a barrier of 1.68 eV and it can account for pertinent experimental data on temperature programmed desorption. We have also considered the effect of compressive and tensile strain on the relative stability of different bonding configurations for excess H.

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