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Ab initio study of hydrogen adsorption on the Si(111)-(7×7) surface

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First-principles total-energy pseudopotential calculations are performed to investigate the adsorption interaction of a H atom with dangling bonds on the Si(111)-(7×7) surface. The binding energies for adsorption of H at the adatom, rest atom, and corner hole sites are calculated to be 2.9, 3.2, and 3.5 eV, respectively. Spectral analysis of the electronic states shows that *nonlocal* changes of chemical reactivity are induced by *charge transfer* upon H adsorption. It is found that H adsorption on the adatoms or rest atoms induces a charge transfer onto the Si-H bond and a shift in energy of the remaining dangling-bond states. Adsorption on the corner hole, however, does not involve any charge transfer. The relationship between charge transfer and binding energies is discussed.

I. INTRODUCTION

First-principles study of the adsorption processes on a surface is important for understanding microscopic processes on the surface, such as the initial stages of epitaxial growth of thin films, initial stages of surface corrosion, and surface catalysis.[1] The interaction of adsorbed atoms with each chemically active site on the surface induces a change of the local electronic structure as well as a relaxation of the local geometry specific to the site. Most experiments provide only limited information about the adsorption process, averaging over a large number of active sites. The study of "atom-resolved surface chemistry using scanning tunneling microscopy" has revealed large differences in electronic spectra at different surface sites.[2] The local properties obtained by first-principles studies can provide complementary microscopic information for understanding the microscopic aspects of the adsorption process.

Adsorption on semiconductor surfaces has been studied extensively because of the technological importance of the surfaces in electronic device fabrication. Specifically, adsorption on the Si(111) surface has been a challenging problem because of the complexity of the stable reconstruction geometry.[3] First-principles studies of the intrinsic (7×7) surface reconstruction became possible only recently with the help of rapid developments in massively parallel processors (MPP).[4,5] The adsorption problem is more challenging than the reconstruction problem for two reasons: First, the strong potential of adsorbed atoms such as H increases considerably the number of basis functions needed to describe the system. Second, it is necessary to investigate several different adsorption sites in order to fully understand the physics and chemistry involved.

The equilibrium structure of the Si(111) surface at temperatures below 870 °C consists of a (7×7) reconstruction in which the surface atoms rearrange to lower the surface energy. The Takayanagi dimer-adatom–stacking-fault (DAS) model is now generally accepted as the model that correctly describes this reconstruction.[3] A ball-and-stick model of the DAS (7×7) reconstruction is shown in Fig. 1. The (7×7) surface unit cell is indicated by the dashed lines in the top panel of Fig. 1. The unit cell consists of two triangles separated by three dimers. The left triangle has a stacking fault between the third layer and the fourth layer as shown in the bottom panel of Fig. 1. Each triangle has six adatoms and three rest atoms indicated respectively as large black dots and gray dots in Fig. 1. The corner hole atoms are indicated as small black dots at the vertices of the unit cell.

There are nineteen chemically active sites on each sur-

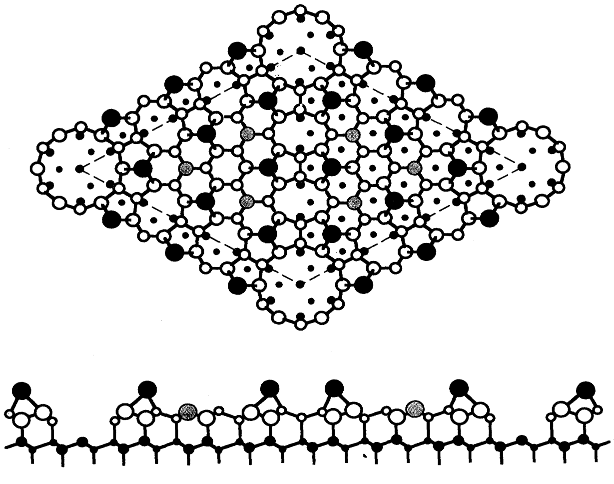

FIG. 1. Ball-and-stick model of the Si(111)-(7×7) surface. Top panel shows the top view, and bottom panel shows side view along the long diagonal of the unit cell.

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face unit cell: twelve adatom dangling bonds, six rest atom dangling bonds, and one corner hole dangling bond. Analysis of local chemical reactivity based on first-principles calculations[6] has shown that these dangling bonds have different capacities to donate and accept electrons and, consequently, different reactivities with various reactants. Specifically, the surface charge donor capacity is proportional to the amount of electrons in dangling bonds so that the donor capacity (and chemical reactivity) follows the order: corner hole > rest atoms > adatoms.

In this work, we choose atomic hydrogen as a prototypical strongly electronegative reactant and investigate hydrogen adsorption on the Si(111)-(7×7) surface. The calculated adsorption energies are consistent with the analysis of local chemical reactivity and the experimental observation that the corner hole is the most active site for hydrogen adsorption. In Sec. II, we describe the method of first-principles calculation. In Secs. III, IV, and V, we discuss the details of the microscopic structural and electronic changes induced by hydrogen adsorption.

II. COMPUTATIONAL METHOD

The Si(111)-(7×7) surface is modeled by a five-layer slab in the supercell (26.6 Å×26.6 Å×16.5 Å), which includes one (7×7) surface unit and 10-Å vacuum between the slabs. These five layers are shown in the bottom panel of Fig. 1 in the ball-and-stick model representation. The top side of the slab is used to construct the DAS (7×7) reconstruction, and the bottom-layer silicon atoms are fixed in the bulk positions. The dangling bonds of the bottom-layer silicon atoms are saturated by hydrogen atoms (which are not shown in Fig. 1).

For the minimization of the electronic energy functional at each ionic configuration, the *ab initio* molecular-dynamics scheme implemented on the MPP CM-5 (Refs. 7 and 8) is used. The ion positions are relaxed according to the Hellmann-Feynman forces calculated from the minimized electron wave functions. At the fully relaxed configuration of the intrinsic (7×7) surface, the Hellmann-Feynman forces on the silicon atoms are smaller than 0.1 eV/Å. Electron wave functions are expanded in a plane-wave basis with 11.5-Ry cutoff energy, which corresponds to about 50 000 basis functions. The Brillouin zone sampling is approximated by the Γ point. Optimized pseudopotentials[9] for the silicon atom and the hydrogen atom are used in the Kleinman-Bylander separable form.[10]

Hydrogen adsorption calculations were performed for three representative surface dangling-bond sites: the corner adatom on the unfaulted side, the rest atom on the unfaulted side, and the corner hole atom. The quality of the pseudopotentials was tested by comparison with SiH_4 and hydrogen adsorption on the Si(111)-(1×1) surface. The optimized geometry of SiH_4 has a Si-H bond length 2.7% larger than the experimental bond length of 1.48 Å. The hydrogen adsorption energies on the Si(111)-(1×1) surface were calculated for the surface both with a stacking fault and without a stacking fault, and were found to be 3.50 and 3.46 eV, respectively. These values are in good agreement with the hydrogen adsorption energy (3.6 eV) calculated independently by Van de Walle using a similar computational scheme.[11] Note that the stacking fault introduces only a 0.04-eV difference in the adsorption energy.

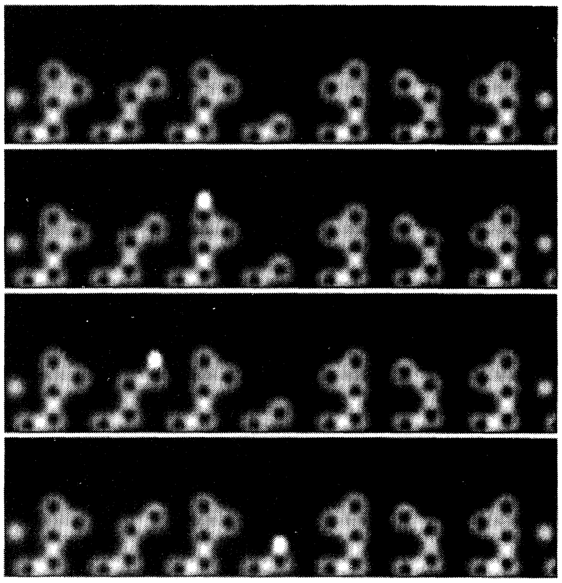

FIG. 2. Plots of the total valence charge density in a plane perpendicular to the surface along the long diagonal. From top panel to bottom panel, each panel corresponds to the intrinsic surface, the surface with hydrogen on adatom, the surface with hydrogen on rest atom, and the surface with hydrogen on corner hole atom.

First, a hydrogen atom was placed 1.5 Å above a corner adatom on the unfaulted side, and the geometry of the surface and the adsorbed hydrogen was relaxed. This procedure was repeated with the hydrogen atom above a rest atom on the unfaulted side and with the hydrogen atom above a corner hole atom. Figure 2 shows the total valence charge density cross sections along the long diagonal of the unit cell. From top to bottom the intrinsic surface, the surface with a hydrogen atom on the adatom, the surface with a hydrogen atom on the rest atom, and the surface with a hydrogen atom on the corner hole atom are shown. The covalent bonds between the three Si sites and the adsorbed hydrogens are clearly visible as white dots on the corresponding surface atoms.

III. ADSORPTION ENERGY AND GEOMETRY

The adsorption energy is calculated from the difference of the total energies of two separate calculations: one with a hydrogen atom adsorbed on a binding site and one with a hydrogen atom fixed in the middle of the vacuum separated from the slabs by 5 Å. The calculated adsorption energies are 2.9, 3.2, and 3.5 eV for the hydrogen atom adsorbed on the adatom, the rest atom, and the corner hole atom respectively. These energies are smaller than the hydrogen adsorption energy (3.5 eV) on the Si(111)-(1×1) surface. Note that because of the surface

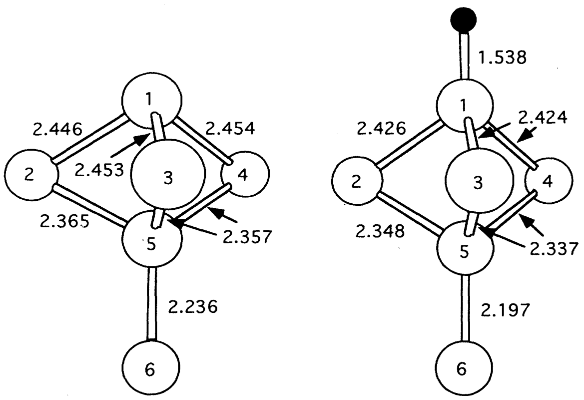

FIG. 3. Ball-and-stick model representation of the change of local geometry of the adatom induced by hydrogen adsorption. The bond lengths are shown in Å.

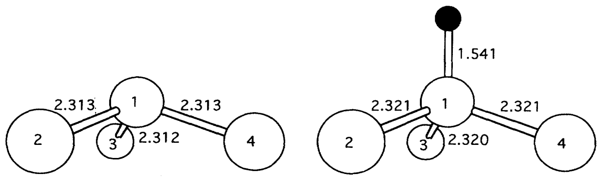

FIG. 5. Ball-and-stick model representation of the change of local geometry of the corner hole atom induced by hydrogen adsorption.

periodicity, one hydrogen atom per unit cell of the (1×1) surface corresponds to 1-ML coverage whereas one hydrogen atom per unit cell of the (7×7) surface corresponds to 0.02-ML coverage.

Figures 3–5 show the changes of the local geometries induced by the adsorbed hydrogen atom. The H-Si bond lengths are 1.538, 1.545, and 1.541 Å for the adatom, the rest atom, and the corner hole sites, respectively. These bond lengths are very close to the Si-H bond length (1.54 Å) on the Si(111)-(1×1) surface.[12] The differences in bond lengths are small, but significant compared to the typical errors in the bond lengths obtained by the calculations (0.001 Å). Typical errors can be seen from the difference between bond lengths, which should be identical by symmetry (e.g., bonds 1-3 and 1-4 in Fig. 3, 1-2 and 1-3 in Fig. 4, and 1-2, 1-3, and 1-4 in Fig. 5). The different Si-H bond lengths, and consequently bonding strengths, cannot explain the large differences in the adsorption energies: for comparison, the results from the SiH_4 calculation show a change of only 0.01 eV in the energy for a change of 0.01 Å in the SI-H bond length. Therefore, the large differences of the adsorption energies are resulting either from the relaxation of the (7×7) surface geometry or from the changes of electronic structure induced by hydrogen adsorption.

Figure 3 shows that the hydrogen saturation of the adatom dangling bond decreases the adatom backbond length by 0.02–0.03 Å, the three next layer bonds (2-5, 3-5, and 4-5) by 0.02 Å, and the bond 5-6 by 0.04 Å. Figure 4 shows that the hydrogen saturation of the rest atom dangling bond decreases the length of three bonds (1-2, 1-3, and 1-4) by about 0.02 Å, while the next layer bond length changes are negligible. Figure 5 shows a very small change of bond length induced by the hydrogen adsorption. An estimate of the energies involved in these distortions can be obtained from the calculations of Ref. 12, giving about 0.05 eV. Thus, these changes of geometries are not large enough to explain the significant differences in adsorption energy. Consequently, the electronic structure effect is crucial in understanding the adsorption energies as we discuss in the next section.

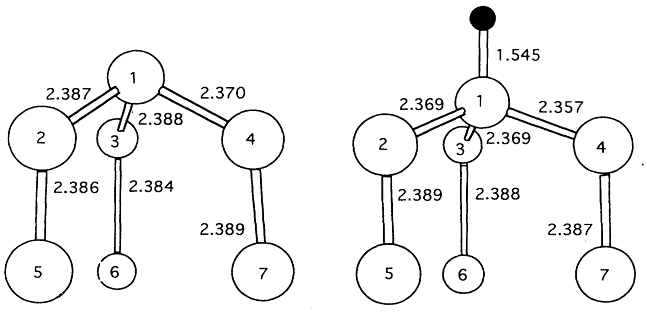

FIG. 4. Ball-and-stick model representation of the change of local geometry of the rest atom induced by hydrogen adsorption.

IV. CHANGE OF ELECTRONIC STRUCTURES

The changes of the surface electronic structure by hydrogen adsorption are illustrated in Figs. 6–9 with the same cross section of the charge densities as in Fig. 2 for the occupied electronic states in the specific energy ranges. Figures 6, 7, 8, and 9 are, respectively, for the intrinsic surface, the surface with a hydrogen atom on the adatom, the surface with a hydrogen atom on the rest atom, and the surface with a hydrogen atom on the corner hole atom. The Fermi energy changes slightly from −0.16 eV for Fig. 6 to −0.13 eV for Fig. 7, −0.09 eV for Fig. 8, and −0.06 eV for Fig. 9.

The top panel of Fig. 6 shows the ball-and-stick model of the intrinsic surface along the long diagonal. In this and the following figures *a*, *r*, *c*, and H indicate the adatom, the rest atom, the corner hole atom, and the hydrogen atom, respectively. The second panel shows four adatom dangling bonds (from left to right, the center adatom and the corner adatom on the unfaulted side, and the corner adatom and the center adatom on the faulted side), two rest atom dangling bonds, and one corner hole dangling bond in the lower center of the panel. Note that the adatom dangling bonds are also present in the seventh panel (−2.5 to −3.0 eV) with larger charge densities in the dangling bonds. The third panel shows the two dangling bonds of the rest atoms: the left on the unfaulted side and the right on the faulted side. The fourth and fifth panels show the adatom backbonds, and the next layer bonds. The sixth panel shows more adatom backbonds (one of them is indicated by an arrow) and the surface dimer bonds at the left and right ends of the panel. The seventh panel shows quite strong covalent bonds between the adatoms and the atoms right below them. The eighth panel shows the difference between the faulted and unfaulted sides: the bonds at the stacking fault on the right side are weaker than the normal bonds at the left side. The ninth panel shows silicon bonds without specific characteristics.

Figure 7 shows the charge density cross-section spectra in the presence of the hydrogen atom on the second adatom from the left, i.e., the corner adatom on the unfaulted side as indicated in the top panel. The spectra of Fig. 7 show very striking changes from those of Fig. 6: the dangling-bond state of the hydrogen-saturated adatom is lowered in energy, from the range [0.0, −0.5 eV] to the range [−1.0, −1.5 eV] and from the range [−2.5, −3.0 eV] to the range [−3.0, −4.0 eV]. The dangling-bond states of the rest atoms are raised in energy from the range [−0.5, −1.0 eV] to the range [0.0, −0.5 eV]. Finally, the dangling-bond state of the corner hole atom is lowered in energy from the range [0.0, −0.5 eV] to the range [0.0, −1.0 eV]. The fourth panel shows the adatom-hydrogen bond as well as the Si-Si vertical bond below the adatom (indicated by a filled arrow) which has higher energy than in the intrinsic surface. The fifth panel and the sixth panel show no change. It is noticeable that the hydrogen saturation removes the bond between the adatom and the atom right below it as indicated by an empty arrow in the seventh panel. The eighth and ninth panels show the Si-H bond states.

Figure 8 shows the charge density cross-section spectra in the presence of the hydrogen atom on the left rest atom as indicated in the top panel. The change of the spectra from those of the intrinsic surface show that the rest atom dangling-bond state is lower in energy by 1.5 eV due to the formation of a Si-H bond. On the other hand, the dangling-bond state of the other rest atom does not change and the dangling bond state of the corner hole atom is lowered in energy as shown in the second and third panels. The fourth and the fifth panels show no

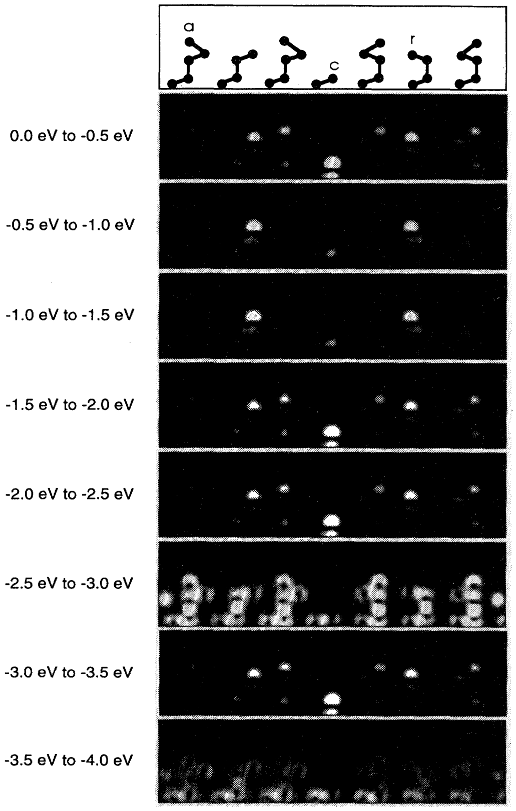

FIG. 6. Plots of the valence charge density in the specified energy ranges for the intrinsic surface. The cross sections are in the same plane as Fig. 2. Top panel shows the ball-and-stick model representation of the atoms in the plane.

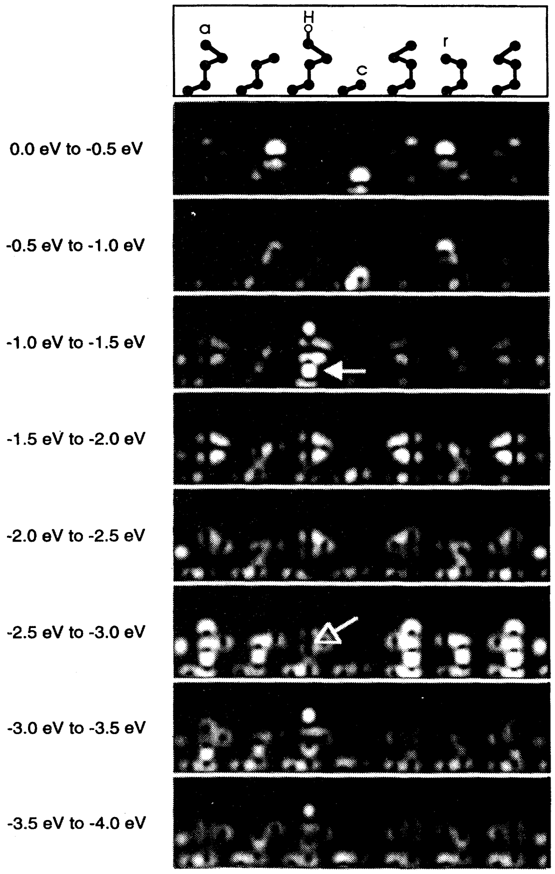

FIG. 7. Plots of the valence charge density in the specified energy ranges for the surface with hydrogen adatom using the same convention as Fig. 6.

change. The sixth through the ninth panels show the Si-H bond on the rest atom. All the remaining properties of the charge density cross-section spectra are identical to those of the intrinsic surface.

Figure 9 shows the charge density cross-section spectra in the presence of the hydrogen atom on the corner hole, as indicated in the top panel. The only significant changes of the spectra from those of Fig. 6 are the lower energy of the corner hole dangling-bond state due to the formation of a Si-H bond, from the range [0.0, −0.5 eV] to the range [−3.0, −4.0 eV] as shown in the eighth and ninth panels. Except for the corner dangling-bond state, all the rest of the charge density distributions remain unchanged from those of the intrinsic surface.

The changes of the surface electronic structure induced by hydrogen adsorption have strong *nonlocal* characteristics. Figures 7 and 8 show that the presence of hydrogen on the unfaulted side changes the dangling-bond state energy of the rest atom on the faulted side. These nonlocal interactions between the surface dangling bonds are induced by *charge transfer* between them. On the intrinsic (7×7) surface the adatom dangling bonds and the rest atom dangling bonds are partially filled, whereas the corner hole dangling bond is completely filled. Since the hydrogen atom is strongly electronegative, when the hydrogen is interacting with a partially filled dangling bond it attracts extra electron charge density to fill the interacting silicon dangling bond. This extra charge comes from the rest of the dangling bonds since they are more chemically reactive and more likely to donate charge than saturated bonds.

The hydrogen on the adatom attracts charge from both rest atom and corner hole dangling bonds so that these states become less filled, and consequently are changed in energy.[13] Furthermore, the bonding charge between the adatom and the atom right below it is also transferred to the silicon-hydrogen bond as noted in the seventh panel of Fig. 7. The hydrogen on the rest atom also attracts charge from the other rest atom dangling bonds and the corner hole dangling bond so that those states become

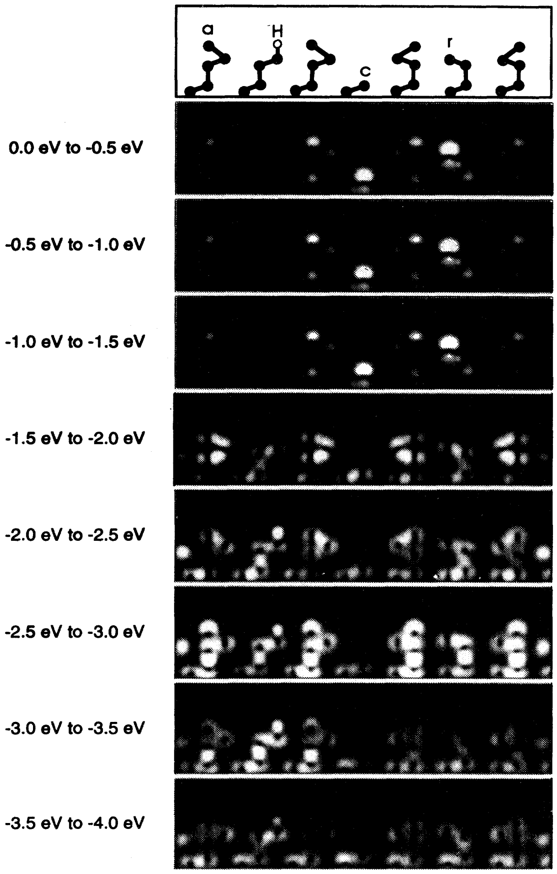

FIG. 8. Plots of the valence charge density in the specified energy ranges for the surface with hydrogen on rest atom using the same convention as Fig. 6.

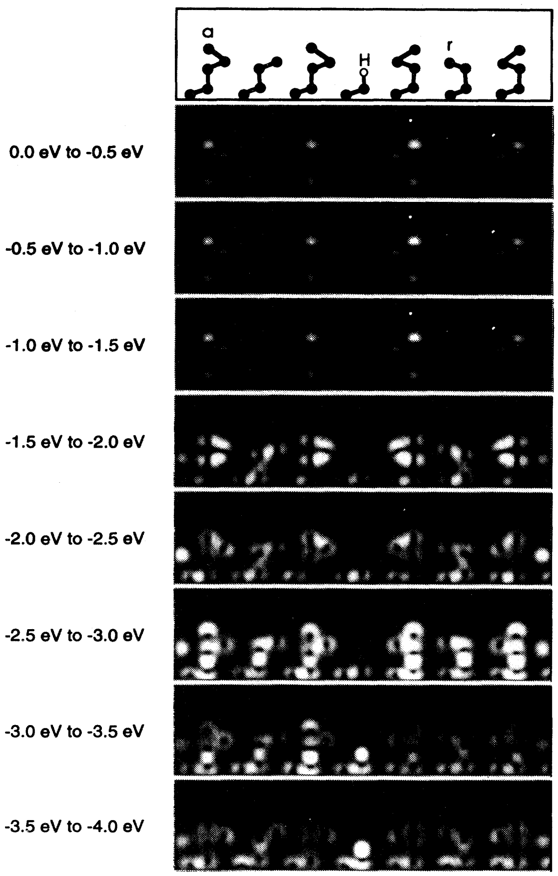

FIG. 9. Plots of the valence charge density in the specified energy ranges for the surface with hydrogen on corner hole atom using the same convention as Fig. 6.

less filled, and their energies are also raised, similar to the case of the hydrogen on the adatom. However, the hydrogen on the corner hole atom does not induce a nonlocal charge transfer from other dangling bonds. The corner hole dangling bond is already completely filled by two electrons, and the hydrogen adsorption actually introduces an excess electron so that there are three electrons to fill the Si-H bond. Two of these electrons form the corner hole Si-H bond, and the remaining electron is placed at the Fermi level as indicated by an upward shift of the Fermi level by 0.1 eV. This extra electron is distributed over 12 adatom dangling bonds and increases the adatom dangling bond fillings by about 8%. This small increase of dangling bond charge density, which is already quite small as shown in the second panels of Figs. 6–9, is difficult to discern in the gray scale of these plots. Nevertheless, a careful comparison of the second panels of Figs. 6 and 9 shows what appears to be a slight increase of the charge on the third dangling bond from the left.

The differences of the adsorption energies for H on adatom, rest atom, and corner hole, respectively, reflect energy costs of the nonlocal charge transfer among the dangling bonds, rather than differences in the Si-H bonding strength at different sites. A charge transfer leads to an increase of the energies of the involved dangling bonds so that a larger charge transfer corresponds to a larger energy cost. The adsorption energy on the adatom is smallest because it involves more charge transfer from the other dangling bonds and the bond between the adatom and the atom right below it. The adsorption energy of the corner hole atom is largest because no charge transfer cost is involved. One can estimate the energy cost of charge transfer for hydrogen on the adatom and on the rest atom as 0.6 and 0.3 eV from the differences of the adsorption energies. It is also noticeable that the adatom and rest atom adsorption energies are smaller than the adsorption energy of 1 ML of hydrogen on the Si(111)-(1×1) surface (3.5 eV). Since the dangling bonds on this surface are uniformly saturated, no charge transfer is required to satisfy the Si-H covalent bonding.

V. LOCAL DENSITY OF STATES

In order to make contact with experimental measurements, the local densities of states (LDOS) on the adatom, the rest atom, and the corner hole are calculated and shown in Figs. 10–12. Figure 10 shows that the LDOS on the adatom is strongly changed only when the hydrogen atom is adsorbed on the adatom, but the effect of the hydrogen atom on the rest atom and the corner hole does not significantly change the position of the peaks in the LDOS. The LDOS peak near the Fermi level indicates that the Si-H bond formation lowers the adatom dangling bond energy by about 1 eV.[14,15] It is noticeable that there are two LDOS peaks that originate from the adatom dangling-bond states, separated in energy by about 3 eV. These correspond to two peaks in the differential conductivity observed in scanning tunneling spectroscopy (STS) measurement at the adatom position.[2]

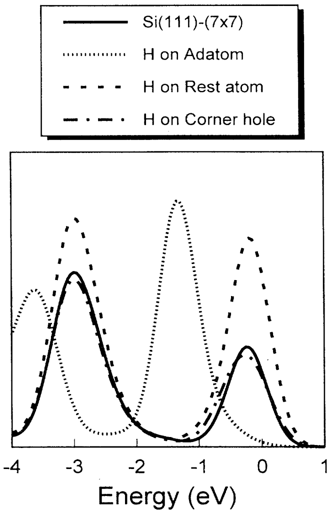

FIG. 10. Plot of the local density of states on the adatom.

Figure 11 shows the LDOS on the rest atom. The Si-H bond formation lowers the rest atom dangling-bond energy by about 2 eV so that no local states are in the energy range between -2.0 and 0.0 eV, in agreement with STS measurements.[2] When the hydrogen atom is adsorbed on the adatom, the LDOS peak moves higher in energy due to charge transfer from the rest atom dangling bond to the adatom dangling bond, but this change is too small to be detected in STS measurements. The effect on the LDOS of hydrogen adsorption at the corner hole site is negligible.

However, Fig. 12 shows significant changes of the LDOS peak position due to hydrogen adsorption. The Si-H bond formation lowers the energy of the corner hole dangling bond by about 3 eV, while the nonlocal charge transfer from the corner hole dangling bond to the Si-H bond on the adatom or the rest atom moves the LDOS

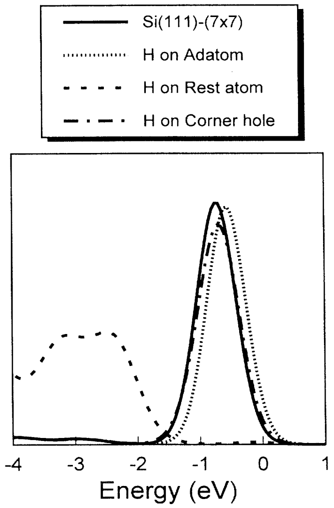

FIG. 11. Plot of the local density of states on the rest atom.

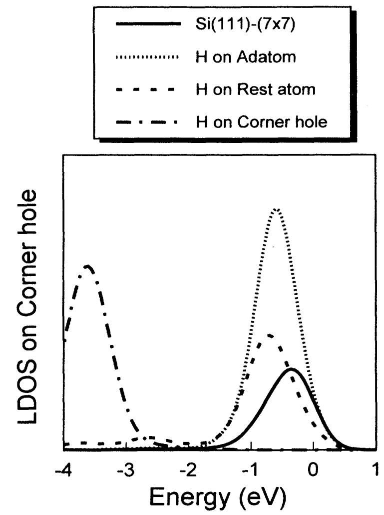

FIG. 12. Plot of the local density of states on the corner hole atom.

peak from the Fermi level. Consequently, the LDOS on the corner hole shows the results of the nonlocal charge transfer. Based on this we expect that the corner hole sites on the (7×7) reconstruction will exhibit significant changes in chemical reactivity induced by the nonlocal charge transfer due to adsorption.

To gauge the detectability of this effect by the STS measurements at the corner hole site, the LDOS on the corner hole is compared to the LDOS on the adatom. Since the depth of the corner hole in the STM measurement is 2 Å, the LDOS on the corner hole is calculated at a vertical position 2 Å lower than that of the LDOS on the adatom. This comparison shows that the intensities of the corner hole LDOS are an order magnitude smaller than the adatom LDOS, and for all practical purposes the corner hole LDOS is not detectable in STS measurements. This finding is consistent with the observations of no specific peak spectra of the corner hole site in the STS experiments.[16] Consequently, the first-principles spectral analysis of the electronic structure provides information of chemical reactivities on the surface sites (i.e., corner holes) which are not detectable by a scanning tip in STS measurements.

VI. CONCLUSIONS

The calculated hydrogen adsorption energies are consistent with the chemical reactivity analysis based on the local charge densities of the surface dangling bonds. The adsorption-induced relaxation of the local geometry is negligibly small, and the variation of the Si-H bond length is also small. However, there is significant charge transfer among dangling bonds induced by hydrogen adsorption, and the charge transfer leads to nonlocal changes of the surface chemical reactivity.

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[13] A small increase of the Fermi level (0.03 eV) indicates the small charge transfer from the rest of the adatom dangling bonds.

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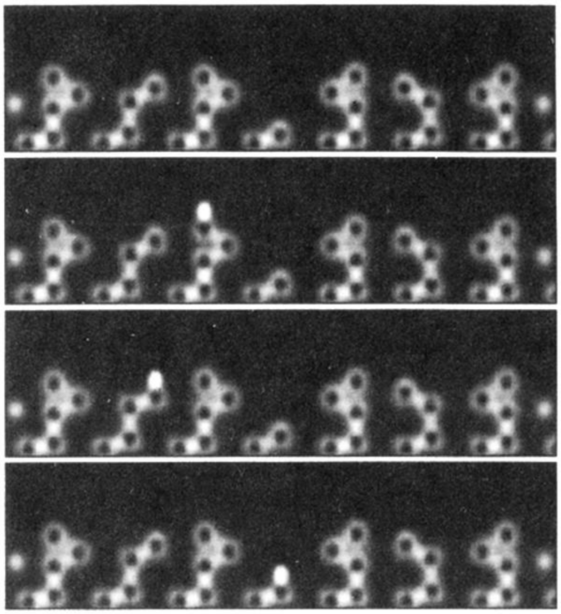

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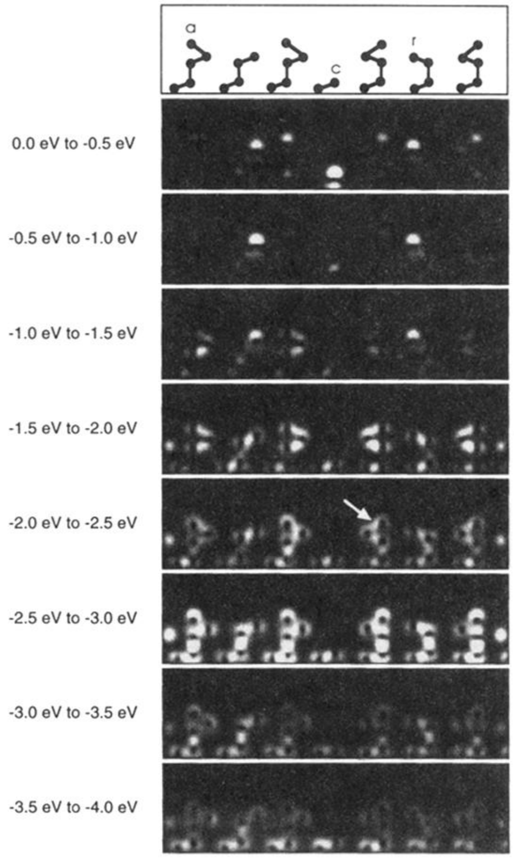

FIG. 6. Plots of the valence charge density in the specified energy ranges for the intrinsic surface. The cross sections are in the same plane as Fig. 2. Top panel shows the ball-and-stick model representation of the atoms in the plane.

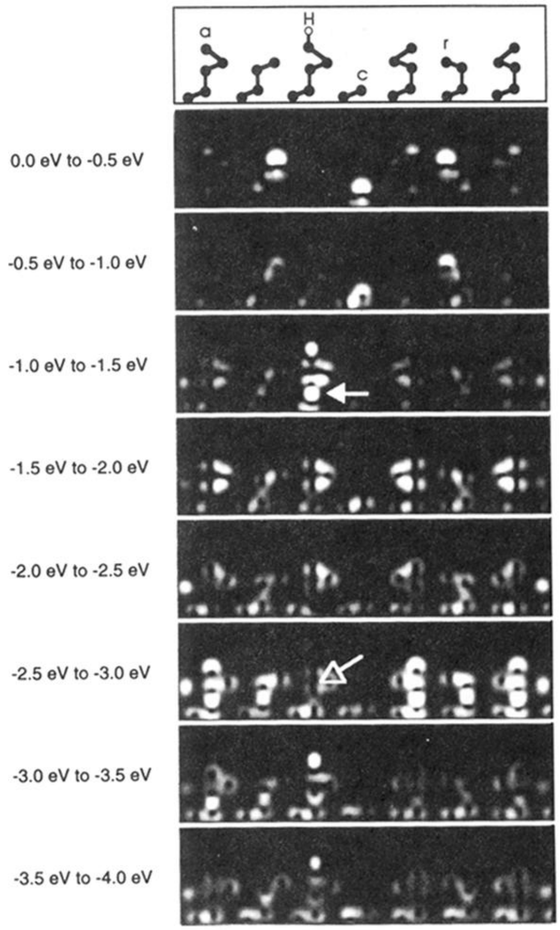

FIG. 7. Plots of the valence charge density in the specified energy ranges for the surface with hydrogen adatom using the same convention as Fig. 6.

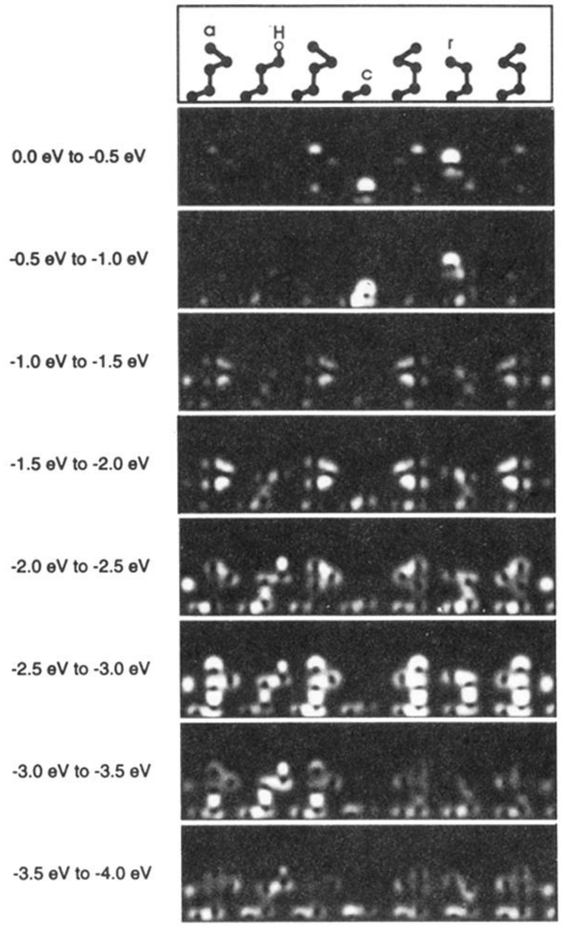

FIG. 8. Plots of the valence charge density in the specified energy ranges for the surface with hydrogen on rest atom using the same convention as Fig. 6.

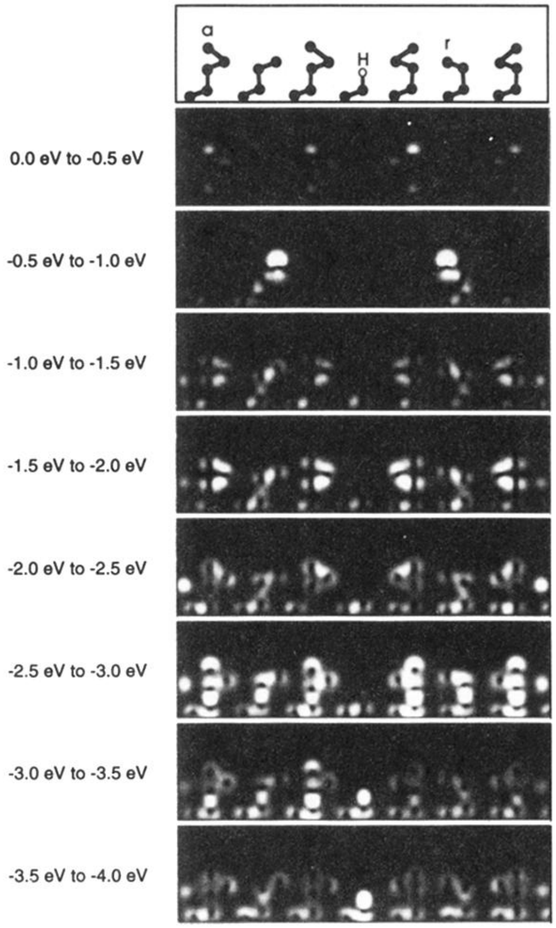

FIG. 9. Plots of the valence charge density in the specified energy ranges for the surface with hydrogen on corner hole atom using the same convention as Fig. 6.