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Dissociative adsorption of Si_2H_6 on the Si(001) surface

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We present results of *ab initio* calculations, based on pseudopotentials and the density functional theory, for the dissociative adsorption of Si_2H_6 on the Si(001) surface. Various models are considered, containing H and the radicals SiH_3 and SiH_2. Models based on the SiH_2 radical were considered with three adsorption sites: (i) an on-dimer position, (ii) an intrarow position between two neighboring Si dimers in the same dimer row, and (iii) an inter-row position between adjacent Si dimer rows. The intrarow and bridge geometries are considered with and without the saturation of the Si dangling bonds with hydrogen. For the 2×1 surface reconstruction, the on-dimer geometry is energetically more favorable than the inter-row geometry. For the 2×2 reconstruction, without hydrogen passivation of the Si dangling bonds, the on-dimer and intrarow geometries leave the system fully passivated. With hydrogen passivation of the Si dangling bonds, the on-dimer geometry is more favorable than the intrarow geometry.

I. INTRODUCTION

In recent years atomic and electronic properties of silicon surfaces have been the most investigated topics in surface science. This is particularly true for clean and covered Si(001) surfaces. The low-temperature clean Si(001) surface is understood to reconstruct to a $c(4\times2)$ phase consisting of alternately asymmetric dimers, while at room temperature the reconstruction becomes 2×1. Surface processes occurring during chemical vapor deposition (CVD) and atomic-layer epitaxy of group-IV elements are currently considered to be very important, such as in the CVD epitaxial growth of Si from disilane and passivation of the Si(001) surfaces with disilane and its radicals.[1]

Disilane (Si_2H_6) is well accepted to chemisorb on the Si(001) surface dissociatively, with the formation of hydride fragments[2–4] such as trihydride (SiH_3) and dihydride (SiH_2). The dissociation pathway is, however, quite complicated. Above 120 K a Si_2H_6 molecule undergoes dissociative chemisorption by breaking the relatively weaker Si-Si bond within the molecule to form two SiH_3 radicals. However, the SiH_3 radical is unstable, and at room temperature it decomposes into a SiH_2 species and a H atom, and the latter subsequently reacts with the dangling bond at a Si dimer atom to form SiH (monohydride).[4] There is further reaction between dihydride SiH_2 and the surface Si atoms, resulting in the formation of monohydride SiH. At higher temperatures two monohydride SiH species desorb in the form of a gaseous hydrogen molecule, leaving the growth of an epitaxial layer of Si on the Si(001) surface.[5] Different stages of the surface reaction can be expected to lead to different atomic geometry and electronic properties. So far only a few theoretical studies have been undertaken to determine the atomic geometry of the surface, with some of the above species chemisorbed.

Recent theoretical calculations using *ab initio* density-functional theory have found that the chemisorption of the SiH_2 radical on the Si dimer (i.e., in the bridge or on-dimer geometry) without hydrogen passivation is more stable and energetically favorable than the intrarow model (between two dimers in the same Si dimer row).[6] However, upon hydrogen passivation this equilibrium ordering is reversed: the intrarow model is found to be energetically more favorable than the on-dimer model. This work concluded that pairing of intrarow SiH_2 species plays an important role in the growth process, and suggested that further studies on the system be undertaken.[6]

In the present work we provide a systematic study of the equilibrium atomic geometry, electronic states, chemical bonding, and stability for chemisorption of various species during the decomposition of disilane on the Si(001) surface. While generally agreeing with recent theoretical works[6–8] for the intercomparison of different geometrical models, we have investigated a few other plausible geometries and discussed their intercomparison.

II. METHOD

Our calculations are made using the density-functional theory of Hohenberg, Kohn, and Sham. The electron-ion interaction was considered in the form of *ab initio* norm-conserving pseudopotentials listed by Bachelet, Hamann, and Schlüter.[9] Electron-electron interaction was considered within the local-density approximation of the density-functional theory, using the correlation scheme of Ceperley and Alder[10] as parametrized by Perdew and Zunger.[11] Self-consistent solutions to the Kohn-Sham equations were obtained by employing a set of four special **k** points for 2×1 and three special **k** points for 2×2 in the irreducible segment of the surface Brillouin zone.[12] Single-particle wave functions were expanded using a plane-wave basis up to a kinetic energy cutoff of 8 Ry. This cutoff was found to be adequate for the structural studies and the electronic struc-

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FIG. 1. Schematic side and top views of the models for possible intermediated steps of disilane at the 2×1 reconstruction. The models are explained in the text.

ture. We do not find any significant changes in structural parameters when the energy cutoff is increased from 8 to 12 Ry. Our earlier works[13–16] also concluded that structural results are well converged for H_2S or S chemisorbed semiconductor surfaces with an 8-Ry energy cutoff. Similar observations regarding converged results for H overlayer systems with an 8–10-Ry cutoff have also been made by other groups.[6,17]

We considered an artificially constructed periodic geometry along the surface normal. The unit cell included an atomic slab with eight layers of Si substrate plus a vacuum region equivalent to about six substrate layers in thickness. The two back substrate layers were frozen into their bulk positions, and each Si atom at the back surface was saturated with two pseudohydrogen (H_{ps}) atoms. All the remaining substrate atoms, the adsorbate atoms and the saturating H_{ps} atoms were allowed to relax into their minimum-energy positions using a conjugate gradient method.[18]

III. RESULTS AND DISCUSSIONS

With the energy cutoff used in this work, our theoretical lattice constant and bond length in silicon are 5.42 and 2.34 Å, respectively. These values are within 0.5% of experimental results. It is well known that on the clean Si(001)-(2×1) surface the Si dimers are tilted by approximately 16°, and have a length of 2.25 Å.[19–21] If a constrained symmetric Si-dimer geometry is enforced, then the dimer is slightly shortened to a length of 2.20 Å.[21] For the asymmetric dimer geometry the dangling bond at the higher-lying dimer component is fully occupied, with the associated electronic state close to the bulk valence-band maximum, and the dangling bond at the lower-lying dimer component is empty, corresponding to the energy state in the upper half of the bulk silicon band gap. For the symmetric dimer geometry there are two overlapping π-derived dangling-bond states:[19] these can be labeled π_u and π_g according to their orbital symmetries. Both of these are partially occupied, making the surface metallic.

Depositions of adsorbates can change the 2×1 reconstruction of the surface, with or without breaking of the Si-Si dimer π-bond, and lead to a new phase. In the present context, dissociation of disilane into various fragments at different temperatures can be expected to lead to a different reconstruction of the Si(001) surface, with different atomic geometry, electronic structure, and chemical bonding. In this section we will describe these changes for the chemisorption of a number of fragments of disilane based on radicals SiH_3 and SiH_2, with a particular emphasis on the electronic structure.

A. Atomic structure, electronic states, and chemical bondings

1. Disilane-dissociated trihydride geometry

Studies using scanning tunneling microscopy[4] as well as temperature, programmed desorption of H_2[2] indicate that at room temperature Si_2H_6 initially breaks into two SiH_3 radicals which are adsorbed as the first basic units on the Si(001)(2×1) surface. Starting with an asymmetric dimer geometry with a tilt angle of 9°, we placed the SiH_3 radical at the dangling-bond position of each of the dimer atoms on the clean surface, as shown in Fig. 1(a). No symmetry was imposed within the 2×1 unit cell, so as to allow the two SiH_3 units to behave independently.

The trihydride species saturate the Si dangling bonds, making all silicon atoms fourfold coordinated. The relaxed geometrical parameters are indicated in Fig. 1(a). The Si-Si dimer becomes symmetric (dimer-tilt angle of <1.1°), and elongated to a length of 2.38 Å. The 6% elongation of the dimer means that its strength has been significantly weakened. An interesting observation we have made is that the two SiH_3 radicals do not adsorb symmetrically with respect to the Si-Si dimer. This is shown in the top view of Fig. 1(a). Although the Si-Si dimer is symmetric, its elongation is accompanied by a relative twist between the two Si-SiH_3 units. The Si atoms in the two trihydride radicals have relaxed to different heights and are at different x coordinates (see Fig. 1 for directions). The distance between the Si atoms in the two trihydride radicals is much shorter (3.50 Å) compared to the similar Si-Si atom separation (3.83 Å) in the bulk along the y direction. This leads to two different bond lengths between the Si in the dimer and the Si in the trihydride. We obtained these bond lengths to be 2.33 and 2.30 Å. Although this difference is very small, it nevertheless provides an indication that one of the trihydride radicals can break away from the surface, or at least decompose into fragments such as SiH_2 and H.

The adsorption of trihydride radicals at both Si dimer dangling bonds results in two occupied surface states below the valence-band edge, as shown in Fig. 2(a). There are no unoccupied states in the band gap, and thus the surface is fully passivated. As seen in Fig. 3(a), the second highest occupied state S_1 shows a strong $pp\sigma$ bonding between the Si atom in the higher lying SiH_3 radical and the Si dimer atom nearest to it. The highest occupied state S_2 is mainly contributed from $pp\sigma$ bonding between Si dimer atoms, but also has an appreciable contribution from $pp\sigma$ bonding between the Si in the lower-lying trihydride radical and the Si dimer atom nearest to it.

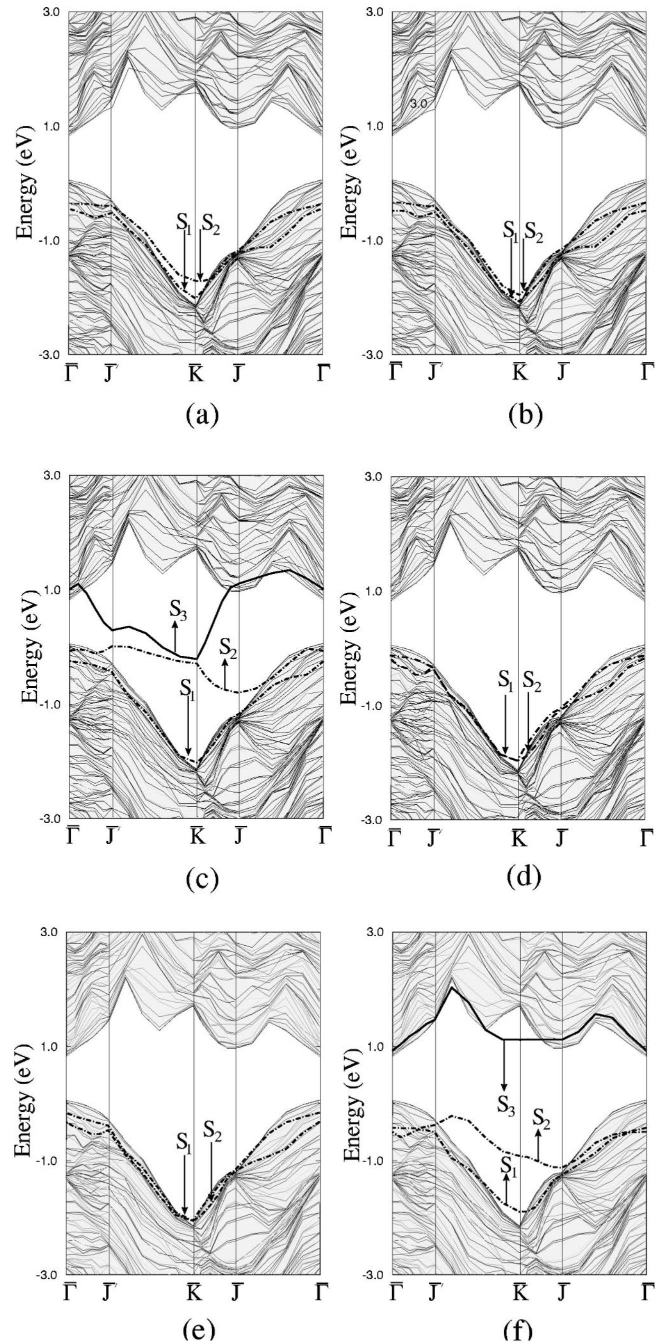

FIG. 2. Calculated band structure for the models shown in Fig. 1. The shaded region is the bulk (2×1)-projected band structure for Si, the dashed lines represent the occupied surface bands, and the thick lines represent the unoccupied surface bands.

2. Silane-dissociated trihydride geometry

Under ultrahigh-vacuum conditions gaseous SiH_4 reacts with Si(001) to produce trihydride (SiH_3) and H species which become attached to each of the dangling bonds at the Si dimer atoms.[8] This is shown schematically in Fig. 1(b).

The relaxed chemisorbed geometry leads to an increased length of 2.39 Å for the Si-Si dimer bond. This value is close to the values of 2.42 and 2.45 Å obtained in cluster calculations by Brown and Doren[8] using density-functional theory and two different basis sets. We find that the Si-Si dimer has turned almost flat, with a small tilt angle of 1.36°. This compares favorably with the values 0.55° and 1.14° obtained in the works by Brown and Doren. Our calculated Si-H bond length is 1.52 Å, very close to the value of 1.54 Å calculated by Nardelli *et al.*[22] using both pseudopotential and linearized-muffin-tin-orbital methods on the hydrogen covered Si(111) surfaces.[22] Brown and Doren[8] also calculated this bond length as 1.50 Å.

The resulting band-structure and orbital bonding characteristics are shown in Figs. 2(b) and 3(b), respectively. Once gain, the system is totally passivated, with two occupied surface states found very close to the bulk valence continuum at the $\bar{K}$ point on the surface Brillouin zone. The electronic state labeled S_1 orginates from the $pp\sigma$ bonding within the

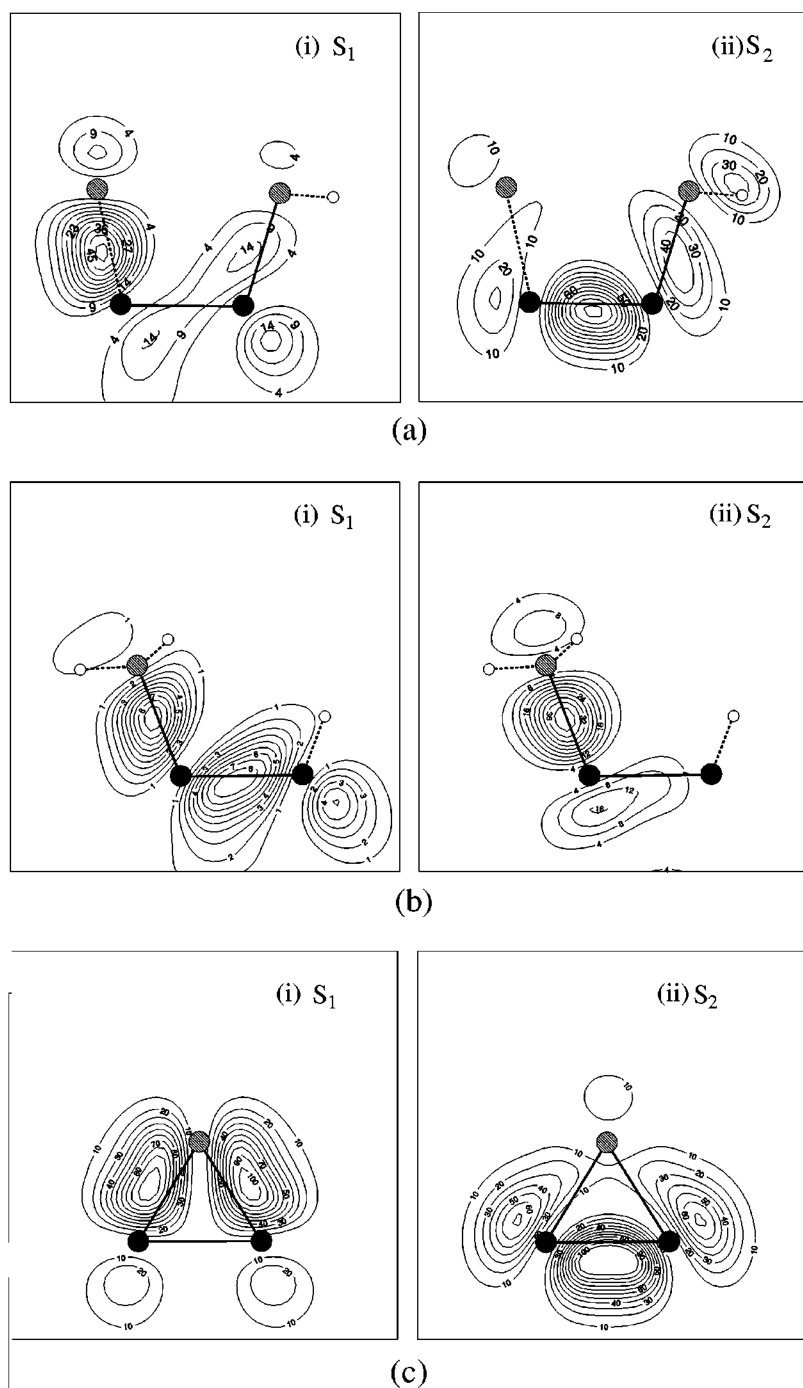

FIG. 3. Electronic charge density plots for the S_1 and S_2 states corresponding to panels (a), (b), and (c) in Figs. 1 and 2. In-plane bonds are indicated by solid lines, whereas out-of-plane bonds are indicated by dashed lines.

Si-Si dimer and the $pp\sigma$ bonding between Si in SiH_3 and the Si dimer atom nearest to it. There is some charge flow from the surface to the bulk region, so this state is almost resonant with the bulk. The highest occupied state S_2 is primarily due to the $pp\sigma$ bonding between Si-SiH_3 and the Si dimer atom.

3. Dihydride-based geometries

Whether produced from the dissociation of disilane or silane, the SiH_3 radical is found to quickly dissociate into SiH_2 and H, both of which may be bonded to the Si dimer atoms.[4,8] There are many possible geometries based on the chemisorption of dihydride radical, with or without the adsorption of the fragmented hydrogen, and with Si-Si dimers intact or broken. In general, there are three basic structural models for the adsorption of SiH_2: (i) inter-row, (ii) on dimer, and (iii) intrarow. Bowler and Goringe[7] studied all these models on the bare silicon surface, i.e., without the adsorption of the fragmented hydrogen. Their work suggested that the intrarow geometry is the most favorable. Hong and Chou[6] considered the first three models. In contrast to the work by Bowler and Goringe, the work by Hong and Chou found that, without the adsorption of the fragmented hydrogen, the on-dimer model is more favorable than the intrarow and inter-row models. Hong and Chou further found that when adsorption of both the dihydride and the fragmented hydrogen is considered, the intrarow model becomes more favorable than the on-dimer model. Moreover, Hong and Chou found that the relative stability of the intrarow model over the on-dimer model decreases slightly

when all surface dimer atoms are passivated with hydrogen, except the ones bonded to SiH_2. In this work we studied atomic geometry and electronic states for a number of models for the adsorption of SiH_2, with or without additional H, including those not considered previously.

(i) *Inter-row geometry*: For the adsorption of SiH_2 on bare Si(001) Bowler and Goringe, as well as Hong and Chou, considered a (2×2)-reconstructed geometry. This leads to two different, but much enlarged, dimer bond lenghts, and a similarly large bond length between a dimer atom and the Si atom in the SiH_2 radical. The system is thus characterized by a large strain energy.

When the density of the SiH_2 radical is doubled, and one radical is absorbed per 2×1 surface unit cell, then we find that the surface dimer is broken and a strong bond is formed between Si atoms from adjacent dimer rows and the Si atom in the SiH_2 radical [Fig. 1(c)]. However, this leads to the creation of two Si dangling bonds per 2×1 unit cell, which turns the surface metallic. This is shown in Fig. 2(c). The dangling bonds at the broken dimer atoms can either be passivated by hydrogen atoms present in the CVD chamber or by the adsorption of another SiH_2 radical per unit cell, as shown in Figs. 1(d) and 1(e), respectively. In both cases the system becomes semiconducting: the highest occupied surface state can only be seen above the bulk valence continuum around the $\bar{K}$ point [cf. Figs. 2(d) and 2(e)], and is mainly derived from the bonding between the surface Si atom and the Si atom in the SiH_2 radical. Both upon passivation by hydrogen atoms and by the adsorption of another SiH_2 radical, all top-layer substrate Si atoms are relaxed back to their bulk sites. The angle involving the Si in SiH_2 and its neighboring substrate Si atoms is close to the tetrahedral value.

If the system is constrained to maintain the Si-Si dimer bond by allowing atomic relaxation only along the surface normal, then the energy goes up by about 0.57 eV per unit cell. This is because even though this constraint stretches the Si-Si dimer bond length to nearly 2.56 Å, there is virtually no bonding between the SiH_2 radical and the substrate Si atoms. A similar observation was discussed in Ref. 4.

(ii) *On-dimer geometry*: As with the inter-row geometry, we considered adsorption of one SiH_2 radical per 2×1 unit cell. On the bare surface, the on-dimer geometry, shown in Fig. 1(f), was found to be more energetically favorable than the inter-row geometry by 0.39 eV per SiH_2. The relative stability of the on-dimer geometry in our case is similar to that obtained by Bowler and Goringe (0.31 eV per SiH_2 for calculation with a 2×2 unit cell), but somewhat smaller than the results obtained by Hong and Chou (0.56 eV per SiH_2 for calculation with a 2×2 unit cell). Our calculations suggest that the Si-Si dimer bond is elongated to 2.43 Å, and the SiH_2 molecule forms an angle of 63.5° at the dimer, similar to the values obtained in Refs. 6 and 7. The bond length between the Si atom in the SiH_2 radical and the Si atom in the dimer is 2.31 Å, closer to the values calculated in Refs. 6–8.

The system is found to be semiconducting in nature, with two occupied surface states lying outside the fundamental band gap but above the bulk valence continuum along the $\bar{J}'$-$\bar{K}$-$\bar{J}$ segments, as seen in Fig. 2(f). The highest occupied state, shown in Fig. 3(c-ii), is due to the bonding between the Si p_z orbital in the SiH_2 radical and the π orbital at the Si-Si dimer. The second highest state has a predominantly p_y character derived from the Si atom in the SiH_2 radical. There is an unoccupied state which lies just outside the band-gap region around the $\bar{K}$ point, and appears to be due to the σ^* bonding between the H atoms in the SiH_2 radical.

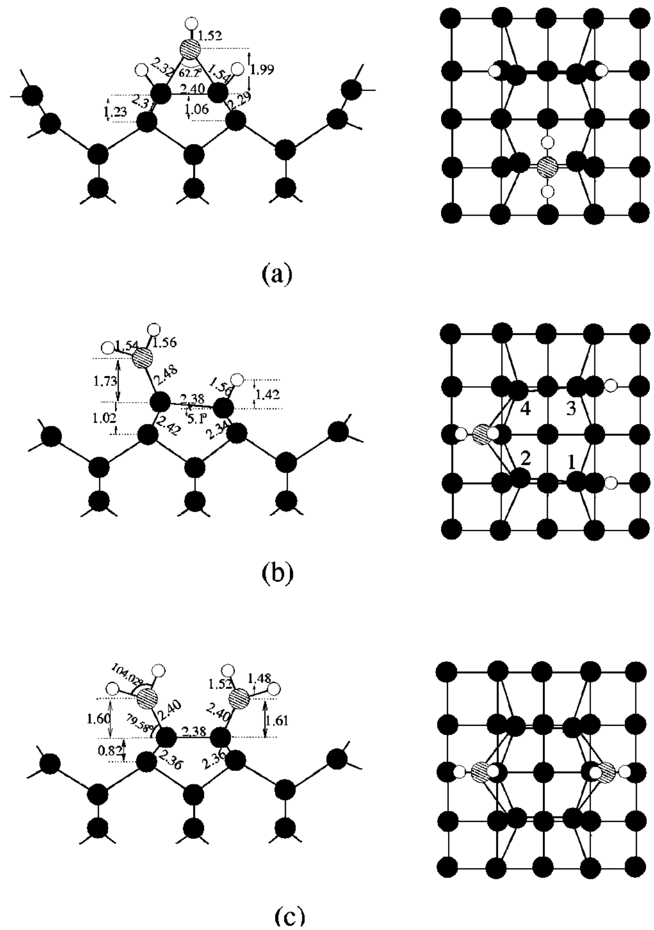

FIG. 4. Schematic side and top views of the models with the 2×2 surface reconstruction. The models are explained in the text.

In order to study adsorption of SiH_2+H, and adsorption of SiH_2 on hydrogen passivated surface, we considered a 2×2 unit cell. We first consider the adsorption of a single SiH_2 group on the bare 2×2 unit cell. The dimer upon which this group is adsorbed becomes flat with a bond length 2.42 Å, while the other (bare) dimer remains tilted. However, the characteristics of this tilted dimer are somewhat different from those of the dimer on the *clean* Si(001)(2×1) surface. In the present case the dimer length is 2.23 Å, and has a tilt of 11.3°. For the SiH_2+H geometry, the H atom saturates one of the dangling bonds of the otherwise bare dimer, making the system metallic and thus undesirable. Adsorption of SiH_2 on the hydrogen-passivated surface saturates both dangling bonds of the second Si-Si dimer by hydrogen. The structural changes for this system with regards to the Si-Si bond lengths and the Si-Si-Si bond angles are within 1.5% of the results obtained for the adsorption of SiH_2 on the bare surface with a 2×1 reconstruction. The geometrical results for the passivated case are indicated in Fig. 4(a). Interestingly, the bond lengths of the two Si-Si dimers in the unit

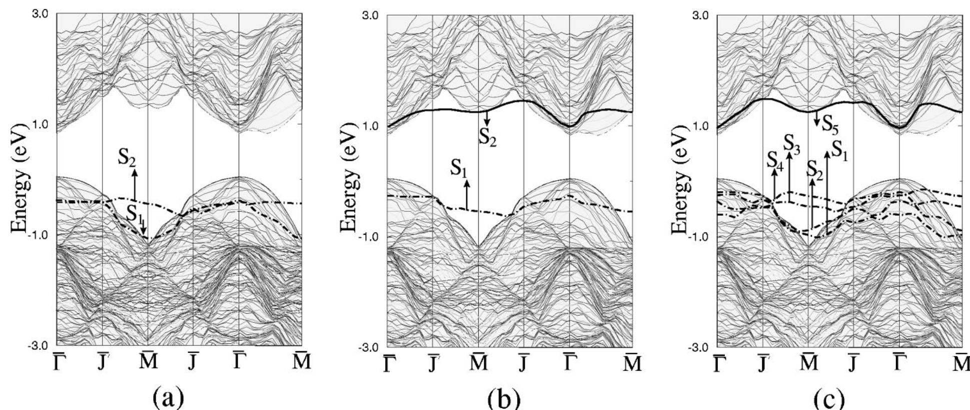

FIG. 5. Calculated band structure for the models shown in Fig. 4. The shaded region is the bulk (2×2)-projected band structure for Si, dashed lines represent occupied surface bands, and thick lines represent unoccupied surface bands.

cell are almost identical to each other. Another interesting feature of this geometry is that the two Si-Si dimers are at different heights from the silicon layer below. These distances are 1.06 and 1.23 Å for dimers bonded to SiH_2 and hydrogen atoms, respectively. This difference can be expected on the basis of the relative heaviness of the adsorbates on the two dimers. The system remains semiconducting, and the corresponding electronic structure is shown in Fig. 5(a). The highest occupied surface state S_2 remains at almost the same energy location and with the same orbital nature as observed for the adsorption of SiH_2 on the bare surface.

(iii) *Intrarow geometry*: Adsorption of SiH_2 in the intrarow configuration on the bare $Si(001)(2\times2)$ surface ''pinches'' the two Si-Si dimers within the unit cell, such that the dimer component bonded to SiH_2 is pulled toward the radical. For the purpose of discussion we can label the four Si atoms forming the two dimers as 1–4, with atoms 2 and 4 bonded to the SiH_2 radical [cf. Fig. 4(b), but without hydrogen saturation of the dangling bonds at atoms 1 and 3]. Atoms 2 and 4 are almost at the same height, and atoms 1 and 3 lie, respectively, 0.48 and 0.04 Å below atoms 2 and 4. Pair 1-2 is almost a flat dimer of length 2.38 Å, and pair 3-4 is an asymmetric dimer (tilt angle 11.5°) of length 2.36 Å. This characteristic of the system can be understood on the basis of charge transfer taking place within the unit cell, leading to the dangling bonds at the atoms 1 and 3 as fully occupied and empty, respectively. A similar atomic configuration was obtained in the work by Hong and Chou, but not discussed in detail. We find that the resulting band structure is semiconducting with a small band gap of about 0.1 eV within the local-density approximation.

The SiH_2+H system can be considered as the dissociated adsorption model for the trihydride radical SiH_3. For this we have placed the H atom at the empty dangling bond at atom 3 mentioned above. This has the tendency of making the dimers flat, and of equalizing the dimer lengths, as noted by Hong and Chou. As expected, the band structure is metallic, and thus undesirable.

When another H atom is attached to the other dimer, making the adsorption of SiH_2 on the passivated surface, then the calculated dimer bond lengths have equalized to an elongated value of 2.38 Å and the dimers are tilted by approximately 5° with the H-terminated end lying lower. The resulting geometry is shown in Fig. 4(b). The adsorption of the SiH_2+H+H unit per 2×2 unit cell compresses the interplanar distance between the surface dimer and the Si surface layer to 1.02 Å. For the equilibrium geometry we have identified one occupied surface state below the valence-band maximum in the valley near the $\bar{M}$ point, and one unoccupied state above the conduction band minimum [cf. Fig. 5(b)]. The highest occupied state is characterized by charge localization between the Si atom in the SiH_2 group and the surface dimer components to which it is bonded. It also has localization of charge between the second and third substrate layers underneath the adsorbate, due to bond distortions as seen in Fig. 6.

The dangling bonds at both ends of the two dimers in the 2×2 unit cell can also be saturated by adsorption of two SiH_2 radicals within the intrarow model, as shown in Fig. 4(c). For this geometry the Si-Si dimers become symmetric with bond a length of 2.38 Å. But now there is some compression between the Si adatom and the dimer (1.60 Å), and between the dimer and the silicon layer below (0.82 Å). The bond length between the Si adatom and the dimer atom is slightly shortened to 2.40 Å, indicating a slightly stronger bond compared with the SiH_2+H+H system. We find that this arrangement also passivates the surface. Total charge-density calculations suggest that there are strong covalent bondings between the dimer atoms and between the Si atoms in adatom and dimer layers. There is also evidence of interdimer bonding between H atoms in the cave region, which suggests pairing between SiH_2 radicals. There are up to four occupied states below the valence-band maximum, but above the bulk valence spectrum around the $\bar{M}$ point. The highest occupied state is characterized by the dimer $pp\sigma$ bonding, with further evidence of pairing between the Si p orbitals in the two SiH_2 radicals.

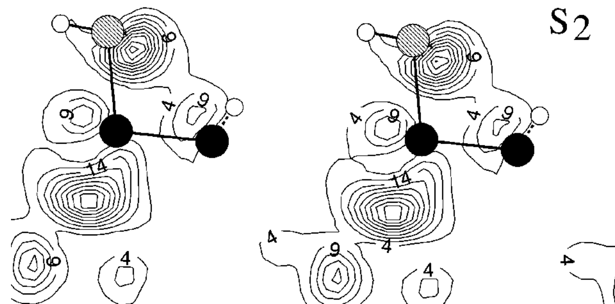

FIG. 6. The electronic charge density plot for the highest occupied surface state shown in Fig. 5(b). In-plane bonds are indicated by solid lines, whereas out-of-plane bonds are indicated by dashed lines.

TABLE I. Relative energies for different configurations of SiH_2, SiH_2+H (hydrogenated) and SiH_2 plus monohydride (passivated) on Si(001). The energies have been compared with the results of earlier theoretical calculations made by Hong and Chou (Ref. 6) and Bowler and Goringe (Ref. 7). The energies are in eV per SiH_2.

	Present			Ref. 6			Ref. 7		
	SiH_2	SiH_2+H	Passivated	SiH_2	SiH_2+H	Passivated	SiH_2	SiH_2+H	Passivated
On-dimer	−0.10	0.15	−0.08	−0.14	0.13	0.11	0.004		
Intrarow	0.00	0.00	0.00	0.00	0.00	0.00	0.00		

B. Energetic stability of systems containing the SiH_2 radical

We first consider systems with 2×1 surface reconstruction. There is an energy gain of 0.57 eV when the Si-Si dimers are broken within the inter-row geometry. However, the on-dimer geometry is energetically more favorable by 0.39 eV than the inter-row geometry with broken dimers. It is interesting to note that the energy of the broken-dimer inter-row geometry upon hydrogen passivation, shown in Fig. 1(e), is comparable to that of the silane dissociated trihydride geometry shown in Fig. 1(b), being only 0.04 eV higher.

We compare the total energies of the on-dimer and intrarow geometries with the 2×2 surface reconstruction in Table I. On the bare surface, the energy of the the intrarow geometry is 0.10 eV higher than that of the on-dimer geometry. Our calculation of this energy difference agrees better with the work of Hong and Chou than with that of Bowler and Goringe. For the adsorption of SiH_2 on a H-passivated surface, we find that the on-dimer geometry is energetically more favorable than the intrarow dimer geometry, in disagreement with the work of Hong and Chou. For the adsorption on the hydrogenated surface (i.e., for the SiH_2+H system), we in general agree with the work of Hong and Chou that the intrarow geometry is energetically favorable to the on-dimer geometry.

IV. SUMMARY

We have studied the equilibrium atomic geometry, electronic states, and chemical bondings on the Si(001) surface with various geometries involving trihydride and dihydride radicals during the dissociative adsorption of Si_2H_6, with and without the presence of extra hydrogen. Our results can be summarized as follows.

Geometry: Deposition of trihydride or dihydride leads to the Si-Si dimer length being elongated by approximately 6% compared to its value for the clean surface. The bond length between the Si adatom and the nearest surface-layer Si atom is approximately bulklike, except for the intrarow geometry for which this length is much larger (between 3% and 6%). The Si adatom is generally located at different heights from the surface Si atoms for different geometrical models and for the adsorption of different radicals.

Electronic structure: All the passivated geometries considered here leave no surface states inside the bulk band gap. For the deposition of the SiH_2 radical on a hydrogen-passivated surface with 2×2 reconstruction, there is a slight difference in the band structures for the on-dimer and intrarow geometries. The latter geometry is characterized by the presence of an unoccupied state slightly above the conduction band minimum.

Stability: For the 2×1 surface reconstruction, the on-dimer geometry is energetically more favorable than the inter-row geometry. For the deposition of the SiH_2 radical on the bare as well as hydrogen-passivated surface, with a 2×2 surface reconstruction, the on-dimer geometry is energetically more favorable than the intrarow geometry.

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