Origin of Surface States on Si(111) (7 × 7)

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First-principles pseudopotential total-energy and electronic-structure calculations are reported for two Si(111)($\sqrt{3}\times\sqrt{3}$):Si adatom geometries. Based on these calculations, a theory of the electronic structure of Si(111)(7 × 7) is formulated, and the binding energy of Si adatoms on Si(111) is determined.

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Recently, there has been significant progress in obtaining a reliable model of the atomic structure of the Si(111)(7 × 7) surface. Scanning-tunneling-microscope images of the surface charge density by Binnig *et al.*[1] revealed the existence of twelve maxima which were interpreted as arising from twelve adatoms in each unit cell. More recently, Takayanagi *et al.*[2] studied the surface with transmission electron diffraction and derived the dimer–adatom–stacking-fault (DAS) model, which contains subsurface dimers, twelve adatoms, and a stacking fault in half of the unit cell. Robinson *et al.*[3] have used glancing-incidence x-ray diffraction to determine the surface structure and also obtain the DAS model. Recent scanning-tunneling-microscope studies by Hamers, Tromp, and Demuth[4] provide further evidence that the DAS model is correct. In light of this progress in determining the atomic structure it is now appropriate to attempt to answer an important remaining question: What is the relationship between the atomic and electronic structure for Si(111)(7 × 7)? In this paper, it is shown how the DAS model[2] accounts for the surface states observed by angle-resolved photoelectron spectroscopy[5-9] (ARPES) on the Si(111)(7 × 7) surface.

A key to understanding the electronic structure of the Si(111)(7 × 7) surface is the similarity observed by Uhrberg *et al.*[9] between the surface states on the (7 × 7) and the Si(111)($\sqrt{3}\times\sqrt{3}$):Al surface. An interpretation of the data for the ($\sqrt{3}\times\sqrt{3}$):Al surface in terms of adatom models[10] can help us identify the atomic structures responsible for each of the surface states on the (7 × 7) surface.

Several groups have observed ($\sqrt{3}\times\sqrt{3}$) reconstructions following $\frac{1}{3}$ monolayer Al[9,11,12] or In[13] deposition on Si(111) and have determined the surface band structure with ARPES. A comparison between first-principles pseudopotential calculations[10,13] and ARPES data indicates that these phases correspond to adatom adsorption in the threefold hollow (H_3) or filled sites (T_4). The geometries corresponding to these sites are shown in Fig. 1. In each of the two geometries the adatom is in a threefold-symmetric site above the second layer (T_4) or the fourth layer (H_3). For Al and In, total-energy calculations[10,13] reveal that the T_4 geometry is preferred.

There are several reasons motivating the present total-energy and electronic-structure calculations for ($\sqrt{3}\times\sqrt{3}$):Si adatom geometries. Since photoemission intensity patterns are governed by the local atomic structure of the surface, it is appropriate to interpret them in terms of surface states associated with the building blocks which make up the structure. The surface layer of the DAS model[2] consists of twelve adatoms in T_4 sites, six rest atoms, and one corner atom in each unit cell. Rest atoms are threefold-coordinated surface atoms not bonded to an adatom. The corner atom is the threefold atom at the bottom of the holes in the corners of the (7 × 7) unit cell. In this paper the electronic structure of the (7 × 7) surface will be interpreted in terms of adatom-induced surface states and rest-atom dangling-bond states. Also, since the DAS model for the Si(111)(7 × 7) surface has adatom bonding sites similar to those found in the ($\sqrt{3}\times\sqrt{3}$) T_4 model, calculation of the atomic structure will be useful in fixing the adatom-substrate distances in the (7 × 7) model.

The total energy and electronic structure of the T_4 and H_3 Si(111)($\sqrt{3}\times\sqrt{3}$):Si models were calculated with use of the first-principles pseudopotential method

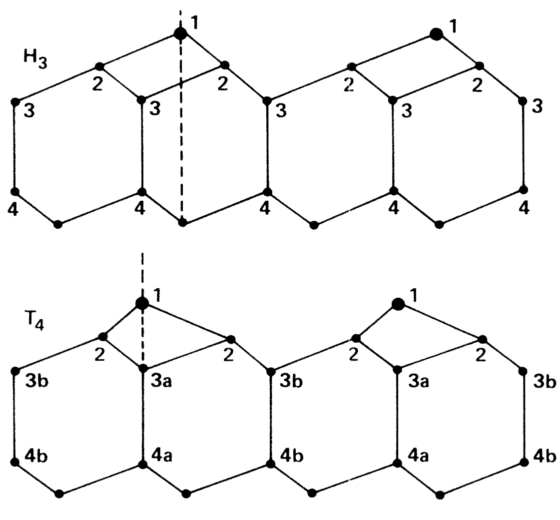

FIG. 1. Sides views of the H_3 and T_4 structures. The dashed line is a threefold axis passing through the adatoms.

TABLE I. Substrate-atom displacements (in a.u.) for $(\sqrt{3}\times\sqrt{3})$ adatom structures. Atom numbers refer to Fig. 1. The r coordinate is the distance to the threefold axis indicated by the dashed lines in Fig. 1.

		Al		Si	
		δz	δr	δz	δr
T_4	2	−0.05	−0.23	−0.15	−0.28
	3a	−0.63	0	−0.74	0
	3b	0.22	0	0.18	0
	4a	−0.33	0	−0.48	0
	4b	0.18	0	0.11	0
H_3	2	−0.18	−0.09	−0.26	−0.16
	3	−0.11	−0.05	−0.15	−0.05
	4	−0.04	−0.02	−0.09	−0.02

and the local-density-functional approximation.[14] The Kohn-Sham[14] equations were solved by use of the momentum space formalism[15] with a plane-wave cutoff of 6 Ry. Forces calculated by use of the Hellman-Feynmann theorem were used to optimize the structures. The calculational technique is very similar to that used to study Si(111)$(\sqrt{3}\times\sqrt{3})$:Al.[10]

The coordinates calculated for the two models are shown in Table I. Also shown there for comparison are the displacements calculated previously for $(\sqrt{3}\times\sqrt{3})$:Al. In the Si T_4 model, the calculated distance between the adatom and the second-layer atom directly below is 4.70 a.u. while the adatom-type-2 distance is 4.71 a.u. These distances should be appropriate for the adatoms in the DAS model as well.

The total energy of the T_4 geometry is found to be lower than H_3 by 0.64 eV/adatom. This energy ordering is the same as that calculated for Al,[10] In,[13] and Ge[16] adatoms. Relative to the ideal unrelaxed surface, the energy of the $(\sqrt{3}\times\sqrt{3})$ T_4 surface is −0.28 eV/(surface atom). Thus, removing an atom from a bulk environment and placing it in a T_4 site lowers the energy of the ideal system by 0.84 eV/adatom. Relaxation lowers the energy of the ideal (1×1) surface by 0.17 eV/(surface atom). Thus, adatom adsorption in a T_4 site is exothermic with respect to a relaxed (1×1) surface. A previous study[17] found that the total energy of a rectangular (2×2) H_3 adatom geometry was −0.17 eV/(surface atom) relative to the ideal unrelaxed surface. The total energy of an optimized (2×2) T_4 geometry has not yet been obtained.

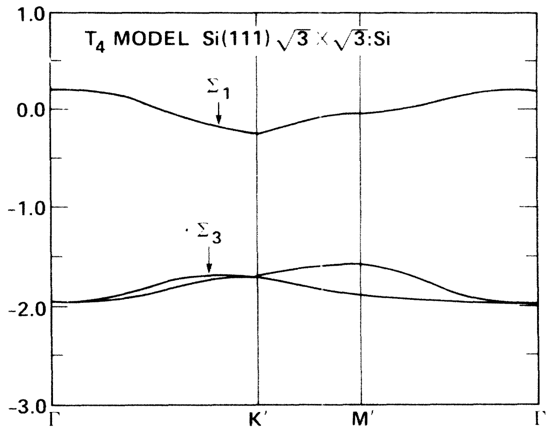

FIG. 2. Calculated surface-state dispersion for the T_4 model. The Fermi level is located at $E=0$.

The theoretical electronic structure for the Si(111)$(\sqrt{3}\times\sqrt{3})$:Si T_4 adatom geometry is shown in Fig. 2. The Σ_1 and Σ_3 bands shown there are adatom-induced surface states derived from the interaction between adatom p orbitals and dangling-bond orbitals on the substrate. The Σ_1 band is half filled and pins the Fermi level near midgap. The lower set of bands, labeled Σ_3, are 1.5 to 2.0 eV below the Fermi level. The character of the Σ_3 bands is that of substrate dangling-bond states coupled to adatom p_x and p_y orbitals. Σ_1 is composed of substrate dangling-bond states coupled to adatom p_z orbitals. Figure 3 shows the experimental surface-state dispersions determined by Uhrberg *et al.*[9] for Si(111)$(\sqrt{3}\times\sqrt{3})$:Al and Si(111)(7×7). These authors observed a striking similarity between the bands labeled A_1 and S_1 and between A_3 and S_3. If the interpretation[10,13] of the electronic structure of the $(\sqrt{3}\times\sqrt{3})$:Al phase in terms of adatom-induced surface states is correct, then this similarity indicates that adatoms are also present on the (7×7) surface. The present calculations indicate that S_1 corresponds to Σ_1 states, and that S_3 corresponds to Σ_3 states.

Uhrberg *et al.*[9] determined the dispersion of the (7×7) surface states in the extended (1×1) surface Brillouin zone. A comparison between the calculated bands for a $(\sqrt{3}\times\sqrt{3})$ T_4 model and the experimental

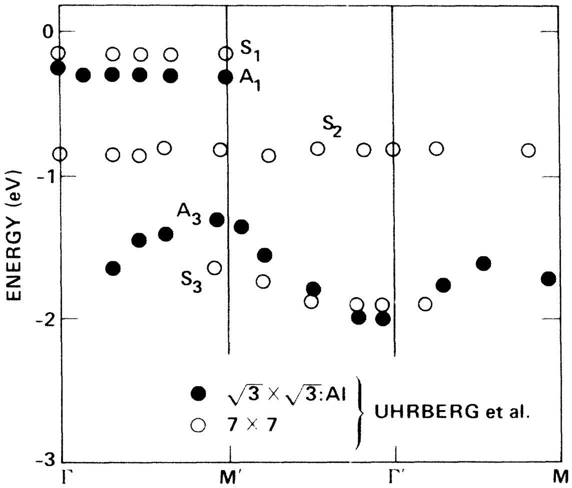

FIG. 3. Experimental angle-resolved photoemission-spectroscopy data for the Si(111)(7×7) and Si(111)$(\sqrt{3}\times\sqrt{3})$:Al surfaces. The figure is adapted from Ref. 9.

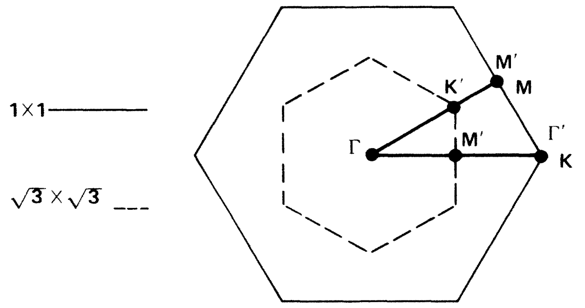

FIG. 4. ($\sqrt{3}\times\sqrt{3}$) and (1×1) surface Brillouin zones.

photoemission data for the (7×7) surface can therefore be made by mapping the calculated bands from the ($\sqrt{3}\times\sqrt{3}$) surface Brillouin zone into the (1×1) zone. The ($\sqrt{3}\times\sqrt{3}$) and (1×1) surface Brillouin zones are shown in Fig. 4. Σ_1 should be most intense along $\Gamma K'$ and $\Gamma M'$, while Σ_3 should be most intense along $K'M'K'$ and $M'\Gamma'M'$. This is because the adatom p_z orbital couples most strongly to substrate dangling-bond states with wave vectors near Γ, while the adatom p_x and p_y orbitals couple most strongly to substrate dangling-bond states with wave vectors near K and M. The comparison between experiment and the mapped theory is shown along two azimuths in Figs. 5 and 6. It is clear that the energy and momentum distribution of S_1 and S_3 can be accounted for by Σ_1 and Σ_3 states, respectively.

The S_2 band exists on the (7×7) surface, but not on the ($\sqrt{3}\times\sqrt{3}$):Al surface. Since S_2 cannot be accounted for in a ($\sqrt{3}\times\sqrt{3}$) adatom structure, its presence indicates that a type of dangling bond exists on the (7×7) surface but not on the ($\sqrt{3}\times\sqrt{3}$):Al surface. In the DAS model for the (7×7) surface there will be additional surface states originating from the six rest atoms in each unit cell. To check this hypothesis, a calculation for a surface geometry with one adatom in a T_4 site and one rest atom was performed in a (2×2) unit cell. In addition to the Σ_1 and Σ_3 surface states associated with the T_4 complex, this calculation indicates the presence of a doubly occupied dangling-bond state localized on the rest atoms. The total dispersion of this state is 0.2 eV and it is centered about 1.2 eV above the Σ_3 states. This state, without doubt, corresponds to the S_2 band observed in ARPES experiments. Since there are no rest atoms on the ($\sqrt{3}\times\sqrt{3}$):Al surface, there is no corresponding "A_2" band. According to previous calculations[10] for ($\sqrt{3}\times\sqrt{3}$):Al the A_1 band, which is very weak in intensity,[9] should not be occupied on an undoped perfectly ordered ($\sqrt{3}\times\sqrt{3}$):Al surface. Its presence suggests that a small fraction of the Al adatom sites are occupied by Si atoms. Such chemical disorder would not be surprising. Each substitutional Si adatom would contribute one electron to the A_1 band.

The number of electrons which occupy states in the S_1 manifold on the (7×7) surface is determined by the relative number of adatoms and rest atoms in the DAS structure. The twelve adatoms and six rest atoms together contribute eighteen electrons to the states in the S_1 and S_2 manifolds. Twelve of these electrons completely fill six rest-atom dangling-bond states in the S_2 manifold leaving six electrons which occupy S_1 states. In this case the S_1 manifold is $\frac{6}{24}$ full, corresponding to three full and nine empty subbands per (7×7) cell.

The preceding paragraph assumes that the corner atom is charge neutral. If it is negatively charged, corresponding to a doubly occupied dangling bond, then the number of electrons in the S_1 manifold drops to five. Thus there are five or six electrons in states in the S_1 manifold which have energies within a few tenths of an electronvolt of the Fermi level. This property of the DAS model is consistent with the electron-energy-loss studies of Demuth and co-

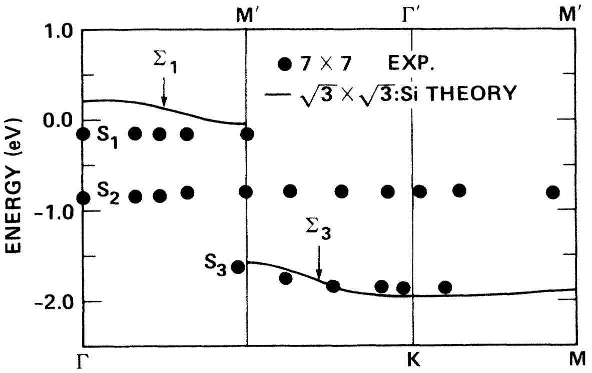

FIG. 5. Comparison between the calculated energy band structure for the T_4 model and the experimental results (Ref. 9) for the (7×7) surface. The comparison is made in the extended (1×1) Brillouin zone along the ΓKM azimuth.

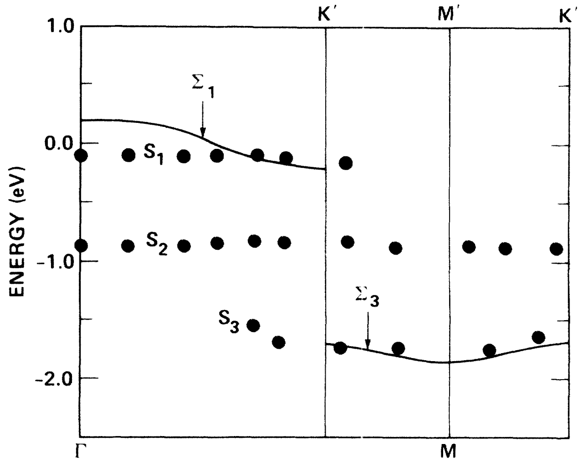

FIG. 6. Same as Fig. 5, but for the ΓM azimuth.

workers.[18] These authors detected 5 ± 1 electrons per (7×7) unit cell in states within 450 meV of the Fermi level. Moreover, three loss peaks (T_1, T_2, and T_3) were observed in this energy range.[18] These loss peaks probably correspond to transitions from the three occupied subbands in the S_1 manifold to an unoccupied subband.

On a (5×5) DAS surface there are six adatoms and two rest atoms. The S_1 manifold would then be occupied by three or four electrons depending on whether the corner atom was negatively charged or neutral. Photoemission spectra taken on the Ge(111)$c(2\times8)$ surface have features which correspond to the S_2 and S_3 peaks observed on Si(111)(7×7). However, no feature corresponding to S_1 is observed. The most likely explanation of this fact is that on Ge(111)$c(2\times8)$ the rest-atom and adatom densities are equal. In this case S_1 is completely empty.

In summary, these calculations show that the T_4 adatom complexes give rise to the surface states S_1 and S_3 while the S_2 states originate from rest-atom dangling bonds.[19] The "metallic" peak S_1 is comprised of three subbands occupied by five or six electrons.

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