RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 58, NUMBER 20 15 NOVEMBER 1998-II

Role of hydrogen in SiH_2 adsorption on Si(100)

Suklyun Hong* and M. Y. Chou†
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430

(Received 7 July 1998)

When disilane (Si_2H_6) is used in the homoepitaxial growth of Si by chemical vapor deposition (CVD), the fragment SiH_2 is believed to be the basic unit adsorbed on the surface. The bonding site of SiH_2 on Si(100) has been proposed in the literature to be either on top of a dimer (the on-dimer site) or between two dimers in the same row (the intrarow site). Since the pathway of SiH_2 combination is dependent on the adsorption site, a first-principles calculation will shed light on the underlying process. We have performed self-consistent pseudopotential density-functional calculations within the local-density approximation. On the bare Si(100) surface, the on-dimer site is found to be more stable than the intrarow site, even though the former has unfavorable Si-Si bond angles. This is ascribed to the extra dangling bond created in the latter geometry when the weak dimer π bonds are broken. However, the presence of hydrogen adatoms eliminates this difference and makes the intrarow site more favorable than the on-dimer site. It is therefore revealed in this theoretical study that hydrogen, an impurity unavoidable in the CVD process, plays an important role in determining the stable configuration of adsorbed SiH_2 on Si(100) and hence affects the growth mechanism. [S0163-1829(98)52544-1]

Epitaxial growth of Si on Si(100) via chemical vapor deposition (CVD) is an important process in the growth industry. Disilane (Si_2H_6) is a promising candidate for low-temperature CVD growth because of its relatively high sticking coefficient and low decomposition activation energy.[1] This system has been studied extensively by many experimental techniques.[1–8] It is widely accepted that disilane dissociatively chemisorbs on Si(100) yielding SiH_3, which spontaneously decomposes at room temperature (under low-coverage conditions) to form SiH_2 bonded to two surface Si atoms plus a hydrogen adatom.[1,5] The fragment SiH_2 is therefore believed to be the basic unit in the growth, while hydrogen is an unavoidable common impurity in the CVD process. The adsorption site of SiH_2 has been suggested to be either on top of a dimer (on-dimer site)[5,6] or between two dimers in the same row (intrarow site).[7,8] Recent scanning tunneling microscopy (STM) experiments by Bronikowski *et al.*[7] and subsequently by Wang *et al.*[8] with low disilane dosage observed SiH_2 located only at the intrarow site. Various pathways have been proposed in the literature[5–8] for two of the SiH_2 fragments to combine, forming a Si monohydride dimer accompanied by the desorption of H_2.

A theoretical determination of the correct bonding site would clarify our understanding of the steps involved in the CVD epitaxial growth of Si from disilane. Therefore, we have evaluated the energies of the SiH_2 bonding sites on Si(100) using the pseudopotential plane-wave method. Three situations are considered: (i) SiH_2 on a bare surface, (ii) SiH_2 on a monohydride surface, and (iii) a SiH_2+H system consisting of SiH_2 and a nearby adsorbed H on a bare surface that mimics the situation in the low-coverage experiment.[8] Quite interestingly, it is found that the stability order between the on-dimer and intrarow sites is reversed in the presence of hydrogen adatoms. In this case, the intrarow site is energetically more favorable than the on-dimer site, consistent with the STM images by Wang *et al.*[8] It is well known that the existence of H adatoms on the surface plays an important role in the the CVD process by affecting the sticking of incoming molecules or by limiting the diffusion of Si adatoms. In a recent study we have shown that hydrogen changes the surface-energy anisotropy on semiconductor surfaces.[9] The present study reveals that hydrogen also affects the stable adsorption site of a fragment such as SiH_2 on Si(100).

While most of the first-principles studies[10–12] on the Si growth on Si(100) have dealt with the molecular beam epitaxy (MBE) process, which does not involve hydrogen, relatively fewer theoretical studies have been conducted for the CVD process, to our knowledge. Recently, an *ab initio* study on the SiH_2 fragments on bare Si(100) has been reported by Bowler and Goringe.[13] Of the four adsorption sites considered, the on-dimer and intrarow sites are found to be low in energy, with an energy difference of less than 0.01 eV. Their study used a relatively smaller (2×2) cell, which is twice smaller than the $\sqrt{8}\times\sqrt{8}$ cell used in the present study. This may be the reason why our results are at variance with theirs, as will be discussed below.

Our calculations are carried out using the pseudopotential method within the local-density-functional approximation. We generate Si and H potentials[14] from the atomic ground states $3s^2 3p^2 3d^0$ and $1s^1$, respectively. The Si potentials have a cutoff radii of 1.90 a.u. and the p potential is chosen as the local potential. These give a lattice constant (bond length) of 5.42 Å (2.35 Å) and a bulk modulus of 0.940 Mbar, in agreement with the experimental values of 5.43 Å and 0.988 Mbar, respectively. In the surface calculation, we use the theoretical lattice constant. The hydrogen potential has a cutoff radius of 1.25 a.u. The wave functions in the surface calculation are expanded in plane waves with an energy cutoff $E_{\mathrm{cut}}=10$ Ry. Increasing the cutoff to 15 Ry in one test case changes the relative energy only by 0.02 eV per SiH_2.

Our slab model for the Si(100) surfaces consists of six silicon layers and a vacuum with a thickness of eight atomic layers (about 12 Å). The bottom of the slab is passivated

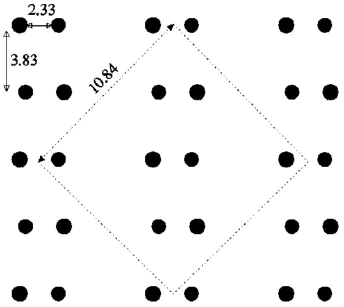

FIG. 1. Geometry of the Si(100) surface with the buckled dimers exhibiting a $p(2\times2)$ surface symmetry. The $\sqrt{8}\times\sqrt{8}$ unit cell used in the calculation is indicated by dotted lines. The distance is in Å. The bond length of a bare dimer is 2.33 Å, and the separation between two dimers in the same row along the crystal axis is 3.83 Å.

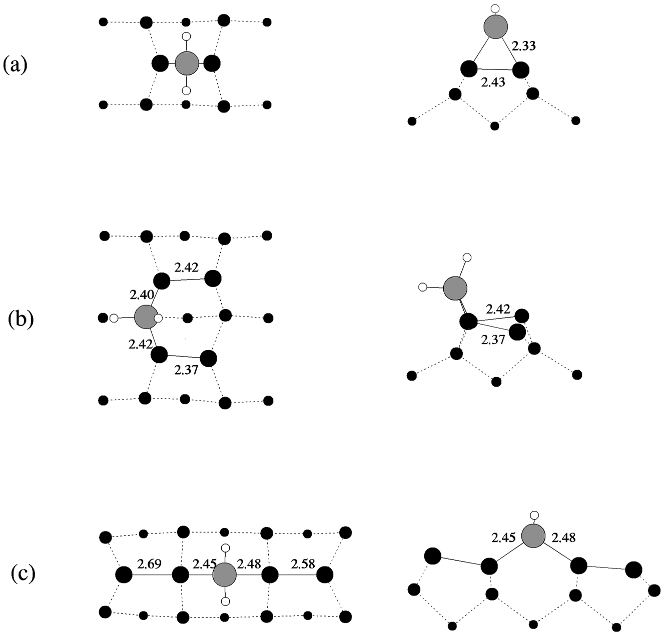

FIG. 2. Configurations of SiH_2 adsorption sites on bare Si(100): (a) on-dimer, (b) intrarow, and (c) inter-row sites. The Si-Si bond lengths in Å are indicated. The filled and open circles represent silicon and hydrogen atoms, respectively. Note that the shaded circles are ad-Si atoms and the dotted circle in the side view in (b) is a dimer atom behind the front dimer atom.

with hydrogen. We use a $p(\sqrt{8}\times\sqrt{8})R45°$ cell with a cell parameter of 10.84 Å, shown in Fig. 1. For the Brillouin-zone integration we use the $2\times2\times1$ grid in the Monkhorst-Pack special point scheme which gives two special k points. A Gaussian broadening with a width of 0.1 eV is used to accelerate the convergence in the k-point sum. A lowest-energy structure for bare Si(100) that can be embedded in a $p(\sqrt{8}\times\sqrt{8})R45°$ cell contains alternating buckled dimers exhibiting a $p(2\times2)$ surface symmetry,[15–17] while the monohydride surface has a $p(2\times1)$ symmetry. The silicon atomic positions at the two bottom layers and passivating hydrogen positions are kept fixed. We then determine the relaxed positions for all other atoms by minimizing the energy and Hellmann-Feynman forces. In our calculations, we use a force convergence criterion of 0.002 Ry/a.u. for the adsorption of SiH_2 at low-energy on-dimer and intrarow sites, and a less strict criterion of 0.005 Ry/a.u. in other cases.

In our study, we investigate two adsorption sites of interest [Figs. 2(a) and 2(b)], along with the inter-row site, shown in Fig. 2(c). The inter-row structure is expected to be energetically unfavorable because it results in much larger Si-Si bond lengths than that of the dimers on the bare surface. Three different surface environments are considered. First, we study SiH_2 on a bare Si(100) surface. This serves as a reference for comparisons. Second, we repeat the calculation for SiH_2 on a hydrogenated Si(100) surface with the stable monohydride configuration, since in the CVD process the surface is usually covered with hydrogen. Finally, we study a situation in the initial stage of growth with low coverage of SiH_2 and an equal number of hydrogen adatoms, as investigated in the experiment.[8]

Our theoretical results of SiH_2 adsorption on bare Si(100) are as follows. The relative energies for the on-dimer [Fig. 2(a)], intrarow [Fig. 2(b)], and inter-row [Fig. 2(c)] configurations are -0.14, 0.0, and 0.42 eV per SiH_2, respectively, as shown in Table I. We find an energy difference of 0.14 eV between the two low-energy configurations, while a difference of less than 0.01 eV was reported in Ref. 13. This may be due to the different size of surface unit cells used. The inter-row site is high in energy as expected, because of the large strain energy caused by the stretch of the bonds: the lengths of two dimers bonded to the SiH_2 unit changes from the bare dimer length of 2.33 Å to 2.58 and 2.69 Å, respectively, while the Si-Si bonds formed upon adsorption are of the order of 2.5 Å.

For the on-dimer configuration, the distance between the silicon atom of the SiH_2 unit and the silicon atoms in the dimer is about 2.33 Å, while the dimer length increases from 2.33 Å before adsorption to 2.43 Å afterwards. One can understand the adsorption process as breaking one dimer π bond and forming two new bonds to the Si atom in SiH_2. With new bond angles of the order of 60° as shown in Fig. 2(a), this is far from the ideal tetrahedral arrangement. This is the reason why it was not considered to be favorable in the past.[7] In comparison, the weak π bond is broken on two dimers for the intrarow configuration in Fig. 2(b), as seen in the increase in the dimer bond lengths. Two new bonds from the Si atom in SiH_2 to two surface atoms (associated with two adjacent dimers in the same row) are formed with a bond length of about 2.4 Å. Although no highly unusual bond angle appears as in the on-dimer configuration, two dangling bonds are not saturated at the Si atoms on the opposite end of the two dimers involved in this case. This raises the energy of this configuration, according to our calculation, to be above that of the on-dimer configuration on the bare surface. Note that the geometry is not completely symmetric in Fig. 2, because the bare surface has an alternating buckled dimer structure.

It is interesting to note that the intrarow location is actually favored by a Si adatom on Si(100), which is the so-called M site.[10,12] We use the same $(\sqrt{8}\times\sqrt{8})$ cell accommodating a $p(2\times2)$ symmetry for this calculation. Our result shows that the M site is lower in energy by 0.59 eV compared to the D site between two Si atoms in a dimer, which is the same as reported in Ref. 10. The single Si ada-

TABLE I. Relative energies for different configurations of SiH_2 adsorbed on bare and hydrogen passivated (monohydride) Si(100), as well as for the SiH_2+H configuration on the bare surface (see text for details), in comparison with the results of an earlier theoretical calculation for the bare surface (Ref. 13). The energies are in eV per SiH_2.

	Bare	Ref. 13	Passivated	SiH_2+H
On-dimer	−0.14	0.004	0.11	0.13
Intrarow	0.00	0.0	0.0	0.0
Inter-row	0.42	0.31	0.42	

tom can go down further to a lower position than SiH_2. The bond lengths of the ad-Si to surface atoms are about 2.4 Å, and the distance between the adatom and the second-layer substrate atom is 2.43 Å. When the hydrogen atoms are attached to the adatom sitting at the *M* site to form the SiH_2 unit, the Si adatom, with four bonds saturated, is pushed up by more than 0.7 Å to be further away from the second-layer substrate atoms.

The preference of the on-dimer adsorption site concluded from the calculation for SiH_2 on the bare surface seems to be inconsistent with the STM results[7,8] that the SiH_2 fragment is observed located at the intrarow site at low coverage. However, the surface is likely to be hydrogenated during the CVD process. We should also consider SiH_2 adsorption on a hydrogen covered Si(100) surface, which may provide the insight in resolving this discrepancy. In the calculation, all surface atoms are passivated by hydrogen, except the ones bonded to the SiH_2 fragment. On this stable monohydride Si(100) surface, the relative energies for SiH_2 at the on-dimer, intrarow, and inter-row sites are 0.11, 0.0, and 0.42 eV, respectively, shown in Table I for comparison. The main difference between the results on the bare and hydrogen passivated Si(100) is the reversed order of stability between the on-dimer and intrarow sites: the on-dimer site is more favorable by 0.14 eV on bare Si(100) while the intrarow site is more stable by 0.11 eV on monohydride Si(100). This can be understood from the bonding configurations on the surface. On hydrogen passivated Si(100), SiH_2 at the intrarow location does not have dangling bonds at the other end of the dimers to raise the energy. Therefore, the intrarow configuration, with more favored bond angles, results in a lower energy than the on-dimer configuration. A comparison of the bonding differences on the two surfaces indicates that the net relative energy change (0.25 eV) should be roughly the energy to break one dimer π bond. This is consistent with the estimated values for the π bond strength from the theoretical H-pairing energies.[18]

The detailed information on the geometry of SiH_2 on the hydrogenated surface is given below. For the on-dimer configuration, the distance between the Si adatom and the surface dimer atoms is 2.33 Å, while the dimer length is 2.44 Å. For the intrarow configuration, the Si adatom is at a distance 2.41 Å from the surface atoms, while the bond length (2.40 Å) of two surface dimers connected to the Si adatom is hardly changed from that of monohydride dimer (2.41 Å). These numbers are all within $\sim 1\%$ of the results on bare Si(100). The result for the inter-row site shows that the Si adatom is at a distance 2.51 Å from the surface atoms, while the length of the two neighboring dimers is stretched to 2.59 Å.

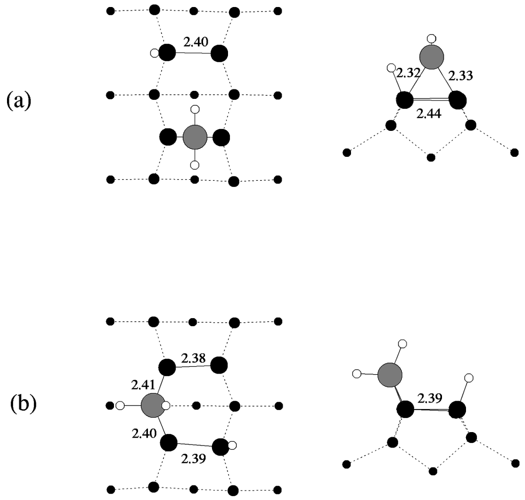

FIG. 3. (a) The on-dimer and (b) the intrarow configurations for the SiH_2+H system on bare Si(100). The Si-Si bond lengths in Å are indicated.

When SiH_3 decomposes into SiH_2, a hydrogen adatom is released to the surface. Therefore, at low coverage, one expects that almost equal amounts of SiH_2 and H exist on the surface, as observed in the STM images.[7,8] We have repeated the calculation for this case by adding one SiH_2 and one hydrogen adatom per unit cell to the bare surface. The hydrogen adatom is placed near the adsorbed SiH_2, as shown in Fig. 3, to mimic the situation right after the SiH_3 decomposition. Energies are calculated for both the on-dimer [Fig. 3(a)] and the intrarow [Fig. 3(b)] locations. We find the intrarow site is again energetically more favorable than the on-dimer site by about 0.13 eV in this SiH_2+H configuration. Adsorption of SiH_2 at the intrarow site breaks two dimer π bonds, and one of the resulting two dangling bonds is saturated by the H adatom. On the other hand, adsorption of SiH_2 at the on-dimer site breaks one π bond, but the nearby H adatom breaks another, leaving also one unsaturated dangling bond. This is supported by the elongation of the dimer from 2.33 to 2.40 Å. Other Si-Si bond lengths, shown in Fig. 3, change by no more than 0.04 Å from those associated with SiH_2 adsorption on the bare surface (Fig. 2). Therefore, the energy of the on-dimer configuration is higher due to the sterically unfavorable angle of about 60°. Wang *et al.*[8] reported sequential images of the Si(001) surface showing the adsorption of SiH_3, and the subsequent dissociation reaction $SiH_3\,(ads) \rightarrow SiH_2\,(ads) + H\,(ads)$. In the STM images, hydrogen seems to have diffused away from the position right after the decomposition of SiH_3, but SiH_2 is almost exclusively observed at the intrarow site, consistent with our energetics result.

Two adjacent SiH_2 fragments located at the on-dimer sites can recombine into a Si monohydride dimer in the normal direction for epitaxial growth, while the product from two intrarow SiH_2 fragments is a ‘‘nonrotated’’ dimer parallel to the substrate dimers and centered in the trough between two dimer rows.[8] In the latter case, a 90° rotation is needed afterward in order to have a growth layer with correct orientation. Our theoretical study indicates that in the presence of hydrogen, SiH_2 prefers the intrarow position. Therefore, immediately after the recombination, we expect the Si monohydride dimer to be parallel to substrate dimers. In fact, pairing of intrarow SiH_2 before recombination is observed in the annealing experiment, as well as the nonrotated dimer species after recombination.[8] Pairing of intrarow SiH_2 plays an important role in the growth and will be the subject of future studies.

In conclusion, we have studied the SiH_2 adsorption problem on bare and hydrogen-covered Si(100), as well as for a SiH_2+H system on bare Si(100). For the bare surface, the on-dimer geometry, despite the unfavorable Si-Si bond angle, is found to have a lower energy than the intrarow site, because extra dangling bonds are created in the latter configuration when the surface dimer π bonds are broken. However, when hydrogen is present on the surface, the energetics order is reversed. This is explained by the passivation role of hydrogen on the surface. Through this comprehensive study, we conclude that in the SiH_2 adsorption problem, hydrogen plays an important role in determining the stable energy configuration.

This work was supported in part by the Department of Energy (Grant No. DE-FG02-97ER45632), the National Science Foundation (Grant No. DMR-9157537), and the National Energy Research Scientific Computing Center (NERSC).

---

*Present address: Oak Ridge National Laboratory, Oak Ridge, TN 37831-6114. Electronic address: hongs@ornl.gov

†Electronic address: meiyin.chou@physics.gatech.edu

[1] S. M. Gates, Surf. Sci. **195**, 307 (1988).

[2] S. M. Gates, C. M. Greenlief, and D. B. Beach, J. Chem. Phys. **93**, 7493 (1990).

[3] W. K. Liu, S. M. Mokler, N. Ohtani, C. Roberts, and B. A. Joyce, Surf. Sci. **264**, 301 (1992).

[4] F. Bozso and P. Avouris, Phys. Rev. B **43**, 1847 (1991).

[5] Y. Suda, D. Lubben, T. Motooka, and J. E. Greene, J. Vac. Sci. Technol. A **8**, 61 (1990).

[6] J. J. Boland, Phys. Rev. B **44**, 1383 (1991).

[7] M. J. Bronikowski, Y. Wang, M. T. McEllistrem, D. Chen, and R. J. Hamers, Surf. Sci. **298**, 50 (1993).

[8] Y. Wang, M. J. Bronikowski, and R. J. Hamers, Surf. Sci. **311**, 64 (1994).

[9] S. Hong and M. Y. Chou, Phys. Rev. B **57**, 6262 (1998).

[10] G. Brocks, P. J. Kelly, and R. Car, Phys. Rev. Lett. **66**, 1729 (1991).

[11] G. Brocks, P. J. Kelly, and R. Car, Surf. Sci. **269/270**, 860 (1992); G. Brocks and P. J. Kelly, Phys. Rev. Lett. **76**, 2362 (1996). Note that the former used a $p(\sqrt{8}\times\sqrt{8})R45°$ surface unit cell, while the latter used a $p(4\times4)$ cell.

[12] T. Yamasaki, T. Uda, and K. Terakura, Phys. Rev. Lett. **76**, 2949 (1996).

[13] D. R. Bowler and C. M. Goringe, Surf. Sci. **360**, L489 (1996).

[14] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[15] N. Roberts and R. J. Needs, Surf. Sci. **236**, 112 (1990).

[16] A. Ramstad, G. Brocks, and P. J. Kelly, Phys. Rev. B **51**, 14 504 (1995).

[17] Although the room-temperature STM image of the bare Si(100) surface shows unbuckled dimers in the symmetric $p(2\times1)$ configurations, it has been pointed out that the tip-surface interaction can effectively flip an asymmetric dimer as it follows the tip motion to produce symmetric images. See K. Cho and J. D. Joannopoulos, Phys. Rev. Lett. **71**, 1387 (1993).

[18] A. Vittadini, A. Selloni, and M. Casari, Phys. Rev. B **49**, 11 191 (1994). The most appropriate value for comparison is the result for the ''*cis*'' configuration in Table II, which is 0.2 eV.