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Surface band structure of Si(111)2×1

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The surface band structures of the three-bond scission (TBS) model and the Pandey-chain (PC) model have been computed using an *ab initio* Hartree-Fock program CRYSTAL 92. In the case of the bulk energy bands, the method gives the correct shapes and structure but overestimates the valence-band dispersion by about 50%. For the TBS model, the calculated valence-band dispersion came out about 50% wider than measured experimentally. This would suggest that the model is consistent with optical data. In the case of the PC model, the valence-band dispersion was qualitatively similar to those of previous calculations, but the width discrepancy was large. The method overestimates the surface band gap for both TBS and PC models. The significance is discussed.

I. INTRODUCTION

Surfaces of Si produced by cleavage in ultrahigh vacuum at temperatures up to a few hundred degrees celsius are known to be reconstructed and to show a 2×1 low-energy-electron-diffraction (LEED) pattern.[1] The surface-state band structure has been measured by angle-resolved photoemission (ARPES) experiments[2-6] and several, although not all, results agree that there is a pronounced upward dispersion in the surface valence band in the Γ-J direction. (We omit the bars sometimes used on surface Brillouin-zone symmetry labels.) The ability of the Pandey chain (PC) model,[7] based on single-bond (shuffle plane) cleavage, to yield such a dispersion, according to several theoretical calculations, has been an important factor in its support.

The three-bond scission (TBS) model[8,9] of the 2×1 surface, based on three-bond (glide plane) cleavage, has been shown to match much experimental data, including scanning-tunneling-microscopy (STM) observations[10] and the phenomena of crack healing.[11] Its nonminimum energy nature accounts for the ready conversion to the low-energy 5×5 structure at the relatively low temperature of 350 °C.[12-14] Although its match to LEED data has been shown,[15] and computations have been made of its energy[16] and of the viability of the three-bond scission process,[17,18] the important surface-state band structure has not been calculated. In this work we have carried out such calculations, and have also determined the band structure of the PC model and other surfaces, and that of bulk Si.

II. COMPUTATIONAL METHODS

The program used was an *ab initio* Hartree-Fock linear combination of atomic orbitals (HF-LCAO) computational package, CRYSTAL 92.[19] The Hartree-Fock-approximation method has been successfully applied to atoms and small molecules, but for solids, the excited-state energies and the band-structure dispersion are generally overestimated. This is believed to be due to the effects of correlation energies which are not properly treated. Nevertheless, it is of interest to apply the method in that the mix of approximations is different from that of other methods used for surface calculations and there is very little scope for adjustment of results. Recent advances in computer power have made it possible to apply the HF technique to low symmetry multicomponent systems such as surfaces.

The [111] direction was chosen as the z direction. Slabs of atoms were taken with various numbers of layers as described below. The surface unit cell (unit mesh) of an ideal 1×1 surface has one atom, whereas there are two for the 2×1 cell. In choosing the slab, the mirror symmetry was taken in the x direction. The atoms in the bottom layer of the slab had their dangling bonds terminated by H atoms in the usual way. Self-consistent-field (SCF) calculations were carried out using the closed-shell restricted-HF method of the program. Gaussian-type functions were used as basis sets. Since the number of symmetry operations of a slab is only 2, a large number of integrals had to be calculated. To conserve disk space, preliminary calculations were made

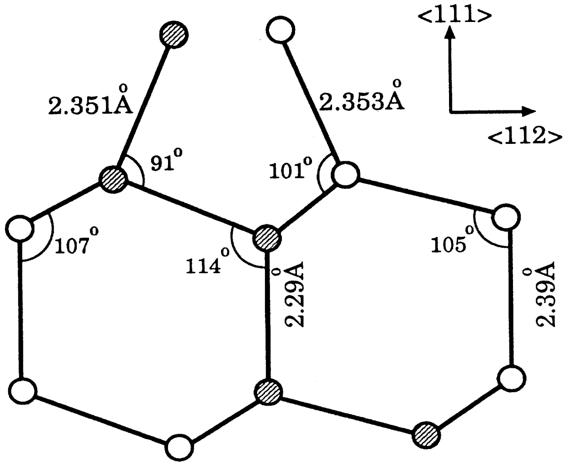

FIG. 1. The minimized strain-energy structure of the TBS model (Ref. 21). Atoms represented by hatched and open circles are in adjacent planes.

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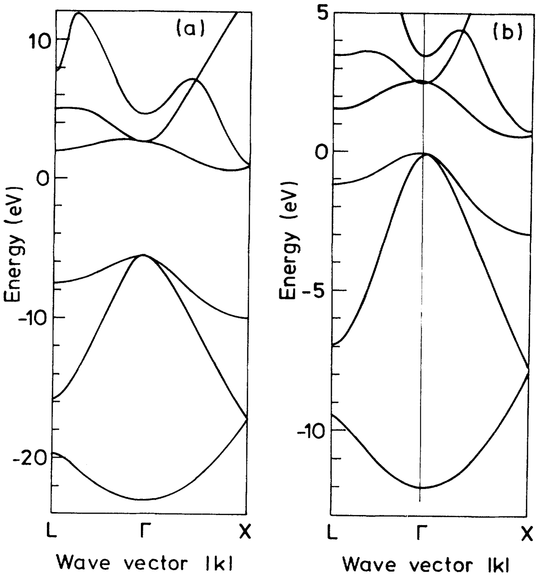

FIG. 2. (a) The band structure of bulk Si calculated by CRYSTAL 92 program. (b) The band structure of Si calculated by pseudopotential methods (Ref. 23).

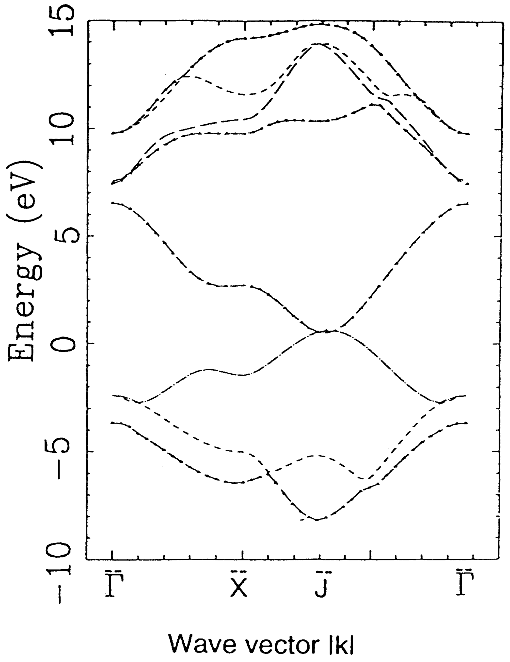

FIG. 3. The band structure of the ideal (111) Si surface.

with the small basis set STO-2G, but later calculations used basis sets STO-3G, STO-6G, and the split-valence basis set 3-21G. No *d* functions were included. The integral thresholds were set to 10^{-4} for large systems and 10^{-5} for small systems. The SCF threshold was set to 10^{-5}. The bond length of Si was 2.3500 Å, and that for Si-H was taken as 1.4235 Å from a self-consistent calculation whose results had been used previously.[18]

Several structures were considered. The undistorted termination of the bulk lattice was used as the ideal (111) surface. To aid comparisons for the PC model, a structure previously computed by Northrup and Cohen,[20] for which parameters were available, was used. The structure for the TBS model was that previously obtained for a minimum-strain-energy calculation,[21] Fig. 1. Note that a cleavage surface is not necessarily the minimum-energy structure, as mentioned in Sec I, but one would expect it to be at least a local minimum-energy structure. Therefore, the strain-energy-minimized structure was checked by computing the energy of structures with various atom displacements from it.

III. CALCULATIONS OF BAND STRUCTURE

A. Bulk structure

The bulk band structure is shown in Fig. 2(a). The parameters are listed in Table I, together with those from a HF calculation by Svane[22] using the linear muffin-tin (LMTO) method. Here, the single-particle wave function for the valence electrons is found as a linear combination of LMTO's. The band structure is similar in shape to that from pseudopotential methods,[23] Fig. 2(b). The bandwidth using the latter is smaller, but, as known, more adjustments are possible. As expected, the HF band gaps and dispersions are overestimated, both by our and by Svane's calculation (which also incorporated relativistic effects). The two methods give slightly different parameters, but the degree of their overall agreement is comparable. Note that the error in valence bandwidth is about 50%.

TABLE I. Calculations for bulk structure. Results of this work, Svane, and experimental values for valence-band width *W*, the direct and indirect band gap, and dispersion (eV).

	Band gap			*W*	
	Indirect	Direct	$E_{L_3'}-E_\Gamma$	$E_{\Gamma_1}-E_{\Gamma_{25}'}$	$E_{L_1}-E_\Gamma$
This work	5.4	7.5	2.26	18.3	10.84
Svane (Ref. 19)	5.6	8.6	1.52	16.2	10.7
Experiment (Ref. 20)	1.2	3.4	1.2	12.4	6.8

B. Ideal structure

The band structure for the ideal shuffle-terminated surface, using six layers, is shown in Fig. 3. It is quite different from that obtained in a much earlier, and more limited, calculation.[24] There is a zero band gap, the valence band disperses upward from Γ-*J* via *X*, and there is a gap between the first and second conduction bands.

An attempt was made to calculate the structure of an ideal glide plane surface by the same closed-shell restricted-HF method. However, it was unstable, the

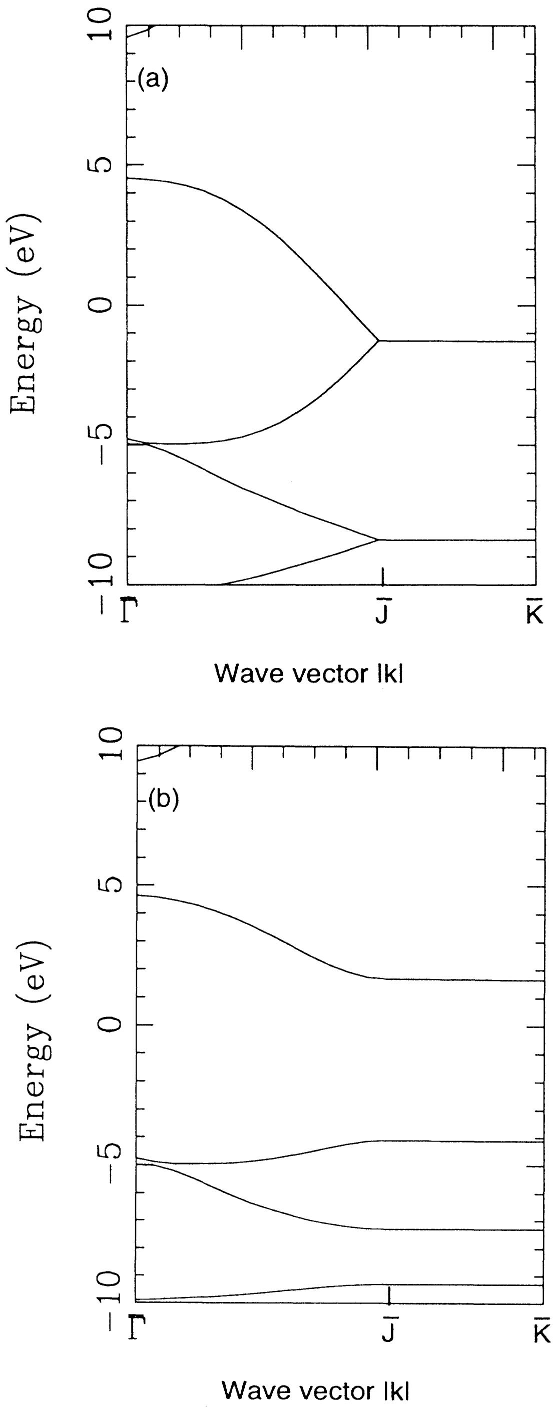

FIG. 4. The band structure of a π-bonded chain alone. (a) No buckling for the two atoms. (b) Two-surface atoms buckled 0.30 Å.

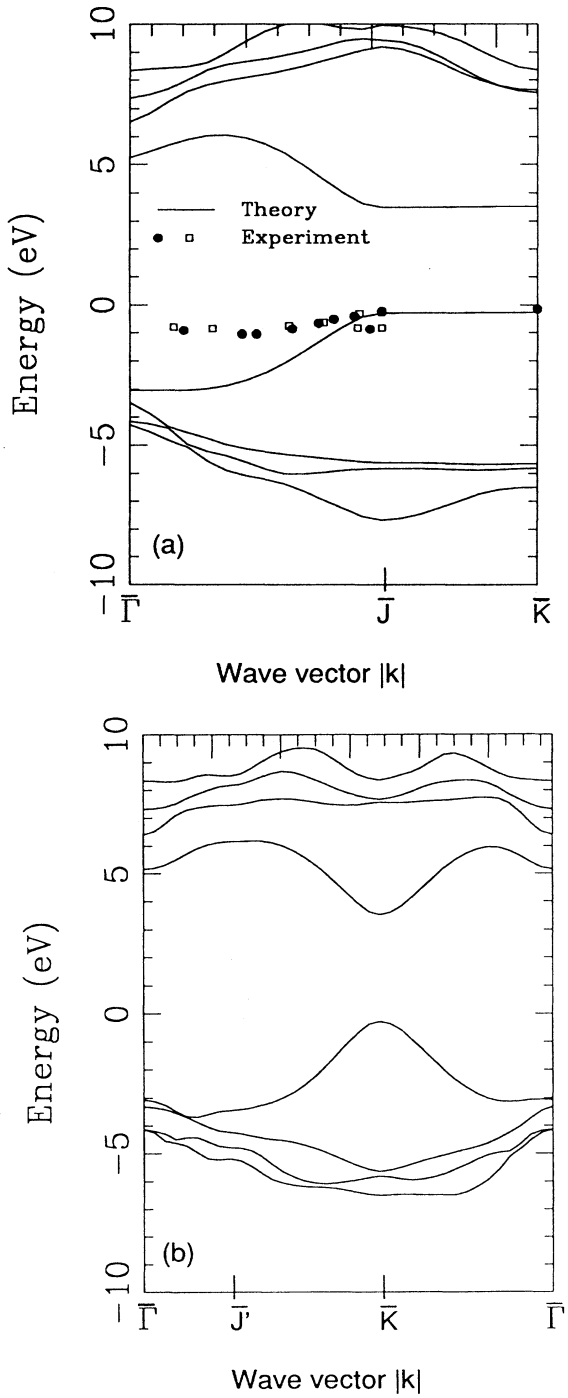

FIG. 5. The band structure (Ref. 26) for the Pandey chain structure. The experimental data were fitted to the valence band at the *J* point. (a) The symmetry path Γ-*J*-*K*, (b) the symmetry path Γ-*J*'-*K*-Γ.

SCF convergence being only 6×10^{-4} a.u., due to too many dangling bonds. This confirms that in a real situation for such a surface, some reconstruction to cause bond overlap would be likely to occur. It is possible that inclusion of spin polarization would enable the convergence.

C. π-bonded surface chain

In order to gain a feel for the role of the chain atoms in a surface calculation, a single chain of Si atoms as would exist on a 2×1 cell, bonded underneath by two H atoms, but with a dangling bond on top, was considered. The Si atom separation was 2.395 Å. The band structure for both a nonbuckled chain, and one with a 0.3-Å buckle, are shown in Fig. 4. The nonbuckled case has a zero band gap with a large dispersion of 3.77 eV from Γ-*J*. The surface band is flat along *J*-*K*′. When buckling is introduced, a band gap appears. The dispersion reduced to 0.87 eV for 0.3-Å buckling. This shows the strong effects of the chain and its buckling on the degree of dispersion.

D. Pandey chain model

The Northrup and Cohen structure for this model[25] was used,[20,26] consisting of six layers. The split-valence basis set 3-21 G was used. The band structure is shown in Fig. 5. The effect of increased buckling is to enlarge the band gap, and reduce the dispersion Γ-*J*, as shown in Table II. This effect was also found in other calculations.[26-28] In this study, the dispersion reduced from 3.67 to 2.74 eV in the case of 0.19-Å buckling. The band gap increased. These dispersions are three or four times those of the above calculation. The band gap is not expected to be reliable, but the valence-band dispersion is only overestimated by about 50% in the case of the bulk. Therefore, the large numerical discrepancy between the dispersions calculated by the different methods is a matter for attention. We note that, following the publication of LEED (Refs. 29 and 30) and ion scattering[31] data indicating large chain buckling (although the LEED fit was poor), subsequent pseudopotential calculations have yielded much larger chain buckling, namely, 0.47 Å (Ref. 27) and 0.49 Å.[28] Use of such buckling would have reduced the dispersion in our calculation (see Table II) although not greatly.

There are no significant adjustable parameters in our calculation. No core level shift was used, but this factor mainly affects the convergence. The shrinking factor in reciprocal space for a dense *k* point net (Gilat net) was 12 for the surface and 8 for the bulk, but these parameters can hardly affect the dispersion. The recommended 30% of the Fock matrix of cycle (I-1) was mixed with the Fock matrix of cycle I, but again this parameter has little effect. We tried the effects of a simpler basis set, STO-2G, and more layers. Thus, use of eight layers with the STO-2G basis set gave a dispersion of 2.5 eV, whereas six layers with 3-21G gave 2.79 eV. The computation, there-

TABLE II. The band gap and dispersion of the Pandey model for various buckling.

Buckling (Å)	Band gap (eV)	Dispersion $\bar{\Gamma}-\bar{J}$ (eV)
0.0	2.55	3.67
0.19	3.93	2.74
0.39	4.56	2.48

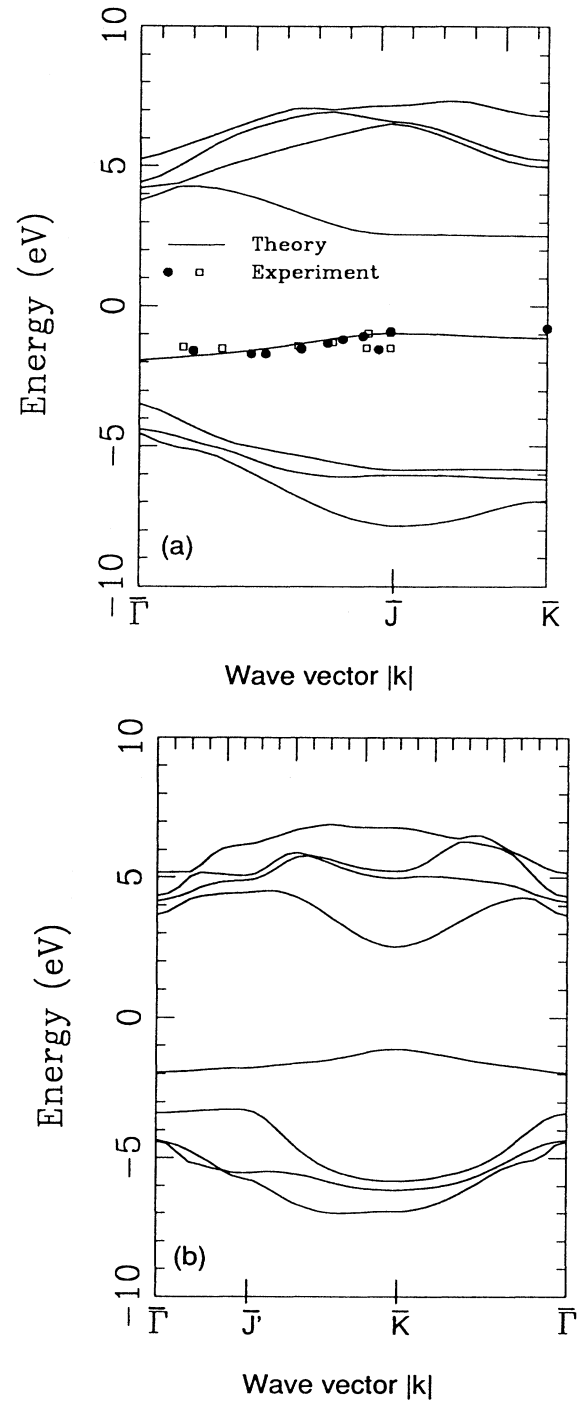

FIG. 6. The band structure of the TBS model strain-energy-minimized structure. The experiment data were fitted to the valence band at the *J* point. (a) The symmetry paths Γ-*J*-*K*, (b) the symmetry paths Γ-*J*′-*K*-Γ.

fore, does not appear to be amenable to significant adjustment.

E. TBS model

Slabs of 5, 7, 9 and 11 atomic layers were calculated using STO-2G basis sets, but no dispersion in the valence band occurred from Γ-*J*, apart from the nine-layer slab which gave 0.22 eV. The STO-2G basis set was clearly inadequate for this model, and STO-6G had to be used. Because of greater disk space demands, only the five and seven-layer slabs were calculated. The band structure for the 0.04-Å buckled seven-layer slab is shown in Fig. 6. The conduction- and valence-band shapes appear generally similar to those of the Pandey model. However, there are differences in magnitude, depending on the buckling chosen for the latter. For example, with a buckling of 0.19 Å, the band gaps are 3.93 eV (PC) and 3.43 eV (TBS), and the dispersions are, respectively, 2.74 and 0.98 eV. The results for a five-layer slab were similar to those of a seven-layer slab, suggesting that the role of the H termination on the bottom surface was minimal, as would be expected.

As a check on whether the structure used for the TBS model corresponded to a local energy minimum, as required for a cleavage structure, the energy was calculated for a series of structures obtained by shifting both the surface chain atoms and the second-layer atoms in steps. It was found that second-layer shifts only increased the energy. In the case of the first-layer atoms, a slight reduction in energy was obtainable by shifting the lower of the two buckled surface chain atoms by 0.04 Å in the [112] direction, i.e., orthogonal to the chain axis and away from it, and the upper buckled atom by 0.06 Å in the same direction. See Fig. 7. However, the lowering in energy was only about 0.006 eV per atom, which is a small fraction of kT. Therefore, the structure used was effectively at a local minimum. The dispersion in the Γ-*J* direction changed from 0.98 eV at the point *B* in Fig. 7 to 0.862 eV at the point *A*. This small change is of little significance.

No dip was found for either model in the dispersion from Γ-*J*. It should be mentioned that although some calculations have produced a small dip, in line with some experimental results,[3,4] there are grounds for doubting whether this dip is, in fact, characteristic of a purely flat surface, due to the impossibility of producing such a surface over the areas needed for obtaining optical data. Thus, although it is possible to find small areas by STM and high-resolution scanning electron microscopy (SEM) where the step content is only about 1% of the surface, there are frequently large rougher regions within the dimensions of several hundred micrometers illuminated under synchrotron irradiation. Such rough portions are seen by SEM on surfaces which nevertheless show a single 2×1 domain structure.[32]

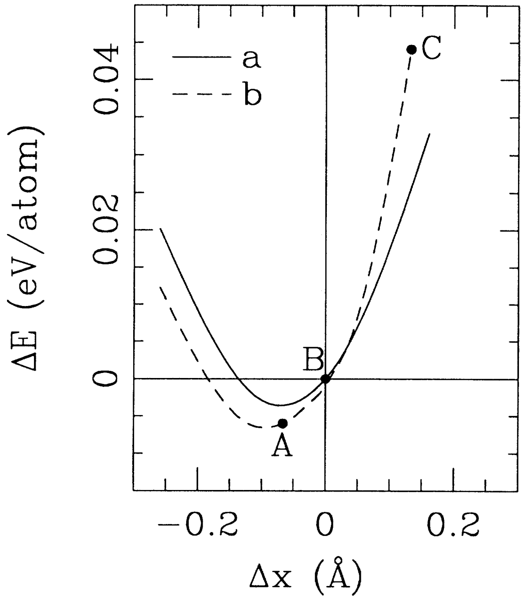

FIG. 7. The variation of the total energy of the strain-energy-optimized TBS structure (in eV/atom) as a function of displacement of surface chain atoms. The direction Δ*x* is in the [112] direction (see Fig. 1). The solid line marked "*a*" refers to displacement of the upper buckled surface atom with the lower atom unchanged. The dashed line marked "*b*" refers to the same displacement, but with the lower surface atom having been shifted by 0.04 Å in the −Δ*x* direction. This results in a slightly lower minimum energy. The dispersion in the valence band in the Γ-*J* direction is 0.862 eV at point *A*, 0.98 eV at point *B*, and 0.086 eV at point *C*.

IV. DISCUSSION

A number of points have arisen from the above computations. The method does not of course give accurate band gaps, either for the bulk or surface case. (In the latter, the direct gap is about 0.45 eV, with about 0.26 eV for the indirect gap.[33]) Local-density-functional methods also have problems with excited states. The most interesting question is that of the dispersion of the surface valence band, since here there exists experimental data which suggests a dispersion along Γ-*J* of about 0.7 eV. Although several computations have been published[25–28] which show dispersions of this order, depending on the parameters chosen for the PC structure and the details of the approximations incorporated in the methods, our HF calculations for one of the above PC models gave dispersions of around 2.5 eV. Since the dispersion for the bulk Si structure is overestimated by about 50%, one would not be surprised by a similar overestimate for the true surface structure. The point of concern is that our HF computation for the PC structure, whether it be the true structure or not, gives a large quantitative discrepancy compared with a calculation for a similar PC structures using a different method.[26] Since a related method[27] in reportedly more thorough form, gave altered parameters (including greatly enhanced chain buckling) which would have significantly reduced the dispersion of the prior calculation, the status of the pseudopotential methods, although generally established, is not above question. The discrepancy between the HF and pseudopotential method for a specific structure could be due to shortcomings in application of the HF method to the surface, or of the other method, or since all are approximate, in both. It is useful to note that there is a general similarity in the shape of the valence and conduction bands in the case of the TBS and PC models, as might be inferred from their possession of a surface chain and the strong effect of this as shown above in the case of the calculations for the chain alone.

In conclusion, we have used an *ab initio* Hartree-Fock self-consistent calculation for small slabs of silicon with a surface on one side and terminated by H atoms on the other. The results for the PC model of the Si(111)2×1 surface were generally similar to those found in a previous calculation, but the valence-band dispersions were much larger. In the case of the TBS model, the dispersion was about 50% greater than that found experimentally, matching the degree of error found for the bulk case. These calculations would suggest that the match of the TBS model to optical data is viable.

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