Model-dependent electronic structure of the Si(111)2×1 surface

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We have used the pseudopotential density-functional total-energy scheme to study the atomic and electronic structure of the Si(111)2×1 surface: we examine and compare in detail both the standard Pandey's π-bonded chain (PC) model and the alternative three-bond scission (TBS) model including their variations. We find that while the PC model is acceptable both in energetics and in spectroscopic examination, the TBS model is energetically unfavored (0.25 eV/surface-atom higher in energy than the PC model) and does not agree in band structure with experiments. This differs from the result of the recent Hartree-Fock cluster calculations where the TBS model produces the experimental band structure. We also find that the reverse-buckled PC model is as favored in energetics as the PC model, and its band structure is also compared well with experiments. The physical relevance of the reverse-buckled PC model and the TBS model is discussed in connection with some unresolved questions concerning this surface. [S0163-1829(96)12027-0]

I. INTRODUCTION

The cleaved Si(111)2×1 surface has been the subject of intensive studies for many years as a prototype of clean semiconductor surfaces. A consensus on the structural model has arrived at the Pandey's π-bonded chain (PC) model[1] with a buckling of the surface-atom chain,[2] mainly because of its ability to yield the experimental surface-state band dispersion.[3–9] Nevertheless, there remain some questions to be resolved for this surface.

First, there has been an alternative structural model for the Si(111)2×1 surface. Haneman[10] argued that the subsurface bond breaking on formation of the PC structure is unlikely, and proposed an alternative three-bond scission (TBS) model. This model was suggested earlier by Seiwatz[11] based on the assumption that cleavage takes place along the (111) plane by scission of three bonds per atom between the closely spaced double layers of Si atoms, but it turned out to be less stable in energetics than the PC model.[12] Chen and Haneman,[13] however, argued that the less stable nature accounts for the ready conversion to the 5×5 structure at the relatively low temperature of 350 °C,[14] and showed that the three-bond cleavage is feasible in the presence of shear stress. Moreover, in their recent Hatree-Fock cluster calculations,[15] Chen and Haneman reported that the TBS model produces the band structure in good agreement with experiments, while the PC model considerably overestimates the experimental band dispersions. This prediction is in strong contrast with the previous pseudopotential density-functional calculations on the PC model[8,9] where the PC band structures agree well with experiments. Hence, it will be interesting to study the band structure for the TBS model using the pseudopotential density-functional scheme.

Second, even within the PC model, there is some discrepancy in surface-state band gap between experiments. The combination of photoemission (PE) and inverse photoemission (IPE) experiments[16] showed a band gap of about 0.6 eV, and this measurement was supported by many-body calculations based on the GW approximation.[9] On the other hand, optical measurement,[17] PE experiment from highly n-doped samples,[6] and scanning-tunneling-microscope (STM) measurements[18,19] gave a smaller band gap of 0.45–0.50 eV. Regarding the optical measurements, excitonic correlation was suggested as the origin of the smaller gap, and two different model calculations[9,20] have estimated the exciton binding energy at 0.15–0.3 eV. But the smaller gap of the PE and STM experiments, which are basically single-particle probes of the gap, is still to be resolved.

In this paper we study the atomic and electronic structure of the Si(111)2×1 surface using the pseudopotential density-functional total-energy scheme. We examine on an equal basis both the PC and TBS models including their reverse-buckled variations (see Fig. 1). In the following, the calculation scheme is described in Sec. II. In Sec. III the energetics and band structures of the considered models are reported, and the physical relevance of the TBS and the reverse-buckled PC models is discussed in connection with the unresolved experimental facts. A summary is given in Sec. IV.

II. THE PSEUDOPOTENTIAL TOTAL-ENERGY SCHEME

Structural determinations are made by total-energy minimization within the local-density approximation[21] (LDA) and the norm-conserving pseudopotential scheme.[22] In LDA, we use the Ceperley-Alder exchange-correlation energy functional parametrized by Perdew and Zunger.[23] Pseudopotentials of Si are generated by the scheme of Troullier and Martins[24] with nonlocal p and d potentials in the separable form of Kleinman and Bylander.[25]

We simulate the Si(111) surface by a periodic slab geometry: the centrosymmetric supercell consists of 12 atomic and 4 vacuum layers. Electronic wave functions are expanded in a plane-wave basis with the kinetic energy up to 10 Ry, and a uniform grid of 10 irreducible k points is used for the surface Brillouin-zone integration. To find the equilibrium atomic geometries, all atoms but in the innermost two layers are relaxed along the calculated Hellmann-Feynman forces[26]

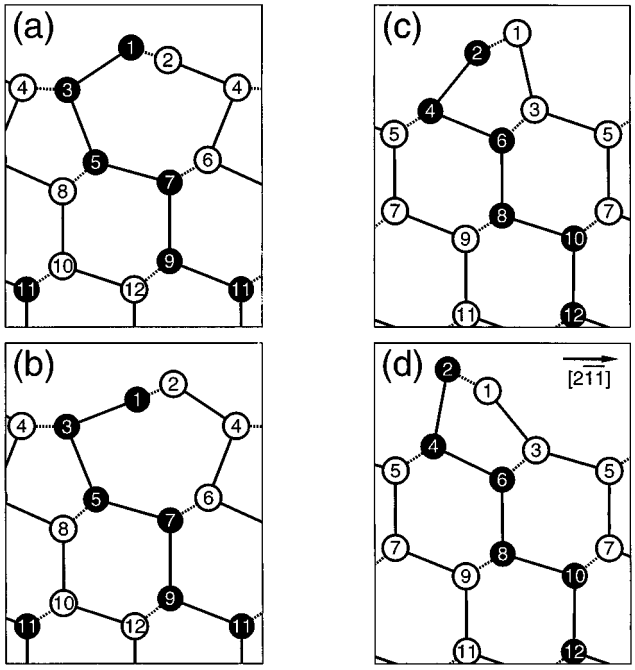

FIG. 1. Equilibrium structures for (a) the PC, (b) the reverse-buckled PC, (c) the TBS, and (d) the reverse-buckled TBS models. Solid and open circles denote atoms in different (011) planes.

until the magnitudes of the forces are within 0.01 Ry/Å. The parameters used in this work were convergence tested.[27]

III. RESULTS

We present the equilibrium atomic geometries for the considered models in Fig. 1 and their structural parameters in Table I. The calculated interlayer spacings for the PC model agrees well with a low-energy electron diffraction (LEED) result,[2] as did the earlier pseudopotential calculations.[8,9] We find, however, the reverse-buckled PC model is as stable as the PC model within the numerical accuracy of our calculations (the difference is about 0.001 eV/surface-atom).[28] The TBS model, which is 0.03 eV more stable than the reverse-buckled TBS one, is 0.25 eV less stable than the PC model.

The band structure of the Si(111)2×1 surface is characterized by two surface-state bands, one filled and the other empty, which are strongly dispersive along the chain direction ($\bar{\Gamma}\bar{J}$) and weakly dispersive perpendicular to the chain

TABLE I. Structural parameters for (a) the PC, (b) the reverse-buckled PC, (c) the TBS, and (d) the reverse-buckled TBS models. z_i is the coordinate of the ith atom (Fig. 1) along the surface normal in Å. The LEED result (Ref. 32) was fitted to the PC model.

	LEED	This work			
		(a)	(b)	(c)	(d)
z_1-z_2	0.38	0.39	−0.48	0.62	−0.67
z_3-z_4	−0.07	−0.07	−0.03	0.05	−0.11
z_5-z_6	−0.07	−0.07	−0.05	0.20	0.27
z_7-z_8	0.20	0.27	0.26	0.14	0.19
z_9-z_{10}	0.13	0.15	0.14	−0.02	−0.02

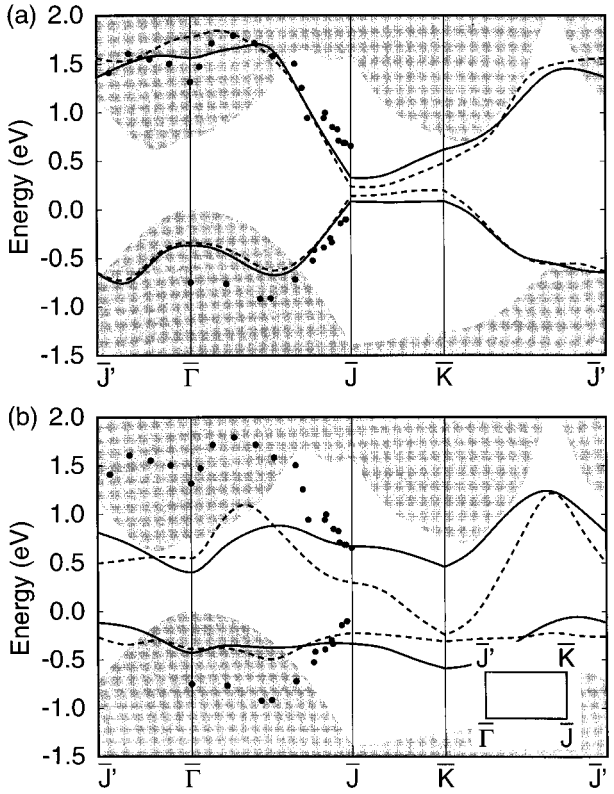

FIG. 2. Calculated surface band structures for (a) the PC model (solid line) and the reverse-buckled PC model (dashed line) and (b) the TBS model (solid line) and the reverse-buckled TBS model (dashed line). All energies are with respect to the valence-band maximum at $\bar{\Gamma}$. Shaded areas are the projected bulk band structures. Solid circles represent photoemission (Ref. 4) and inverse photoemission (Ref. 7) data.

($\bar{J}\bar{K}$) as shown in Fig. 2(a). The band structure calculated for the PC model agrees well with experimental data in accord with the earlier pseudopotential calculations.[8,9] It is also noticeable that the reverse-buckled PC model has a similar band structure to the PC model except the region around the band gap: the direct band gap at $\bar{J}$ is 0.10 eV, a little smaller than 0.25 eV for the PC model. In Fig. 2(b), band structures for the TBS and the reverse-buckled TBS models are much different from both the PC models and experiments. The TBS band dispersion along $\bar{\Gamma}\bar{J}$ is 0.1 eV, in contrast to 0.75 eV for the PC models. The present pseudopotential band structure for the TBS model disagrees with that of the Hartree-Fock cluster calculation by Chen and Haneman[15] where the TBS band structure fits well to experiments, while the PC model does not. Their scheme, compared with the present one, tends to greatly overestimate the band dispersion for both the PC and TBS models.

Besides confirming the known fact that the PC model is compatible with energetics and spectroscopic data, the present results shed some light on the previously unresolved problems with this surface. We discuss first the gap discrepancy between experiments. In our result, the reverse-buckled PC model is as stable in energetics as the PC model. It is also compatible with PE and IPE experiments and, moreover, has a 0.15 eV smaller band gap than the PC model. We note that the many-body calculations based on the *GW* approximation[9] corrected the LDA band gap of 0.25 eV to

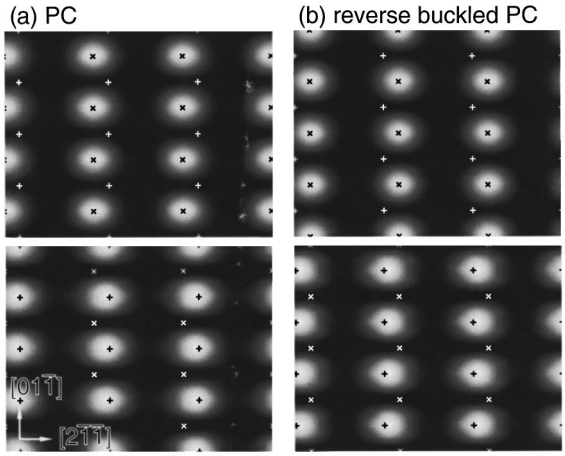

FIG. 3. Simulated STM images for (a) the PC and (b) the reverse-buckled PC models. The filled-state images (upper) are simulated by integrating $\rho(r,\varepsilon)$ from -0.5 to 0 eV with respect to the band-gap center; for the empty-state images (lower) the interval is from 0 to 0.5 eV. Crosses and plusses represent the upper and the lower top-layer atoms, respectively, in each model.

0.62 eV for the PC model. When we assume the same correction, the exact band gap of the reverse-buckled PC model would be about 0.47 eV. Then, the gap of 0.45–0.5 eV found in optical,[17] PE,[6] and STM[18,19] experiments could be explained as originating from the reverse-buckled PC structure. In fact, we have found that the STM experiments by Stroscio *et al.*,[18] which were presented as supporting the PC model and have raised the unresolved problem of the smaller gap, have actually imaged the reverse-buckled PC structure. This fact is inferred by observing the change of the STM images induced by the change of the voltage bias. Figure 3 shows the simulated STM images—contour maps of the local charge density, $\rho(r,\varepsilon)=\Sigma_{nk}|\psi_{nk}(r)|^2\delta(\varepsilon-\varepsilon_{nk})$, integrated over states near ε_F, at a fixed height (~ 3 Å) above the surface. For the PC model, the bright spot images along the chain direction ([011̄]) shift by about 0.9 Å in the [211̄] direction by changing the voltage bias from negative to positive (i.e., from filled to empty state). The reverse-buckled PC model produces very similar images to the PC model but a shift of the image in the opposite direction, reflecting the fact that in the two models the positions of the upper and the lower top-layer atoms are reversed. Experimentally, Stroscio *et al.* observed a shift of about 0.7 Å in the [211̄] direction, which is consistent with the reverse-buckled PC model both in direction and in magnitude.[29]

Second, we note that the TBS model, although energetically unfavorable, has some bearing on the earlier PE experiments for the Si(111)2×1 surface. Himpsel *et al.*[3] and later Houzay *et al.*[5] reported the existence of two surface bands at -0.15 eV and -0.7 eV (at $\bar{J}$) with respect to the valence-band maximum, which exhibited different sensitivities to hydrogen exposure. The first band was attributed to the PC structure, but the origin of the second one with a very small dispersion (~ 0.1 eV) along $\bar{\Gamma}\bar{J}$ was not explained. A similar band structure has been found more clearly on the Ge(111)2×1 surface, which is believed to have a similar structure to the Si(111)2×1 surface: in a PE experiment, Solal *et al.*[31] found a prominent valence band with a bandwidth of 0.25 eV along $\bar{\Gamma}\bar{J}$, which was inconsistent with the other PE experiment[32] exhibiting a valence-band dispersion of 0.8 eV corresponding to the PC model.[33] Based on the STM observation that 30–60 % of the cleaved Ge(111) surface was covered with adatoms, Feenstra[19] suggested that the ordered structure of the adatoms may have relevance to the weakly dispersive band. He found such adatom structures on the Si(111) surface, too. We find that the observed weakly dispersive band agrees well in position and in bandwidth with the present TBS band structure. Moreover, the TBS model is also compatible with the geometrical condition of the adatoms on the PC-type reconstructed surface. These strongly suggest that the weakly dispersive band originates from the ordered adatom structure corresponding to the TBS model.

IV. SUMMARY

We have examined, using the pseudopotential total-energy scheme, the atomic and electronic structure of the Si(111)2×1 surface within the PC and TBS models. We have found that while the PC model is acceptable both in energetics and in spectroscopic examination, the TBS model is energetically unfavored (0.25 eV/surface-atom higher in energy than the PC model) and does not agree in band structure with experiments. This is in contrast with the recent proposal based on Hartree-Fock cluster calculations where the TBS band structure agrees better with experiments than the PC one. The present study has also shown that the reverse-buckled PC model is as favored in energetics as the PC model, and its band structure is compared well with experiments. Finally, we have discussed some experimental facts as indicating a physical realization of the TBS and reverse-buckled PC models. The present result points out that a careful examination of the structural variation depending on the cleavage condition is essential in proper understanding of the Si(111)2×1 surface.

ACKNOWLEDGMENTS

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