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Dissociative adsorption of NH_3 on Si(001)-(2×1)

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Using the first-principles pseudopotential–local-density-approximation approach, we have studied the dissociative molecular adsorption of NH_3 on Si(001)-(2×1). We find that upon adsorption the Si dimer becomes symmetric and somewhat elongated. We also find that the Si-N bond is inclined at 10° with respect to the surface normal, the N-Si bond length is 1.75 Å, and the N-H bond length is 1.05 Å. Finally, our electronic structure calculations suggest that the adsorption of ammonia almost completely passivates the silicon surface. [S0163-1829(98)05636-7]

I. INTRODUCTION

Studies of adsorbate covered semiconductor surfaces have attracted a great deal of attention in the past few years. In particular, due to their role in device manufacturing, the electronic and atomic structure of adsorbate covered silicon surfaces have been studied most widely. One example is the adsorption of the reactive NH_3 molecule on Si(001). This molecule is an excellent nitration agent, useful in the production of ultrathin, sharp silicon nitride (SiN_x) interfaces with potential application in future ultra-large-scale integrated (ULSI) circuits.[1]

For a complete understanding of the nitration process, it is essential to study details of the geometry and electronic structure of the interaction of ammonia with the Si(001)-(2×1) surface. One of the first studies on this issue, by Bozso and Avouris[2,3] using x-ray and ultraviolet photoemission techniques, found that the Si(001) surface is highly reactive to ammonia and that the surface dangling bonds promote dissociation of the molecule at low temperatures (around 90 K). The same group,[4] using the scanning-tunnelling-microscopy technique, showed that even at 300 K the silicon-ammonia reaction not only preserved the Si-Si dimer bonds but that these dimers were virtually all symmetrically terminated. From this observation, they concluded that the Si dangling bonds are predominantly hydrogen terminated and that the nitrogen occupies subsurface sites. This view is not upheld by subsequent experimental work. Using the electron stimulated desorption ion angular distribution technique, Johnson, Walczak, and Madey[5] found that NH_x fragments on the surface, indicating low-temperature dissociation of NH_3. Dresser *et al.*[6] employed a number of different experimental techniques to conclude dissociative adsorption of NH_3, with the formation of Si-NH_2 and Si-H bonds. The work by Fujisawa *et al.*,[7] using the high-resolution vibrational electron energy-loss spectroscopy, confirmed the presence of Si-NH_2 and Si-H bonds at room temperature. Using the same experimental technique, Larsson and Flodstrom[8] concluded that the NH_2 group and H are attached to different components of the Si-Si dimer. Dresser *et al.*[6] and Fujisawa *et al.*[7] suggested a trigonal pyramidal geometry for the Si-NH_2 group, with the H-N-H bond angles essentially the same value as in the ammonia molecule.

More recently Franco and co-workers[9,10] have used the scanned-energy mode photoelectron diffraction (PhD) technique to determine the local atomic structure of the NH_2 species on Si(001)-(2×1) and its effect on the asymmetry of the Si-Si dimer. This technique exploits the coherent interference of the directly emitted component of the photoelectron wave field resulting from an adsorbate core level with other components of the same wave field elastically backscattered from surrounding (mainly substrate) atoms[10] and is able to provide firm evidence concerning the location of the N atom. Their work determines the N-Si bond to be of length 1.73±0.08 Å inclined at $\phi = 21° \pm 4°$ with respect to the surface normal (see Fig. 1). However, due to the absence of the H core level this technique is unable to provide any information[11] about the N-H and Si-H bonds. Furthermore, being a local probe, this technique does not have sufficient precision to determine the tilt angle of the Si-Si dimer. The reported dimer tilt angle is $8° \pm 8°$, meaning that it could be anything between 0° (totally symmetric case) and 16° [the full asymmetry on the clean Si(001)-(2×1) surface[12]]. These authors have, however, employed an alternative route and *indirectly* concluded that the dimer tilt angle is substan-

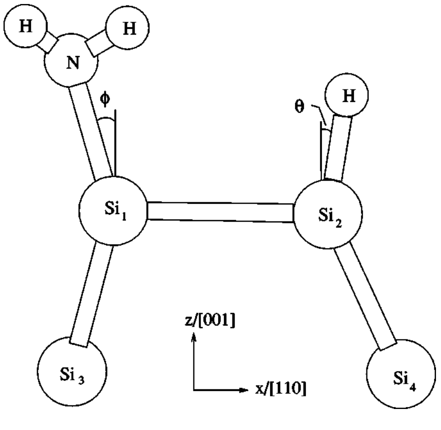

FIG. 1. Schematic side view of the dissociative adsorption model of NH_3 on Si(001)-(2×1).

tially reduced, or possibly removed.

From the theoretical point of view, as far as we are aware, only three investigations have been reported. Zhou, Cao, and Fu[13] used a DV-$X\alpha$ (discrete variational $X\alpha$) and atom superposition and electron-delocalization–molecular-orbital theory. Moriarty and Smith[14] employed the modified intermediate neglect of differential overlap (SLAB-MINDO) molecular-orbital method presenting different structural results. In the third work, where a detailed energetic investigation of the system was made, Fattal *et al.*[15] used the complete-active-space self-consistent-field/multireference single-and-double-excitation configuration-interaction (CASSCF/MRSDCI) theory by modeling a Si-Si dimer within a Si_9H_{12} cluster. The theoretical work of Fattal *et al.* predicts that dissociative adsorption of NH_3 on Si(001)-(2×1) takes place in two steps: the molecule NH_3 is first chemisorbed on a single Si dimer component. This is followed by activated N-H bond cleavage of NH_3, leading to adsorption of NH_2 on one dimer component and the adsorption of H on the other. While the results from the three approaches agree on the tilt angle of the Si-N bond from the surface normal, the planar structure of the Si-NH_2 calculated by Moriarty and Smith is in serious disagreement with the trigonal-pyramidal orientation predicted by the other two groups.

In this work we employ the state of the art pseudopotential method, within the local-density approximation, to accurately calculate the atomic and electronic structure of the coadsorbed NH_2/H system on Si(001)-(2×1). We provide a critical discussion on the available theoretical and experimental results on the system.

II. THEORETICAL CONSIDERATIONS

The surface was modeled in a supercell geometry, with an atomic slab of 8 Si layers and a vacuum region equivalent to four atomic layers. The theoretical bulk Si lattice constant of 5.42 Å is used in the surface calculations. On the top side of the slab we placed the coadsorbed NH_2 and H species, and the back surface was passivated by H atoms arranged in a dihydride structure. The pseudopotentials for Si, N, and H were derived by using the scheme of Troüllier and Martins[16] and the electron-electron exchange correlation was considered by using the scheme of Ceperley and Alder as parametrized by Perdew and Zunger.[17] The single-particle orbitals were expressed in a plane-wave basis up to the kinetic-energy cutoff of 30 Ry and eight special **k** points were used for the Brillouin-zone summation. Increasing the energy cutoff to 40 Ry did not change the key structural parameters by more than 0.6%.

III. ATOMIC STRUCTURE

A. NH_3 molecule

The plane-wave pseudopotential method has very successfully been applied for many years in studies of atomic and electronic structure of solids. However, the size of the basis set increases enormously when dealing with systems comprised of first-row elements that generally are characterized by sharp pseudopotentials due to the lack of a *p* core state. In a previous study[12] it was noted that the N pseudopotential listed in the paper by Bachelet, Hamann, and Schlüter[18] would require a very large kinetic-energy cutoff for reasonably converged geometrical and electronic results. It was also noted that a softer N pseudopotential generated by using a scheme such as that due to Troüllier and Martins[16] can produce well-converged results for a relatively smaller energy cutoff. In this study we thus begin by investigating the application of our method and the pseudopotentials to the structural determination of the ammonia molecule.

In order to do so, we found that placing the NH_3 molecule in a cube of size 17 a.u. provided well-converged results, with the N-H bond distance 1.05 Å and the H-N-H angle 104°. These values are in good agreement with experimental values available in the literature,[19,20] where the N-H bond length of 1.01 Å and the bond angle H-N-H between 106° and 107° are reported. The same level of agreement is observed when we compare our results with two recent *ab initio* studies. Northrup, Felice, and Neugebauer,[21] using a first-principles pseudopotential framework similar to ours, obtained the bond length of 1.01 Å and the bond angle 107° for the molecule, while using the CASSCF/MRSDCI theory Fattal *et al.*[15] obtained 1.03 Å for the bond length and 106.4° for the bond angle. Furthermore, we observe that increasing the cube size first to 20 a.u. and then to 23 a.u. did not have a significant effect on the bond length and bond angle obtained previously.

B. Si(001)-(2×1) surface

In order to understand the adsorption of NH_3 on the Si(001) surface, it is instructive to examine first the clean Si(001)-(2×1) surface. Although the clean surface has long been known to reconstruct by the formation of dimers,[22–24] only recently has there developed consensus for the asymmetric model[25–27] characterized by a charge transfer from one dimer component to the other, as discussed later. Our calculations are in full agreement with the asymmetric dimer model. The clean Si(001)-(2×1) structure was calculated to have the length 2.25 Å with a tilt angle of 16°, in agreement with experimental[28,29] and other theoretical studies.[25–27] Another interesting point concerns the backbond, expected to be most strongly stressed in the substrate because it deviates considerably from the tetrahedral configuration around the second-layer atoms. In fact we find that the distance in the growth direction [001] between the first- and second-layer atoms can be as great as 1.37 Å for the upper dimer atom, or just 0.73 Å for the lower dimer atom. The bond lengths are found to be 2.39 Å for the Si bonded to the upper dimer atom and 2.33 Å for the Si bonded to the lower dimer atom, the average of these values being only slightly greater than the bulk bond length of 2.35 Å. It should be pointed out that the results obtained by Fattal *et al.* for this surface are at variance with the well-converged results obtained by us and other groups. In particular, their work suggests an almost symmetric Si-Si dimer [cf. Fig. 2(a) in their paper], with a bond length of 2.42 Å, which is 7.5% larger than the value obtained in our work.

C. The NH_3/Si(001)-(2×1) surface

Our total-energy calculations confirm the prediction made by Fattal *et al.*[15] that the adsorption of NH_3 on the Si(001)-(2×1) surface is an exothermic process. The chemisorption energy of (NH_2+H):Si(001) relative to free

TABLE I. Comparison of structural parameters for NH_3/Si(001)-(2×1) obtained in this work and in previous theoretical and experimental works. The symbols are explained in Fig. 1.

Bond lengths (Å)	Pres. work	Refs. 9, 10	Ref. 13	Ref. 14	Ref. 15
Si-Si	2.36			2.42	2.496
Si-N	1.75	1.73	2.04	1.71	1.768
Si-H	1.51		1.38	1.52	1.516
N-H	1.05		1.14	1.02	1.025
Bond angles (deg)					
Si-Si dimer tilt	1.9	8±8		2.2	
Si-N (ϕ)	10	21±4	25	22.7	24
Si-H (θ)	16		25	19.5	20.7
H-N-H	105		105	106	110.7

NH_3 and clean Si(001) obtained from our calculations is 100 kcal/mol. This result is consistent with the findings of Fattal *et al.*,[15] who calculated a value of 75 kcal/mol. Table I lists the important structural parameters calculated in this work for the dissociative molecular adsorption of NH_3 on Si(001)-(2×1). To facilitate discussion previous theoretical and experimental results are also listed.

Upon the adsorption of ammonia, the Si dimer gets elongated by approximately 5% with bond length 2.36 Å and becomes almost symmetric with a tilt angle of only 1.9°. This finding is in very good agreement with the theoretical work of Moriarty and Smith[14] where a bond length of 2.42 Å and a tilt angle of 2.2° is reported. The theoretical work by Fattal *et al.* also predicts an elongation of the Si-Si dimer by approximately 3% with an almost symmetrical configuration. There is no information in the paper by Zhou, Cao, and Fu about the Si-Si dimer. As mentioned earlier, although there is no direct information available about the Si-Si dimer in the experimental work by Franco *et al.*, their *indirect* conclusion is that the dimer is inclined at an angle $8°\pm8°$ and is of length 2.8 ± 0.7 Å. Because of the large error bars of the experimental measurements by Franco *et al.*, it is difficult to reach a definite conclusion about the level of agreement between our predictions and their results. The expanded Si dimer length predicted in our work would indicate softening of the dimer bond. Similar findings were presented concerning the Si-Si dimer length upon the adsorption of other elements.[26,30]

Our calculated N-Si bond length of 1.75 Å is in very good agreement with the experimental value of 1.73 ± 0.08 Å by Franco *et al.*,[10] with the theoretical value of 1.71 Å by Moriarty and Smith,[14] and with the theoretical value of 1.77 Å obtained by Fattal *et al.*,[15] but is slightly different from the 2.04 Å obtained by Zhou, Cao, and Fu.[13] The work of Fattal *et al.*[15] has reported the Si-Si-N angle to be 114°, which compares favorably with the approximately 102° obtained in our work.

With respect to the surface normal, we calculated the inclination of the N-Si bond as $\phi=10°$ (see Fig. 1). This value is appreciably smaller than that of all three experimental estimates available: the optimum fit structure in the work of Franco *et al.*[10] gives a value of $21°\pm4°$, while Fujisawa *et al.*[7] and Dresser *et al.*[6] *estimated* values of 20° and 35°, respectively. While we discuss a possible reason for the difference between our result and the findings of Franco *et al.* later on, it is worth emphasizing that the biggest difference lies between our result and that of Dresser *et al.* This is not surprising as Dresser *et al.* estimated their results by assuming Si(001)-(2×1):F bond angles in their electron-stimulated desorption ion angular distribution (ESDIAD) analysis of the Si/NH_3 system. Similarly, the theoretical values of 22.7° obtained by Moriarty and Smith[14] and 25° obtained by Zhou, Cao, and Fu[13] are more than twice as large as those of our prediction. The difference between our result and previous theoretical calculations for the angle ϕ is possibly due to (a) the lack of self-consistency in the works of Zhou *et al.* and Moriarty and Smith and (b) the use of a small cluster by Fattal *et al.*

As a consequence of the symmetric dimer, we expect a lowering of the stress on the layer immediately below the dimer. Our calculations showed that the distances in the growth direction are 1.17 Å for the upper dimer atom and 1.18 Å for the lower dimer atom, in opposition to the large dimer buckling (0.6 Å) found in the clean surface case. We find that the height of the dimer in the growth direction is slightly bigger on the adsorbate covered surface when compared to the clean surface. The backbond lengths are slightly greater in the clean surface case (2.39 Å for the upper dimer atom and 2.33 Å for the lower dimer atom) when compared to the adsorbate case (2.38 Å and 2.31 Å, respectively). This behavior is not observed upon the adsorption of Cl on the same surface, as reported by Casagrande, Srivastava, and Ferraz.[30]

In addition, we find that the NH_2 species preserves its trigonal character with the H-N-H angle as 105°, exactly the same found for the NH_3 molecule, and as suggested by Dresser *et al.* and Fujisawa *et al.* Similarly, the N-H bond distance is 1.05 Å, again the same value as for the NH_3 molecule. Our prediction of the trigonal-pyramidal orientation of the Si-NH_2 group is in agreement with the theoretical works by Zhou, Cao, and Fu and by Fattal *et al.*, but is contrary to the planar structure calculated by Moriarty and Smith. Our calculated results for the N-H distance and the H-N-H angle are also in good agreement with the results presented by Zhou, Cao, and Fu and Fattal *et al.*

The H adsorbed by the other Si dimer component is at a distance 1.51 Å, in very good agreement with the value of 1.52 Å obtained by Moriarty and Smith and Fattal *et al.* and in reasonable agreement with the value of 1.38 Å calculated

TABLE II. Comparison of structural parameters for the relaxed NH_3/Si(001)-(2×1) structure, with the photoelectron diffraction experiment by Franco *et al.* The origin is taken at the Si atom labeled Si_3 in Fig. 1, which is almost at its bulk position. The symbols are explained in the text.

Parameter (Å)	Pres. work	Ref. 10
x_{N1}	-0.30	-0.63 ± 0.06
z_{N1}	1.72	1.61 ± 0.02
x_{13}	0.71	0.50 ± 0.25
z_{13}	1.18	1.12 ± 0.06
x_{23}	3.09	$3.3\ \pm0.3$
z_{23}	1.10	$1.5\ \pm0.4$

by Zhou, Cao, and Fu. The H-Si bond is found to be inclined at $\theta = 16°$ with respect to the surface normal, against 25° and 19.5° calculated by Zhou, Cao, and Fu, and Moriarty and Smith, respectively. The angle between the Si-Si dimer and this H is 104°, slightly different from the 110.7° obtained in the work of Fattal *et al.*

In Table II the structural parameters of our relaxed structure are compared with the best-fit model obtained from the photoelectron diffraction by Franco *et al.* The coordinate system and the notation used are the same as in Franco *et al.*, where x is along [110] and z along the surface normal [001]. The atomic positions are measured with respect to the second substrate Si atom labeled Si_3 in Fig. 1. In this notation x_{13}, for example, is the x coordinate of Si_1 relative to that of Si_3 (see Fig. 1). In general large uncertainties have been quoted by Franco *et al.* for the lateral position (i.e., the x coordinate) of the dimer atoms (labeled Si_1 and Si_2) and the vertical position (i.e., the z coordinate) of the dimer atom labeled Si_2. Surprisingly, our predicted x coordinate of the N atom (x_{N1}) is approximately 0.3 Å shorter than the value measured by Franco *et al.* The calculated z coordinate of N is approximately 0.1 Å larger than the value obtained by Franco *et al.* These differences lead to the difference in the angle ϕ given in Table I.

IV. ELECTRONIC STRUCTURE

The electronic band structure for the clean Si(001)-(2×1) surface with the optimized asymmetric dimer geometry is shown in Fig. 2. The shaded area represents the projected bulk band structure. The states labeled s_i are predominantly s like, while the ones labeled p_i are strongly p like, with small s and p admixture. The s_1 state, with a binding energy between 10 and 12 eV is due to the second-layer atoms, while s_2 and s_3, lying around -9 eV are due to the third-layer atoms. The p_1 and p_2 states with energies around -8 eV and -4.5 eV are due to the second-layer atoms, while the p_3 state around -2 eV originates from the third layer. The states labeled D_u (upper dimer atom) and D_d (lower dimer atom), which lie in the fundamental band-gap region, can be thought to originate from a fully occupied p_z-like dangling bond on the upper dimer atom and an empty p_z-like dangling bond on the lower dimer atom, although in truth the charge transfer is not quite complete and rehybridization occurs so that the more fully occupied orbital become more s^2p^3 like, while the other becomes more sp^2 like. This rehybridization drives a shift of the dimer atoms towards an asymmetric geometry, as the component with the more fully occupied dangling bond is pushed away from the surface, while the other component moves closer.[25] The energy location and dispersion of the D_u and D_d states are in very good agreement with other theoretical calculations.[25–27] Finally, the unoccupied p_4 state is derived from the first-layer atoms.

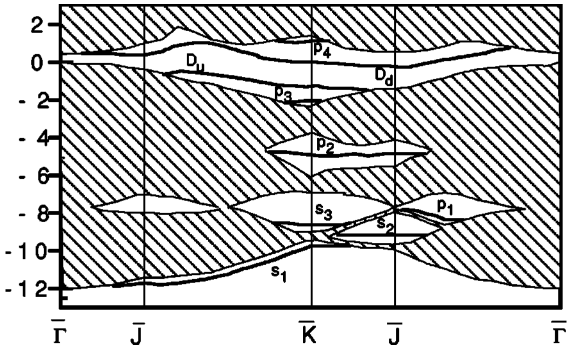

FIG. 2. Surface band structure for the clean Si(001)-(2×1) surface. The shaded area represents the projected bulk band structure.

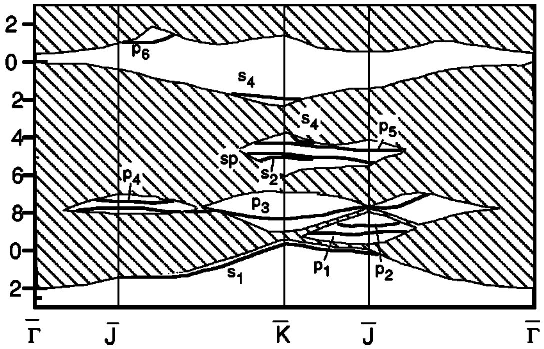

FIG. 3. Surface band structure for the NH_3/Si(001)-(2×1) surface. The shaded area represents the projected bulk band structure.

Some dramatic changes are observed in the band structure upon the adsorption of the ammonia molecule. As shown in Fig. 3, the occupied and unoccupied surface states situated within the semiconducting gap region have nearly vanished, which indicates an almost complete passivation of the dangling bonds of the Si dimer. Again we have labeled the states according to their physical origin, as in Fig. 2. The total charge density plots in Fig. 4 indicate the character of each bond associated with the dissociated NH_3 molecular adsorption. A highly covalent bond is maintained between the Si dimer atoms [Fig. 4(a)]. Ionic character can be noticed for the N-H [Fig. 4(d)] and Si-H [Fig. 4(c)] bonds, although some covalent contribution is also evident. The ionic character is more remarkable in the Si-N bond [Fig. 4(b)].

Although the adsorption of ammonia preserves the covalent character of the dimer bonds, it has a strong passivation effect as can be appreciated by examining the energy-resolved charge-density plots for the clean and chemisorbed surfaces in Fig. 5. In the case of the clean surface, some charge is transferred from one dimer component to the other, resulting in one fully occupied dangling bond band [Fig. 5(a)] and one empty dangling bond band [Fig. 5(c)]. In contrast, for the adsorbate case the uppermost occupied surface

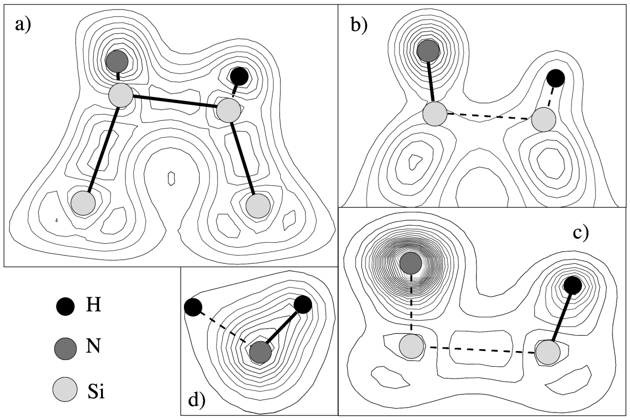

FIG. 4. Total valence charge density contour plots for NH_3/Si(001)-(2×1). Bonds in the drawing plane are plotted as solid lines, while bonds that form an angle with the drawing plane are given by dashed lines. The drawing planes are chosen to highlight each bond.

state (s_4) is a s-like nitrogen state [Fig. 5(b)] and the lowermost unoccupied surface state (p_6) is a p_x dangling bond on the Si atom bonded to the N atom [Fig. 5(d)]. On the clean surface most of the surface states are localized on the second layer and even the third layer [Figs. 5(e) and 5(g)]. In contrast, on the covered surface the great majority of the surface states are due to the first (adsorbate) layer, with small contributions from the second (Si dimer) layer [Figs. 5(f), 5(h) and 5(i)]. In other words, while on the clean surface the electronic perturbation extends up to the third layer, on the adsorbate surface the perturbation is restricted to the first and second layers. In fact, this is also suggested by the calculated relaxed atomic geometries, as the relative movement from bulk positions of the Si atoms in the adsorbate case is slightly smaller than in the clean surface case.

Some interesting features of the covered surface deserve attention. The s_4 state is due to the hydrogen s orbital [Fig. 5(f)] and lies at a binding energy of around 4.5 eV. The state p_5 is largely contributed by the p_y orbital of the N atom [Fig. 5(h)]. The state p_1 [Fig. 5(i)] is derived from the σ bonding between the dimer atoms and the p_z orbital of the nitrogen, with a binding energy around 9 eV. It is interesting to notice that the Si-Si σ state is also reported by Jenkins and Srivastava[31] in a recent work on the growth of Ge upon Si substrates. The s_1 and s_3 states, at binding energies of 11 eV and 3.0 eV are due to the first (adsorbate) layer atoms, while the s_2 state around -4.5 eV is localized on the first (adsorbate) and second (Si dimer) layer atoms. The sp state at an energy of -4 eV is due to s and p orbitals of the hydrogen and nitrogen, with some contribution from the Si dimer. Finally, the p_2, p_3, and p_4 states around an binding energy of 8 eV are due to the first- (adsorbate) and second- (Si dimer) layer atoms.

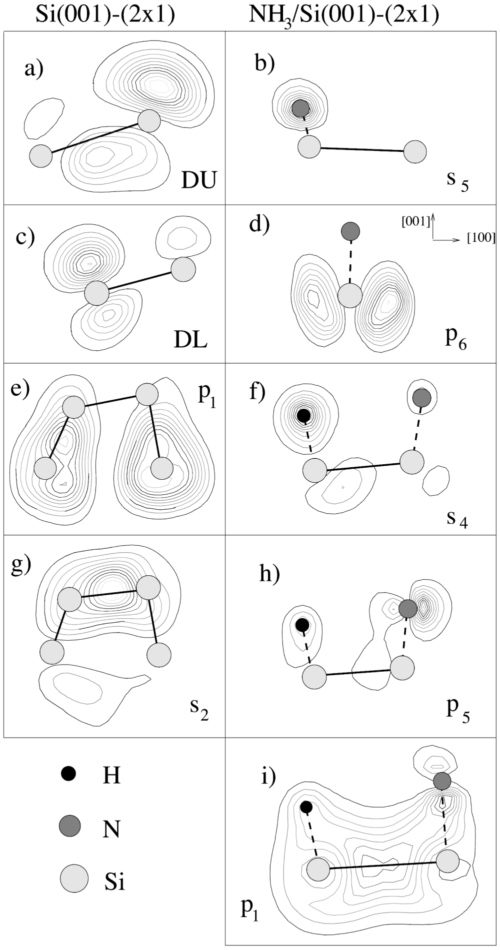

FIG. 5. Energy-resolved charge-density contour plots for the clean Si(001)-(2×1) surface (left side) and NH_3/Si(001)-(2×1) (right side). All drawings are on the [001]-[110] plane unless otherwise indicated. Bonds in the drawing plane are plotted as solid lines, while the bonds that form an angle with the drawing plane are given by dashed lines.

V. SUMMARY

In summary, from a first-principles pseudopotential study we have made an accurate determination of the atomic geometry and electronic structure of the dissociative adsorption of ammonia on Si(001)-(2×1). We find that the chemisorbed system is characterized by elongated and symmetric Si dimers, and by the fact that the Si-NH_2 group retains the pyramidal geometry of the ammonia molecule. On the whole, the experimental results are in better agreement with our calculations than the previous theoretical findings.[13–15] Some of the key geometrical parameters calculated in our work differ appreciably from those presented in previous theoretical works. In particular, the studies by Zhou, Cao, and Fu and by Moriarty and Smith have calculated the inclination ϕ of the N-Si bond to be at least twice as large as our work predicts. Finally, our electronic structure calculations suggest that the adsorption of ammonia almost completely passivates the silicon surface and decisively removes the perturbation experienced by deeper-layer atoms on the clean surface.

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