H$_2$ adsorption/desorption at Si(111)-(7 x 7): a density functional study

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Abstract

The interaction of H$_2$ with the Si(111)-(7 x 7) surface is investigated by means of density functional slab calculations on a (4 x 2) reconstructed model surface. A viable mechanism for F$_2$ desorption is identified, which involves thermally activated SiH$_2$ units at adatom sites. This mechanism leads to adsorption and desorption barriers of 1.0 and 2.4 eV, respectively, in agreement with experiment. An explanation for the two components observed in the F$_2$ peak of temperature-programmed desorption spectra is proposed. The lattice deformation energy at the transition state for desorption is large (~ 0.6 eV). If we assume that this remains in the surface after H$_2$ desorption, the low translational energy of desorbing molecules which has been observed experimentally can in part be explained. © 1997 Elsevier Science B.V.

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The interaction of hydrogen with silicon surfaces is a subject of intensive research [1-3]. In particular, the question of the mechanism for the recombinative desorption of H$_2$ has been widely debated [3]. The interpretation of the experimental data is controversial, especially in the case of Si(100)-(2 x 1), for which several theoretical calculations have been performed. Density functional (DF) calculations carried out on slab models [4-7] suggest the viability of the so-called “pre-pairing” mechanism, where the two hydrogens desorb from the same dimer unit. In contrast, cluster calculations of various degrees of computational sophistication [8-10] rule out such a pre-pairing mechanism because of the activation energy is too high (> 3 eV), and instead predict desorption paths based on isolated silicon dihydride (SiH$_2$) defects [11-14]. In an attempt to understand the origin of such a discrepancy, ab-initio and DF calculations for small silicon-based molecules have been compared [15]. The results, however, are not conclusive, as the relative accuracy of the different gradient-corrected exchange-correlation functionals used in DF calculations has not yet been established in the case of extended systems, for which high-level ab initio calculations are not practical [16].

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In this paper we focus our attention on the adsorption/desorption of H\textsubscript{2} at Si(111)-(7 × 7). For this surface, experiments have shown that desorption obeys an approximately second-order kinetics with an activation barrier of \( \sim 2.5 \text{ eV} \) [17–20]. As for Si(100)-(2 × 1), sticking-coefficient measurements have shown that adsorption is activated with an effective barrier of \( 0.87 \pm 0.1 \text{ eV} \) [21]. Vice versa, time-of-flight measurements have shown no excess translational kinetic energy of desorbing H\textsubscript{2} molecules [22].

Because of the complexity of the surface reconstruction [23], no theoretical calculation has so far been performed for H\textsubscript{2} adsorption/desorption at Si(111)-(7 × 7). We have previously found that H binding and diffusion on this surface can be modeled satisfactorily using a smaller (4 × 2) supercell taken on a (2 × 2) adatom-reconstructed surface [24] (see Fig. 1). Results obtained for H diffusion reproduce the experiment well [25], and also yield binding energy differences between restatom (R) and adatom (A) sites which agree with calculations performed on the full (7 × 7) surface [26]. Moreover, these calculated energy differences compare well with estimates obtained from desorption studies [20]. In contrast, cluster calculations [27] give poorer results, with too large a binding energy difference between A and R sites. In this paper we intend to extend our DF studies of hydrogen interactions with the (7 × 7) surface by identifying a possible mechanism for H\textsubscript{2} adsorption and desorption on this surface.

Our calculations have been performed using the DF pseudopotential plane wave method within the framework of the Car–Parrinello (CP) scheme [28]. Geometry optimizations have generally been carried out using the local density approximation (LDA), while the energies of all the relevant minima and saddle points have been recalculated using the generalized gradient approximation (GGA) in the form proposed by Becke [29] and Perdew [30]. Norm-conserving pseudopotentials and a local pseudopotential have been used for Si and H, respectively. LDA and GGA pseudopotentials were taken from Ref. [31] and Refs. [32, 33], respectively. The wave functions were expanded in plane waves with energy up to 16 Ry, and only the \( \Gamma \) point of the Brillouin zone was sampled.

The Si(111) surface is modeled as a repeated slab, each slab consisting of six layers. The experimental value of the bulk lattice constant is adopted. The unit cell has eight Si atoms per layer, corresponding to two primitive (2 × 2) cells, plus two Si adatoms on the top surface. The Si adatoms are located at the so-called \( T_4 \) sites, i.e. the three-fold sites above second-layer Si atoms. Each of these unit cells has four dangling bonds (DBs), two associated to the restatoms and two to the adatoms. Because the energy of the restatom DBs is lower, the DBs at the A sites turn out to be empty, whereas it is known that the adatom DB states are partially filled in the (7 × 7) surface. To model this property, we introduce an extra H on the surface to saturate one of the two restatoms. In this way, the number of available adatom DBs is twice the number of restatom DBs, and the adatom DB states are partially filled, as in the true (7 × 7) surface. The fulfillment of such conditions was found to be crucial in order to describe H diffusion and binding on the (7 × 7)-reconstructed surface [24].

All relevant H atoms are chemisorbed on the top surface only. The other surface is kept in a bulk-terminated structure and is saturated by eight (irrelevant) H atoms. The four topmost Si layers as well as the Si adatoms and the chemisorbed hydrogen(s) are allowed to relax. Constraints in the optimization procedure (as used, for example, in the search of transition states, or more generally...
in sampling of the potential energy surface) were introduced via the shake algorithm [34].

The reference configuration for our H$_2$ desorption calculations consists of two hydrogens sitting at A and R sites. A further hydrogen, adsorbed on the other restatom site (R', see Fig. 1), is introduced with the sole purpose of keeping the correct A/R ratio of available DBs on the surface (see the discussion above). All the energies in the following will be given relative to this configuration. In particular, for the desorption energy, i.e. the difference between the energy of non-interacting H$_2$ and the surface and the energy of our reference configuration, we obtain $\Delta H = 1.42$ eV (LDA: 1.74 eV). Unless otherwise stated, all reported energies are at the GGA level.

In a first series of calculations, we explored the possibility of desorbing H$_2$ by simply approaching the two H atoms at the A and R sites, without causing any major surface deformation (e.g. backbond breaking). We placed the center of mass of H$_2$ at different positions along the R–A direction between the two on-top sites, and for each position we considered a number of (fixed) values of the H–H distance between 1.0 and 1.5 Å, while all other structural parameters of the system were fully relaxed. In this way a two-dimensional sampling of the potential energy surface was obtained (see Fig. 2). The preferred orientation for the molecule was always found to lie in the vertical plane containing R and A, with an approximately horizontal orientation. On-top A and R sites are local maxima on the potential energy surface, similarly to results obtained for the unreconstructed Si(111) surface by Wu and Cheng [35]. The energy at these sites is higher than 2.5 eV even at the LDA level, which is known to considerably underestimate desorption barriers. Vice versa, the "canyon"-shaped valley in Fig. 2 corresponds to configurations in which the H$_2$ molecule is located approximately halfway between A and R in a bridging geometry. However, no transition state was found for such a bridging state, and energies are always larger than $\Delta H$. This means that the potential energy surface of Fig. 2 simply describes a repulsive interaction (larger at A and R, smaller at hollow sites) between H$_2$ and the surface. Thus, it does not contain the pathways of dissociative adsorption/recombinative desorption of H$_2$ in which we are interested.

In the light of the preceding results, we decided to explore the possibility of the desorption of H$_2$ from SiH$_2$ surface species. The occurrence of dihydride units following intermediate/high H exposures on Si(111)-(7 × 7) is well documented [37–41]. We first considered the formation of dihydride species at the adatom site, as qualitative arguments [36] suggest that H$_2$ adsorption and desorption occur mainly at the adatom DBs. We found that the creation of the dihydride species has an energy cost of 0.73 eV (LDA: 0.65 eV) and leads to the disruption of one of the adatom backbonds, e.g. the A–B1 backbond (see Fig. 3a). Contrary to "defect" species, whose existence has been invoked on the monohydride Si(100) surface, these dihydride units on Si(111) can be formed reversibly, and at the desorption temperature (~ 800 K) can be thought of as being in thermodynamic equilibrium with the monohydride species resulting from H adsorption at the atop A and R sites. We have also computed the formation energy of dihydride unit from the restatom, and found it to be 0.67 eV (LDA: 0.38 eV) higher than for the adatom case. Thus, under equilibrium conditions, desorption...
Fig. 3. LDA structures corresponding to side views of (a) a SiH₂ unit at the adatom site, (b) the H₂ desorption TS related to (a), (c) the configuration obtained at the end of a short (~25 fs) MD run, starting from a point just after the TS, on the desorption side, and (d) the configuration obtained at the end of a short (~15 fs) MD run, starting from a point just before the TS, on the adsorption side. Note that in all these structures the A-B₁ bond (present on the clean surface, see Fig. 1) is broken. The adatom is represented by the gray circle, the silicon atoms by the large white circles, and the hydrogen atoms by the small white circles. All distances are in Å.

From a hypothetical restatom-based dihydride is negligible.

The transition state (TS) for desorption from an adatom-based dihydride unit was searched for by means of constrained CP-shake minimizations. In this case, the search was first performed on a coarse grid where the H–H distance was decreased in steps of 0.1 Å, while a finer spacing (0.01 Å) was used in the region of the saddle point. This was found at a H–H distance of 1.11 Å, and corresponds to an activation barrier $E_{\text{des}} = 2.42$ eV (LDA: 2.16 eV). A sketch of the structure of the TS is reported in Fig. 3b. The authenticity of the TS was tested by slightly contracting/elongating (0.01 Å) the H–H bond, reoptimizing the system, and finally carrying out a free molecular dynamics (MD) run (see Fig. 4). The structures obtained after these MD simulations are reported in Figs. 3c and d. Although these runs were rather short, we can see that the resulting structures correspond to a desorbed H₂ molecule and to a SiH₂ species, respectively.

Fig. 4. Evolution of (a) the H–H distance, (b) the H₂ center of mass (COM) height, (c) the total energy of the H–H distance during MD runs performed starting from configurations on the desorption (solid line) and adsorption (dashed line) sides of the desorption TS. Energies are relative to the absolute minimum (R–H + A–H configuration), while the H₂ COM height is relative to the TS value.

In order to build a complete desorption curve starting from the absolute minimum (R–H + A–H configuration), we tried to estimate the barrier of
the diffusive process leading to the formation of SiH$_2$. We first moved H from R to B$_1$, to obtain a configuration in which the adatom–H unit had one broken backbond (step 1), and then we moved H to A–H to form the SiH$_2$ species (step 2). The TS for both processes were obtained via constrained CP-SHAKE minimizations. Step 1 was found to have a barrier of 1.97 eV (LDA: 1.76 eV), with a TS in which H bridges R and B$_1$ symmetrically. The local minimum (A–H+B$_1$–H) has an (LDA) energy of 0.78 eV. The second diffusion step (step 2), yielding the dihydride unit, was found to occur very easily, with an (LDA) barrier only 0.3 eV above the local minimum obtained in step 1.

The complete curve for the whole SiH$_2$-related desorption path, starting from the R–H+A–H configuration, is reported in Fig. 5. For clarity, the diffusion process leading to the formation of the dihydride species has been represented as a single step. The desorption barrier (2.42 eV) compares favourably to experiment, and should be considered as an estimate for a situation of intermediate H coverage ($\theta_H$), i.e. $\theta_H \approx 0.2$–0.38 in the temperature-programmed desorption (TPD) spectra simulations of Flowers et al. [20]. In the case of low H coverage, all the H atoms are expected to be bonded to restatoms, so we must add the extra energy required to promote a H atom from an R to an A site (0.2 eV [24]) to the previously calculated barrier. This can explain the presence of two components in the TPD spectrum of Flowers et al. [20]. We also note that when referred to the SiH$_2$ configuration, the barrier for desorption is reduced to 1.7 eV. This is in fair agreement with the energy of the $\beta_2$ TPD peak (1.99 eV [20]), which is attributed to desorption from SiH$_2$ units in the adatom islands formed on the surface at high H coverages [40,41].

Turning now to consider the case of H$_2$ adsorption, it appears from Fig. 5 that the incoming molecule has to overcome a barrier of 1.00 eV. This agrees with the adsorption barrier of $0.87 \pm 0.1$ eV obtained in second-harmonic generation measurements by Bratu and Höfer [21]. The increase in the adsorption rate found with increasing surface temperature can be attributed to the strong distortion of the lattice which is necessary to disrupt the adatom backbond. The energy associated with such a distortion can be estimated by computing the energy difference between the relaxed clean surface and the energy of the slab obtained by removing the desorbing H$_2$ molecule from the TS structure. The resulting value is 0.57 eV. If we consider H$_2$ desorption to be a sudden event, we can assume that a large fraction of the lattice deformation energy remains in the surface (see, e.g., Ref. [36]). In this way, the excess energy of the desorbing molecules should be $\sim 0.4$ eV. This picture is also supported by our short MD simulations: from Figs. 3c and 4 it appears that at the end point of the desorption trajectory the energy of the system is still quite close to its value at the TS although H$_2$ is already practically desorbed. This is related to the fact the A–B$_1$ backbond has not yet been restored (Fig. 3c). Such a dynamical behavior can to some extent explain the puzzling observations of a very large adsorption barrier in sticking-coefficient measurements [21] and at the same time of a negligible translational energy for the desorbing H$_2$ molecules [22].

In summary, we have performed first-principles calculations of the interaction of H$_2$ with the Si(111)-(7 × 7) surface. Our results are in quantitative agreement with the available experimental data. In particular, the $\beta_1$ TPD peak is attributed to H$_2$ desorption from a SiH$_2$ species in thermal equilibrium with the surface, and a dependence of
the related barrier on the coverage is correctly predicted. Our results also suggest that the large lattice deformation at the desorption transition state is largely responsible for the apparent discrepancy between the values of adsorption barriers inferred from adsorption and desorption experiments.

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