Multidimensional Energy Barrier Surface Study for the Dissociative Adsorption of H₂ Impinging on a Si(111)(1×1) Surface: First-Principles Calculations†

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With a first-principles method the energy barrier surface of the dissociative adsorption for hydrogen molecules impinging on a Si(111)(1×1) surface was investigated. A large corrugated energy barrier surface was found and the corrugation of the surface is much larger than that of H₂ on a Cu(100) surface. The energy barrier strongly depends on the orientations of the molecule and the position of H₂ on the surface. The large corrugation of the energy barrier surface and the strong orientation effect are the main cause for the low sticking coefficient of the hydrogen molecule impinging on a Si(111) surface.

I. Introduction

The interaction of hydrogen with a silicon surface has been widely investigated as it is vital to some industrial technologies, e.g., the chemical vapor deposition process in device manipulation.[1−3] Despite those extensive studies, some unresolved problems still exist, and the one we are most concerned with is the controversy over the adsorption energy barrier yielded from the adsorption and the desorption experiments.[4−6] In the adsorption experiments, a quite low sticking coefficient of H atom on the Si(111) or Si(100) surface was measured at room temperature[2,7,8] and a large energy barrier (E_b) was assumed to be the cause of the low sticking coefficient during the dissociative adsorption of H₂ on a Si surface. However, no such adsorption barrier was found in the desorption experiment[2,9,10] and the lack of adsorption barrier apparently contradicted the prediction based on the adsorption experimental result. Furthermore, the existence of various possible initial surface structures for the Si(111) surface complicates the problem. Among them, the unreconstructed Si(111) surface is the simplest one and the hydrogen adsorbed Si(111) surface structure was identified as the (1×1) structure with H atoms bound to the surface silicon atoms.[11,12] Studies on the system would help further investigations on more complex systems.

Even with the simplest neutral diatomic molecule, H₂, the interaction of the Si(111)(1×1) surface with molecular systems is still very complicated and at least six coordinates are required to well describe the system. In addition to the position of the hydrogen molecule on the surface, the orientation of the molecule (θ and ϕ in Figure 1a) and the interatomic distance of the molecule (denoted as d) should also be specified. In our previous papers on this system,[13,14] two of the authors presented the orientation effect of H₂ and the energy curves of H₂ approaching the Si(111)(1×1) surface (both with fixed d equal to that of free H₂), and some interesting results were found. The energy of H₂ on the Si(111)(1×1) surface is very sensitive to the orientation of the molecule and the effect of orientations depends strongly on the position of H₂ on the surface and the distance of H₂ from the surface. H₂ prefers to have the molecular axis parallel to the surface and directed to a nearest
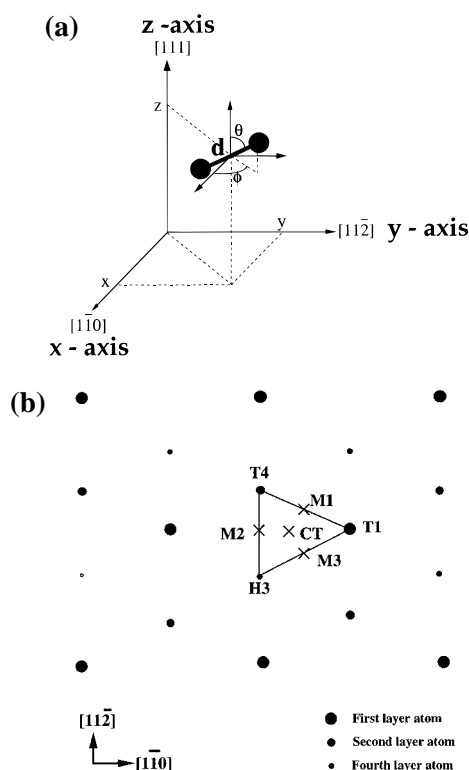
Figure 1. (a) The description of H₂ on the surface. The x and y denote the position of the center of mass of H₂ on the surface; z is the height of H₂ above the surface; polar angle θ and azimuth angle ϕ describe the orientations of molecule, and d is the interatomic distance of H₂. The x-, y-, and z-axes are along [$1\bar{1}0$], [$11\bar{2}$], and [111] directions, respectively. (b) Top view of the Si(111)(1×1) surface. The shaded area is the irreducible zone of the surface.

chemisorbed site of H atom on the Si(111)(1×1) surface. As stated earlier, the adsorption energy barrier is, in general, one of the important factors affecting the sticking coefficient. The study of the multidimensional energy barrier surface would help to understand the low sticking coefficient of hydrogen on the Si(111) surface. In this paper, we present the study of the adsorption barrier for the dissociative adsorption process of hydrogen molecules on the Si(111)(1×1) surface.

For Si(111)(1×1) surface structure, the irreducible zone is represented by the shaded equilateral triangle in Figure 1b. The Si(111)(1×1) surface contains three 3-fold symmetry sites,

which correspond to positions right above the first, the second, and the fourth layer of silicon atoms denoted as T1, T4, and H3, respectively. The M1, M2, and M3 sites are located individually at the middle point between (T1, T4), (T4, H3), and (H3, T1) sites. The CT site is the center of the irreducible zone. The dangling bonds of the surface silicon atoms make the T1 site the perfect position for bonding with hydrogen atoms. This is the chemisorbed position for hydrogen atoms on the Si(111)(1×1) surface. On the potential energy surface (PES) of the H atom on the Si(111)(1×1) surface, T4 and H3 sites correspond to local maxima[15] and the M2 site is a saddle point. On the other hand, T1 and M2 sites correspond to the global maximum and global minimum of the PES for H_2 moving on the Si(111)(1×1) surface.[14]

Seven adsorption trajectories right above the seven specific sites in the irreducible zone were selected for the study of the E_b on different positions of the Si(111)(1×1) surface, while the E_bs of different orientations were calculated for H_2 incoming the surface with the center of mass right on the M2 site (the M2 trajectory). A large corrugated energy barrier surface was obtained and the E_b was found to strongly depend on the orientation of hydrogen molecule. This suggests that only a small portion of the hydrogen molecule with a specific orientation which impinges the Si(111)(1×1) surface at the right positions can be successfully dissociated and adsorbed on the surface.

The calculation method is presented in the next section, while details of the results and discussions are in the third section. A concluding remark is given in section IV.

II. Calculation Method

The calculations were based on the density functional theory[16] with local density approximation[17] (LDA). The Ceperley–Alder form[18] was used to calculate the exchange-correlation energy. Recently, the general gradient approximation (GGA) was found to raise the energy barrier of adsorption more than that obtained with LDA.[19,20] Although the absolute value of the energy barrier calculated with LDA is lower than that of GGA, the relative value among the energy barriers of LDA results is similar to that of GGA results which were reported by White and Bird in the study of the dissociative adsorption of H_2 on the Cu(100) surface.[20] The underestimate of E_b was also pointed out in their paper as emerging from the overestimation of the total energy of free H_2 within the LDA and that led to a constant shift of the adsorption energy barriers. In this calculation, GGA is not included. To be consistent with our previous studies the norm-conserving pseudopotentials for the silicon and hydrogen ions were taken.[21] Using the bare Coulomb potential for hydrogen ions gives only a small difference (less than 20 meV/H_2) in the formation energy. A similar result was also reported in the paper of Chang and Chadi.[22]

All the structures in the calculations are periodic systems with slab configurations. The unit cell contains six double layers of silicon along the [111] direction with a period of nine double layers. The surface area which corresponds to $^1/_3$ monolayer coverage of H_2 on the surface was used as the unit cell. The wavefunctions were expanded with plane waves and the calculations were done in the momentum space.[23] The samplings of k points for integration over the first Brillouin zone were chosen with the scheme of Monkhorst–Pack.[24] Details of the convergence tests in the k-point sampling (using up to 25 points in the first Brillouin zone) and the basis-set expansion (up to 12 Ry for the energy cutoff of the basis set) were explained elsewhere[14] and the error bar was estimated to be less than 0.1 eV/H_2.
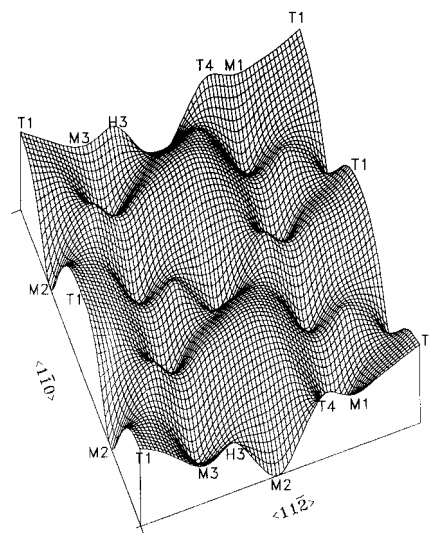

Figure 2. Energy barrier surface of the dissociative adsorption of H_2 impinging on the Si(111)(1×1) surface. The energy barrier surface for a large rectangular area of the surface (as the one of Figure 1b) is shown.

III. Results and Discussions

As stated in the first section, six coordinates are required to specify the pose of H_2 on the Si(111)(1×1) surface (Figure 1a). In our calculations the position of H_2 is represented by the location of its center of mass, (x, y, z). The x-, and y-, and z-axes are defined as those along the [$1\bar{1}0$], [$11\bar{2}$], and [111] directions of the Si(111)(1×1) surface. The orientation of the molecule is described by the polar angle θ and the azimuthal angle ϕ. The molecule is perpendicular to the surface at $\theta = 0°$ and parallel to the surface at $\theta = 90°$. The azimuthal angle ϕ describes the projection of the molecular axis on the Si(111)(1×1) surface. The $\phi = 0°$ and $\phi = 90°$ correspond to the projection of the molecular axis being along the [$1\bar{1}0$] and the [$11\bar{2}$] directions, respectively.

In order to have a thorough picture of the dissociative adsorption of H_2 on the Si(111)(1×1) surface, the energy barriers E_b were calculated for dissociative adsorption of H_2 on the surface with various molecular orientations and different impinging positions of H_2 on the surface.

A. E_b of H_2 Impinging at Different Positions on the Si(111)(1×1) Surface. For the study of different impinging positions of H_2 on the surface, seven perpendicular surface trajectories passing through the seven sites in the irreducible zone (as shown in Figure 1b) were selected. During these adsorption processes, the hydrogen molecule is in the most favorable pose, i.e., with the molecular axis parallel to the Si(111)(1×1) surface and with the H atom directing to the nearest T1 site,[13,14] and the bond length of H_2 was increased until one H atom of the molecule reached the nearest T1 site. From the seven adsorption trajectories, only the E_b of the M2 trajectory is negative; the other six trajectories all have positive energy barriers to overcome during these adsorption processes and a large corrugated energy barrier surface (EBS) was found for the dissociative adsorption of H_2 on Si(111)(1×1) surface (see Figure 2). The global minimum of the EBS is found at the M2 site where the direct dissociative adsorption process occurred,[15] while the global maximum of EBS is found at the T1 site, the chemisorbed site of the H atom on the surface. The E_b at the T1 site is much higher than that at the M2 site by a magnitude of over 4.5 eV and the difference is much larger than that of H_2 on the Cu(100) surface (0.28 eV).[20] It reveals that the corrugation of the EBS of H_2 on the Si(111)(1×1)
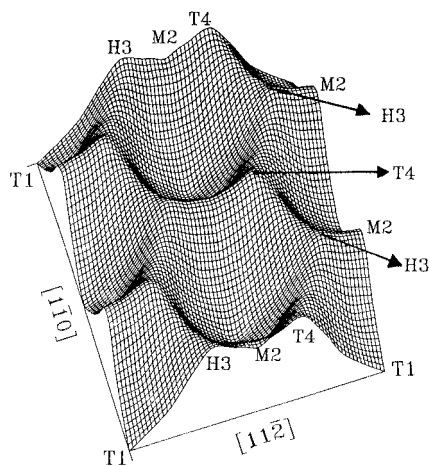
Figure 3. Potential energy surface for hydrogen atoms diffusing on the Si(111)(1×1) surface. The large rectangular area of the surface is the same as in Figure 2.
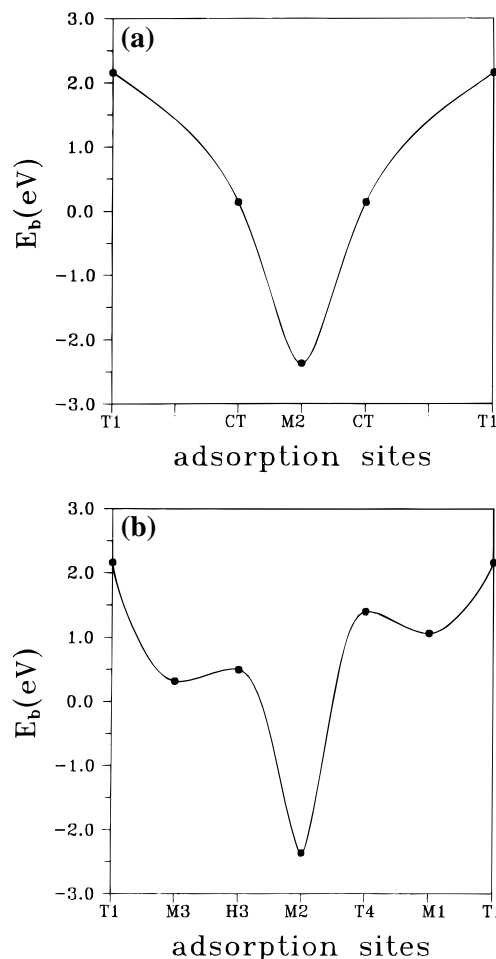

Figure 4. Energy barrier of the dissociative adsorption of H₂ impinging on the Si(111)(1×1) surface along the (a) [1$\bar{1}$0] direction and (b) [11$\bar{2}$] direction (see Figure 1b).

surface is much larger than that of H₂ on the Cu(100) surface. As mentioned earlier, the T1 and M2 sites also correspond to the global maximum and global minimum of the PES of H₂ on the Si(111)(1×1) surface.[14] However, a site with higher energy on the PES of H₂ on the Si(111)(1×1) surface does not necessarily have a higher energy barrier of adsorption.

On the other hand, a large corrugated EBS can be expected as the PES of H atom on the Si(111)(1×1) surface and the surface effect on the interatomic interaction of the H dimer (the details will be published elsewhere[25]) are the two main factors involved in the dissociative adsorption of H₂ on the Si(111)(1×1) surface. The effect of the Si(111)(1×1) surface usually weakens the interatomic interaction of the H dimer on the surface and makes the dissociative adsorption of H₂ feasible. If the interatomic interaction of the dimer is weak enough, the PES of the H atom on the Si(111)(1×1) surface plays a key role in the dissociation of the H dimer. For the purpose of completeness and clarity, the PES of the H atom on the Si(111)(1×1) surface (Figure 4b in ref 14) is redrawn in Figure 3. As shown in the PES of the H atom on the Si(111)(1×1) surface, when one H atom moves from a T1 site to its nearest neighboring T1 site, it is required to overcome a large energy barrier of over 2 eV. On the other side, it is an exothermic process as one H atom moves from a M2 site to its nearest neighboring T1 site. A large energy difference between a hydrogen molecule dissociated at a T1 site and at a M2 site can be anticipated.

To have a further insight on the EBS of the dissociative adsorption of H₂ on the Si(111)(1×1) surface, E_b along the [1$\bar{1}$0] and [11$\bar{2}$] directions is drawn in parts a and b of Figure 4, respectively. Besides a global minimum and maximum on the EBS, there are two local maxima at T4 and H3 sites and two saddle points at M1 and M3 sites. The EBS of H₂ on the Si(111)(1×1) surface shows that only a small region around the M2 site has a negative E_b. This indicates that only a small portion of hydrogen molecules on the Si(111)(1×1) surface might succeed to dissociate and adsorb on the surface and it leads to a low sticking coefficient of H₂ on the Si(111)(1×1) surface.

B. The Orientation Effect on E_b. Being the global minimum of the EBS, the dissociative adsorption process of H₂ impinging on the M2 site was chosen to further study the orientation effect on E_b. For this purpose, several sets of calculations for H₂ at (i) various polar angles θ with fixed ϕ equal to 0°, i.e., the molecular axis parallel to the [1$\bar{1}$0] plane, and 90°, i.e., the molecular axis parallel to the [11$\bar{2}$] plane, and (ii) various azimuthal angles ϕ with fixed θ equal to 90°, i.e., the molecular

axis parallel to the surface, were done. As can be seen in Figure 5a, for ϕ fixed equal to 0° (solid line), the energy barrier is increased to a maximum at $\theta = 45°$ and then decreased when θ continuously increased to 90°. The path with the molecular axis parallel to the surface has the lowest E_b. For fixed ϕ equal to 90° (dashed line in Figure 5a), the variation of E_b is less significant than that for $\phi = 0°$, however, the path with the molecular axis parallel to the surface ($\theta = 90°$) still has the lowest energy barrier. In Figure 5b, E_b is plotted as function of ϕ and the curve shows that the energy barrier is sensitive to the azimuthal angle ϕ. The lowest energy barrier occurs as the molecular axis directs to the two nearest T1 sites (i.e., $\phi = 0°$), and the highest energy barrier occurs as the molecular axis is parallel to the line joining T4 and H3 sites (i.e., $\phi = 90°$).

In summary, the adsorption energy barrier is strongly orientation dependent, and the lowest barrier trajectory, i.e., the M2 trajectory, is found to involve the hydrogen molecule with its axis parallel to the Si(111)(1×1) surface plane and with the H atom directed to the T1 site during the dissociative adsorption process. The trajectory involving the H₂ molecule with its axis perpendicular to the surface encounters a larger energy barrier.

According to the highly corrugated EBS and the strong orientation effect on E_b, there is quite a low probability for a successful dissociative adsorption of H₂ on the Si(111)(1×1) surface. The probability might even be lowered as the GGA is included in the calculation, the small region of negative E_b on the EBS would be reduced and the value of the energy barrier is expected to be raised.[19,20] Furthermore, when the initial surface is the reconstructed surface, e.g., Si(111)(2×1) or -(7×7)
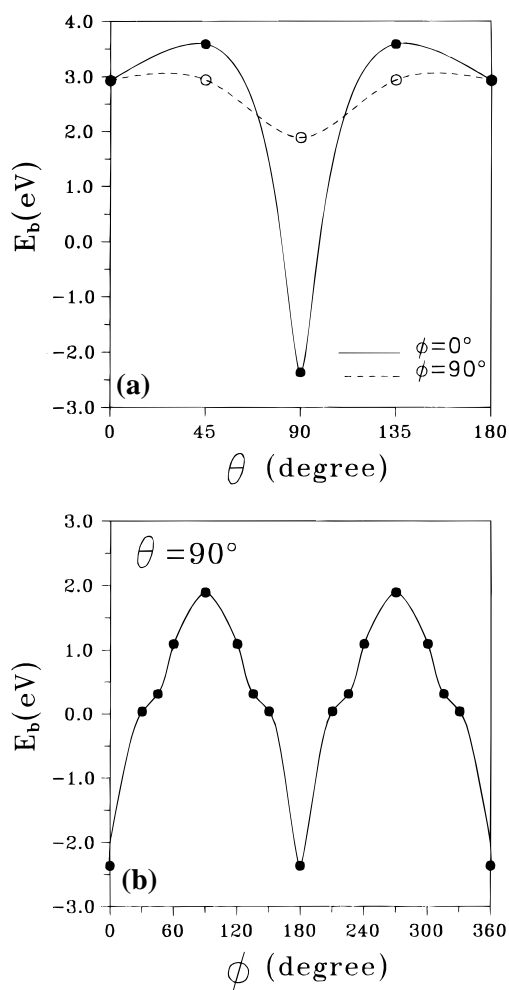
Figure 5. Energy barrier of H_2 impinging the M2 site (a) with various polar angles θ for the angle ϕ fixed at 0° (solid line) and 90° (dashed line) and (b) with various azimuthal angles ϕ for the polar angle θ fixed at 90°.

surfaces, a successful dissociative adsorption event of H_2 on these surfaces might be more difficult than that on the unreconstructed surface, i.e., Si(111)(1×1) surface.

Based on the discussions above, the hydrogen molecule, impinging on a right position of the surface with a specific orientation, could have a successful dissociative adsorption, otherwise, the large energy barrier makes the dissociative adsorption of H_2 on the Si(111)(1×1) surface quite difficult. The strong position- and orientation-dependent character of the dissociative adsorption of H_2 on the Si(111)(1×1) surface reduces the probability of successful dissociative adsorption largely. In other words, only a small portion of H_2 impinging on the surface would dissociate and adsorb on the Si(111)(1×1) surface successfully. Namely, the large corrugated EBS and strong orientation effect on E_b lead to a low sticking coefficient

for the dissociative adsorption of H_2 on the Si(111) surface and the results support the Kolasinski's proposition.[5]

IV. Conclusions

With a first-principles method, we have performed the calculations of a multidimensional energy barrier surface for the dissociative adsorption of a hydrogen molecule on the Si(111)(1×1) surface. A large corrugated energy barrier surface is found, and the difference between the highest and the lowest energy barrier is much larger than that of H_2 on the Cu(100) surface. The lowest energy barrier of hydrogen on the Si(111)(1×1) surface occurs during the process of hydrogen impinging the M2 site with the molecular axis parallel to the surface and directed to a nearest neighboring T1 site. The large corrugated EBS and the strong orientation effect on E_b are considered as the main cause for the low sticking coefficient of the hydrogen molecule on the Si(111) surface.

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