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SiH₂ adsorption on the single dimer vacancy of the Si(100) surface

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Abstract

The energetic and structural properties of SiH₂ adsorbed on the single dimer vacancy (SDV) of the Si(100)-c(4 × 2) surface have been studied by using empirical tight-binding (ETB) total energy calculations. The adsorptions of SiH₂, SiH₂ with a hydrogen adatom (SiH₂ + H) and SiH₂ with two hydrogen adatoms (SiH₂ + 2H) on the Si(100) surface with SDV structure have been studied. Three possible sites (A, B and C) are found in each case. Adsorbing of SiH₂ or H on the SDV makes the structure of the SDV change. When a unit of SiH₂ is adsorbed on the SDV, the A site is more stable than the B site. If SiH₂ + H or SiH₂ + 2H is adsorbed on the SDV, the relative stability of the A site and B site reverses. The C site is found to be the least stable site in all cases.

1. Introduction

Epitaxial growth of Si film on a silicon base via chemical vapour deposition (CVD) is an important method in the growth industry. Silane and disilane are commonly used for low-temperature CVD growth because they have high sticking coefficient and low decomposition activation energy [1]. These systems have been the subject of intensive studies, both theoretically and experimentally. It is widely accepted that Si₂H₆ or SiH₄ decomposes to form SiH₃ in the adsorbing process. Then the SiH₃ spontaneously decomposes to form SiH₂ at room temperature [1–6]. Therefore, the SiH₂ and H atoms are considered as the basic units in the CVD growth. There are two adsorption sites for them on the Si(100) surface: one is on the top of a dimer (on-dimer site), and the other is between two dimers in the same row (intra-row site). A scanning tunnelling microscopy (STM) study with low disilane dosage has observed that SiH₂ is located only at the intra-row site [4].

Theoretically, Hong and Chou [5] have evaluated the energies of the SiH₂ bonding sites on a bare Si(100) surface using the pseudopotential plane-wave method. They found that the

on-dimer site is more stable than the intra-row site on the bare Si(100) surface. However, the presence of H atoms eliminates this difference and makes the intra-row site more favourable than the on-dimer site. They argue that the reason why SiH₂ is located only at the intra-row site in the STM images may be due to the presence of hydrogen. By using a first-principles total energy calculation Takeuchi [6] also found that in the absence of H atoms, SiH₂ prefers to be adsorbed in the on-dimer site on the Si(100)-c(4 × 2) surface. However, if the two H atoms produced in the dissociation of SiH₄ are considered, the relative stability of the two sites is reversed.

However, their calculations are all based on a clean silicon surface. Actually, the defects in the surface may play an important role in the growth, and influence the adsorbing sites. Thus practically, the study of adsorption of SiH₂ on a defect-induced Si surface is more meaningful. Since the SDV is the simplest defect of the silicon surface, the SDV defect is introduced in our study. In this paper, the energetic and structural properties of SiH₂ adsorbed in the SDV of a Si(100)-c(4 × 2) surface have been studied by using empirical tight-binding (ETB) total energy calculations.

2. Method

Our calculations are carried out using the ETB total energy calculation with the steepest descent (SD) relaxation method [7–10]. We adopt the scheme of Goodwin, Skinner and Pettifor (GSP) for Si–Si interactions [11]. These schemes introduce the parameters from the first-principles calculation and experimental results. It has proved to be both efficient and accurate enough in studying various Si–H systems [7–16].

Our slab model for the Si(100)-c(4 × 2) surface consists of five Si atomic layers and 16 atoms for each layer in this work. H atoms have been used to saturate the dangling bonds of the Si atoms at the bottom layer to mimic the bulk Si. The bottom hydrogen layer and two Si layers are fixed to get rid of any fictitious forces when we study the adsorption of Si adatom on the surface. The dimerization bonds are along the *x* direction [110], and the dimer rows are parallel to the *y* direction [110]. The periodic boundary conditions are applied to the *x* and *y* directions. The potential cutoff is 3.20 and 1.80 Å to consider the nearest atom–atom interaction of Si–Si and Si–H, respectively.

3. Results and discussion

We have first calculated two stable adsorption sites, which are the on-dimer site and intra-row site, on the Si(100)-c(4 × 2) surface. In agreement with other theoretical calculations [5, 6], the dimer length increases when SiH₂ deposits on the clean Si(100)-c(4 × 2) surface on the dimer site. The total energy of this structure is 0.32 eV lower than that of the intra-row structure. This energy difference is 0.26 eV by the first-principles calculations [6], and 0.14 eV by the pseudopotential plane-wave method [5]. The differences in the data are probably due to the different calculation methods. Our calculation results are in accord with their results. Therefore, these calculation results show that our ETB method is accurate and reliable for this study.

To mimic the SDV structure, an arbitrarily chosen dimer is simply removed from the perfect Si(100)-c(4 × 2) surface structure and then the system is fully relaxed via the ETB method with SD. We investigate three adsorption sites of SiH₂ in the SDV and mark them as A site (figure 1(a)), B site (figure 1(b)) and C site (figure 1(c)), respectively. The relative total energies for the A site, B site and C site are 0.0, 0.20 and 1.23 eV, respectively.

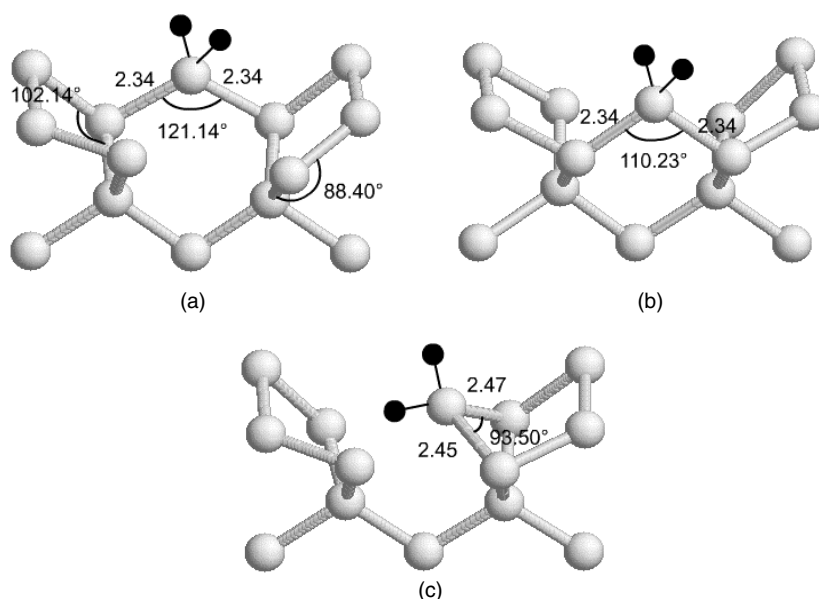


Figure 1. Side views of possible adsorption sites of SiH₂ on the Si(100)-c(4 × 2) surface: (a) A site (b) B site (c) C site. The bond lengths in Å are indicated. Black balls represent H atoms and grey balls represent Si atoms, respectively.

In site A (see figure 1(a)) the Si atom of SiH₂ bonds with the back atoms of two upper atoms of two dimers on opposite sides of the SDV. The two new bonds are as long as 2.34 Å, close to the bulk Si bond length. The bond angle between the two new bonds is 121.14°. It is noted that the two angles of the back Si atoms have changed from 96.87° and 83.77° to 102.14° and 88.40°, respectively (as shown in figure 1(a)). These changes lower the structure energy considerably. Site B is shown in figure 1(b). On two sides of the SDV, the Si atom of SiH₂ binds to the back atoms of two lower atoms of dimers. The two new bonds have length 2.34 Å. The bond angle between two new bonds at site B is 110.23°, which is close to the angle of sp³ hybridization and more favourable than that of site A. However, the structure of the SDV has been changed a little, so the total energy of site B is slightly higher than that of site A. In the C site, the Si atom of SiH₂ makes two bonds with two Si atoms, which are located on the same side of the SDV. The bond lengths are 2.45 and 2.47 Å, respectively, which are about 0.10 Å longer than that of the Si–Si bond in bulk silicon. The bond angle between the two new bonds turns out to be 93.50°, which is far from the ideal tetrahedral arrangement. The stretched bonds and the improper bond angle raise the total energy, which makes the structure unfavourable. Thus the total energy is much higher than that of sites A and B. The structure of site C is the least stable of the three sites.

As mentioned before, SiH₃ is metastable, and it can easily decompose into SiH₂ and a hydrogen atom. Therefore, we further consider possible adsorption geometries for SiH₂ + H or SiH₂ + 2H on the SDV.

Following the labels for different adsorption positions of SiH₂ in the SDV, several energetically favourable adsorptive geometries are shown in figure 2 and named as A-H, B-H, C-H(1), C-H(2), respectively. The relative total energies for the A-H site (figure 2(a)), B-H site (figure 2(b)) and C-H(1) site (figure 2(c)), C-H(2) site (figure 2(d)), are 0.35, 0.0, 1.54, and 1.81 eV, respectively.

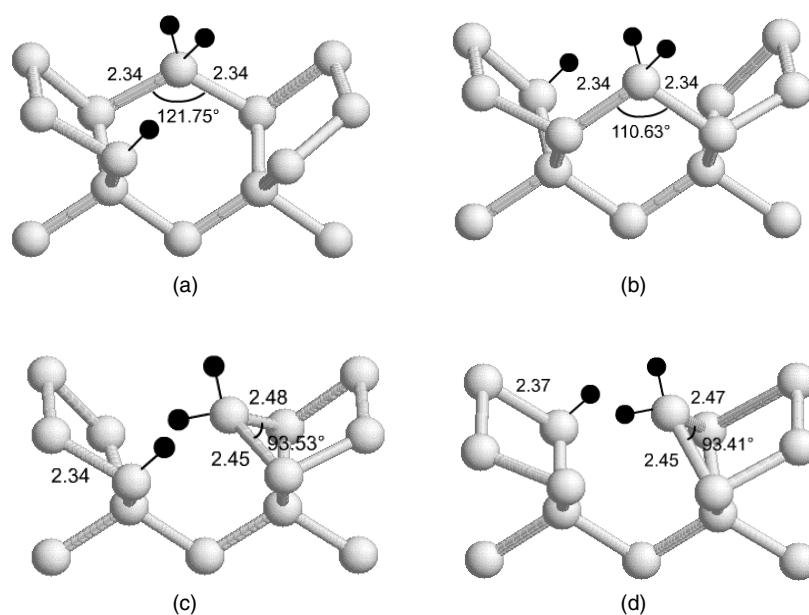


Figure 2. Side views of possible adsorption sites of SiH_2 and a hydrogen adatom on the $\text{Si}(100)\text{-}c(4 \times 2)$ surface: (a) A-H site, (b) B-H site, (c) C-H(1) site, (d) C-H(2) site. The bond lengths in Å are indicated. Black balls represent H atoms and grey balls represent Si atoms, respectively.

When a hydrogen atom is introduced into the SDV, it prefers to saturate one dangling bond. It is found that the presence of a hydrogen adatom causes the relative stability of the A site and B site to be reversed. We argue that the additional H atom saturates one dangling bond of the SDV, and does not change the structure of the SDV much either for the A-H site or for the B-H site. Thus the structure property of the additional $\text{SiH}_2 + \text{H}$ unit plays an important role in determining the relative stability of the total critical geometry. It is worth noting that the angle between the two new Si–Si bonds of the B-H site is 110.63° , which is very close to that of sp^3 hybridization, while that of A-H site is 121.75° , close to that of sp^2 hybridization. Thus comparing to the adsorption of SiH_2 , the relative energies of the A-H site and B-H site are reversed. In the C-H sites (C-H(1) and C-H(2)), the additional H atom also causes the SDV structures to change a little. The Si atom of SiH_2 makes two new bonds with two Si atoms located on the same side of the SDV. The new bond lengths are 2.45 and 2.48 Å in the C-H(1) site, and 2.45 and 2.47 Å in the C-H(2) site, respectively. The bond angles between the two new bonds are 93.53° in the C-H(1) site and 93.41° in the C-H(2) site, respectively. The improper bonds and bond angle raise the total energy, which makes the C-H sites less stable than site A-H or B-H. The differences between C-H(1) and C-H(2) exist only in subtle structures. For example, in the C-H(1) site, the bond between the silicon atom attached to the H atom and the lower site atom of the dimer is 2.34 Å, which is close to the length of the Si–Si bond in silicon bulk. However, in the C-H(2) site, this bond is 2.37 Å (see figure 2(d)). All these cases cause the total energy of the C-H(2) site to be a little higher than that of the C-H(1) site.

Finally, $\text{SiH}_2 + 2\text{H}$ is introduced and three geometries are found to be stable, following above, which are named as A-2H, B-2H, C-2H (shown in figure 3). The relative total energies of the three geometries are 0.09, 0.0 and 1.54 eV, respectively.

The two hydrogen adatoms can saturate the two dangling bonds. For A-2H and B-2H sites, all dangling bonds are saturated and they have the symmetry structure. Because the bond angle

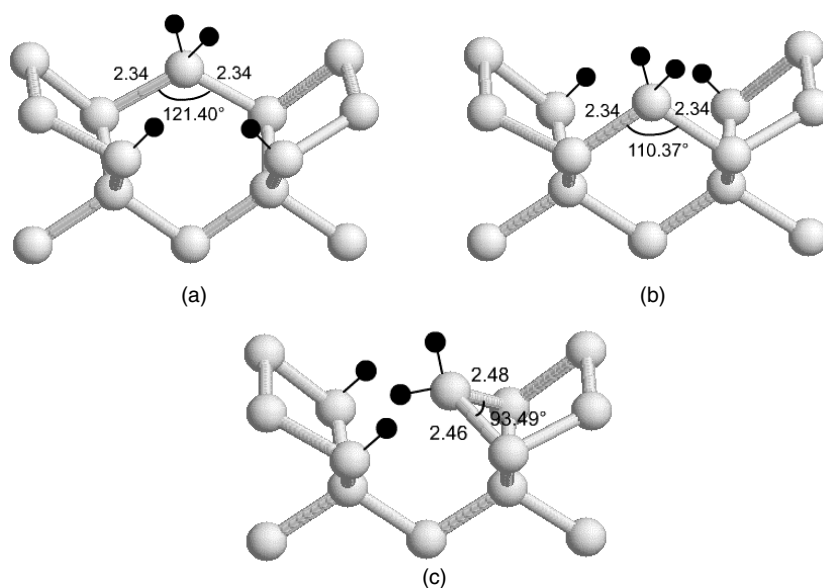


Figure 3. Side views of possible adsorption sites of SiH₂ and two hydrogen adatoms on the Si(100)-*c*(4 × 2) surface: (a) A-2H site (b) B-2H site (c) C-2H site. The bond lengths in Å are indicated. Black balls represent H atoms and grey balls represent Si atoms, respectively.

Table 1. Relative energies for different configurations of SiH₂, SiH₂ + H and SiH₂ + 2H adsorbed on the single dimer vacancy (SDV) of the Si(100)-*c*(4 × 2) surface. The lowest total energy is set as the energy zero point in each case. The energies are in eV.

| | SiH ₂ | SiH ₂ + H | SiH ₂ + 2H |
|---|------------------|----------------------|-----------------------|
| A | 0.0 | 0.35 | 0.09 |
| B | 0.20 | 0.0 | 0.0 |
| C | 1.23 | 1.54 or 1.81 | 1.54 |

between the two new bonds of the B-2H site is 110.37°, close to the angle of sp³ hybridization, its total energy is a little lower than that of the A-2H site. Similar to the C-H(1) and C-H(2) structures, the unfavourable configuration of SiH₂, again, increases the structural energy. Thus the C-2H site has higher total energy than the others. We compare the total energies of various configurations in table 1.

From the table, we can see that the C site (C, C-H(1), C-H(2) and C-2H) is always the least stable of the three situations. When a unit of SiH₂ adsorbs on the SDV, the A site is more stable than the B site. However, the presence of hydrogen makes the B-H (or B-2H) site more favourable than the A (or A-2H) site. This is ascribed to the dangling bonds saturated by the hydrogen, which make the structure of the SDV to hardly change, and the geometries of the adsorbed SiH₂ play the critical role in determining the total energy.

4. Conclusion

The ETB total energy calculation has been used in studying the energetic and structural properties of SiH₂ adsorbed on the SDV of a Si(100)-*c*(4 × 2) surface. We have discussed the adsorption of SiH₂, SiH₂ + H and SiH₂ + 2H, which are fragments of silane produced in CVD, on a Si(100) surface with an SDV.

Various different adsorption geometries have been discussed in detail. We find that SiH₂ adsorbed on two sides of the SDV is much more stable than that by the same side. The presence of hydrogen atoms may change the relative stabilities of different adsorption sites and further change the surface deposition of SiH₂ on a Si surface.

Acknowledgments

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