Dimer-plus-Chain Structure for the Si(100)-$c(4\times 2)$ Surface

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A new $c(4\times 2)$ structure for the Si(100) surface is proposed in which the second-layer atoms are dimerized and the top-layer atoms form π-bonded chains. Pseudopotential total-energy calculations indicate that this $c(4\times 2)$ dimer-plus-chain structure has a lower energy than the (2×1) dimerized surface. The bond topology of the structure explains the streaking and weakness of the $\frac{1}{4}$-order diffraction spots observed in low-energy electron and He-atom diffraction.

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The structure of the Si(100) surface has been a central, but unresolved, issue in semiconductor surface physics since Schlier and Farnsworth[1] observed an apparent two-domain (1×2) reconstruction with low-energy electron diffraction (LEED). Later, Lander and Morrison[2] obtained a two-domain $c(4\times 2)$ LEED pattern with streaks through the $\frac{1}{4}$-order spots. A sharp two-domain $c(4\times 2)$ LEED pattern having $\frac{1}{4}$-order spots with intensity 0.03 relative to the integral spots was observed by Poppendieck, Ngoc, and Webb[3] following careful annealing procedures. Cardillo and Becker[4] also observed a streaked $c(4\times 2)$ pattern using He-atom diffraction. Their results indicate that the Si(100) surface structure is a weakly ordered $c(4\times 2)$ with much more disorder in the 4 direction than in the 2 direction.[4] Evidently, much more energy is required to destroy the twofold periodicity than the fourfold periodicity in the $c(4\times 2)$ structure. In this paper I propose a structure which is consistent with this fact, and present total-energy calculations which show that it has a lower total energy than the Si(100)2×1 dimer models.[1,5,6]

Is the Si(100) dimer model stable with respect to the addition of Si atoms? Consideration of this question led to the construction of the model shown in Fig. 1. It was constructed by adding chains of atoms onto a (2×1) dimerized surface. The top two layers of atoms are strongly reconstructed, i.e., the ring structure is altered from the bulk. The atoms in the second layer (5,6,7,8) form subsurface dimers and participate in fivefold rings. The top-layer atoms (1,2,3,4) are bonded together in linear chains, and participate in sevenfold rings. Other layers are close to the ideal positions. The possibility of a Si(100) structure of this type was forseen by Seiwatz.[7] In dimer models[1,5,6] each surface atom has a π bond with one other surface atom, its partner in the dimer. In the present dimer-plus-chain model, or DC model, the surface atoms each have two nearest-neighbor surface atoms. The DC model is energetically favorable, compared to the dimer models, because of the increased surface-atom π bonding.

Figure 2 shows two kinds of long-range order which can be obtained with different alignments of neighboring chains. A $c(4\times 2)$ structure is shown in Fig. 2(a), and I propose that it is the ground state of the Si(100) surface. Translation of a chain along the chain direction by one (1×1) lattice vector does not change the local bond topology, but does change the interaction energy of neighboring chains. Evidently, the $c(4\times 2)$ ordering minimizes the interaction energy of a chain

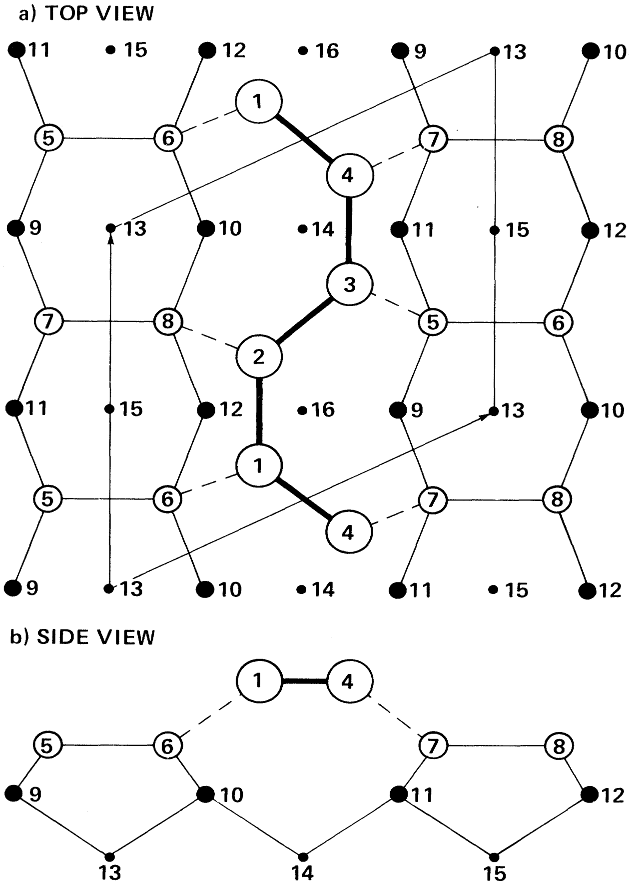

FIG. 1. Top and side views of the $c(4\times 2)$ surface reconstruction. Atoms 1–4 are surface atoms and form chains. Atoms 5–8 are dimerized second-layer atoms. Atoms 9–12 are third-layer and 13–16 are fourth-layer atoms with bulk-like coordinates. Arrows indicate primitive translations.

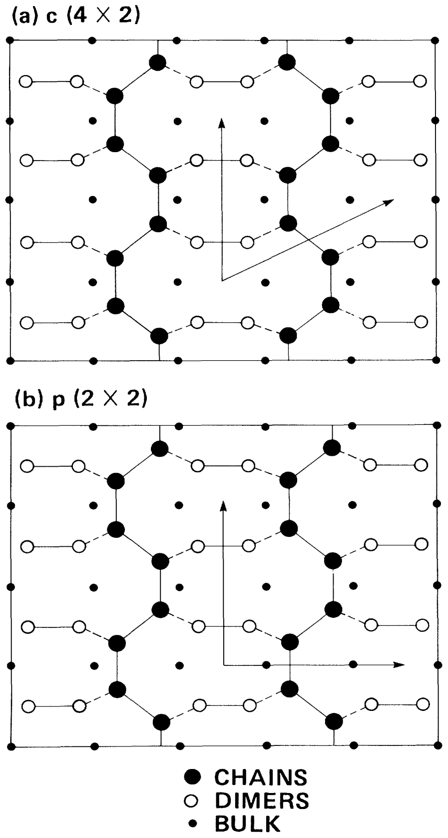

FIG. 2. Top view of the (a) $c(4\times2)$ and (b) $p(2\times2)$ ordering. Arrows indicate primitive translations.

with its neighbors. A $p(2\times2)$ ordering is shown in Fig. 2(b). Because the $p(2\times2)$ and $c(4\times2)$ structures have similar local bonding topology, they are very close in total energy. Thus, a large number of misaligned chains can occur leading to a weakly ordered $c(4\times2)$ surface. Misalignment preserves twofold periodicity in the 2 direction but destroys the fourfold periodicity in the 4 direction. This topological property of the model explains the streaking and the weakness of the $\frac{1}{4}$-order features observed in LEED[2,3] and He diffraction.[4]

The total energy of the $c(4\times2)$ chain model was calculated with the momentum-space pseudopotential formalism[8,9] and the local density approximation.[10] A norm-conserving pseudopotential was generated with the method of Hamann, Schluter, and Chiang,[11] and the local density approximation was implemented by use of the correlation energy functional of Ceperley and Alder, as parametrized by Perdew and Zunger.[12] The Kohn-Sham equations[10] were solved in a plane-wave basis. A plane-wave cutoff of 5 Ry limits the number of plane waves used in the expansion of the single-particle wave functions to ~1300. A supercell[13] containing 32 atoms was used to model the surface. Inversion symmetry was imposed on the atomic positions to facilitate the computations. This scheme is similar to others used to study Si(111)[13-15] and Si(100)[16] surfaces. Forces calculated with the Hellmann-Feynman theorem were used to optimize the structure. The resulting structure has an energy 1.10 eV/(surface atom) lower than the ideal Si(100)1×1 geometry. I have also performed total-energy calculations for the energy-optimized (2×1) dimer model[16] and find it to be 0.99 eV/(surface atom) lower than the ideal surface. Thus, I conclude that the DC model is preferred over the dimer model by ~0.1 eV/(surface atom). The uncertainty in the calculated energy difference is 0.1 eV/(surface atom). Total-energy calculations[15] show that an energy reduction of similar magnitude arises from an analogous increase in π bonding on Si(111)2×1. For the Si(111)2×1 surface, the structure analogous to the DC model is the π-bonded chain[17] and the structural analog of the dimer is the π-bonded molecular model.[18]

Calculated atomic coordinates for the DC model are listed in Table I. For this structure, most of the bonds are within a few percent of the bulk bond length (2.35 Å). The exception is the subsurface dimer bond between atoms 5 and 6 (and between 7 and 8), which is 2.52 Å. Here, the increased length arises from the elastic forces generated in the fivefold rings. In the chains, the *cis* bonds are 2.29 Å and the *trans* bonds are 2.25 Å. The backbonds connecting the chains to the dimers are 2.33 Å. These bond lengths should be accurate to within 0.05 Å.

Many spectroscopic experiments[19-22] show that dangling-bond surface states exist on the Si(100) surface. These experiments have all taken place on two-domain surfaces with disorder within each domain, i.e., the $\frac{1}{4}$-order LEED streaks were not observed. Despite these unavoidable difficulties, structure in the photoemission spectra[19,20] indicative of *two* occupied dangling-bond surface bands could be resolved. The DC model accounts for these two features as π bands. The dispersion calculated for the DC model along the $\Gamma J'$ direction, which is parallel to the chains, is shown in Fig. 3. Two occupied π and two empty π^* bands exist. The dispersion of these π bands is not completely independent of the long-range order in the 4 direction. For example, on a $p(2\times2)$ ordered surface, the Γ and J' points (defined in Fig. 3) would be equivalent by translational symmetry, so that the energies of the surface states at Γ would be the same as at J'. For the $c(4\times2)$ ordering, no such equivalence is required, and, as Fig. 3 shows, does not occur. Therefore, it is most appropriate to compare the dispersion shown in Fig. 3 with photoemission experiments performed on $c(4\times2)$ ordered surfaces when such experiments are possible.

TABLE I. Coordinates for the DC model. Listed numbers (r_1, r_2, r_3) are coefficients of the vectors $\mathbf{R}_1 = 2a\hat{\mathbf{x}} + a\hat{\mathbf{y}}$, $\mathbf{R}_2 = -2a\hat{\mathbf{x}} + a\hat{\mathbf{y}}$, and $\mathbf{R}_3 = c\hat{\mathbf{z}}$. $a = (\frac{8}{3})^{1/2}b$, $c = (\frac{1}{3})^{1/2}b$, b is the bulk bond length. Atom numbers 1–16 correspond to Fig. 1. B1–B4 are fifth-layer bulk positions.

Atom	r_1	r_2	r_3	Atom	r_1	r_2	r_3
1	0.173	−0.221	3.85	11	0.007	0.243	1.8875
2	0.471	0.077	3.85	12	0.243	0.007	1.8875
3	−0.221	0.173	3.85	13	0.625	0.625	0.975
4	0.077	0.471	3.85	14	0.875	0.375	1.0125
5	−0.200	−0.036	2.8625	15	0.125	0.125	0.8875
6	−0.036	−0.200	2.8625	16	0.375	−0.125	1.0125
7	0.286	0.450	2.8625	B1	−0.625	−0.625	0.0
8	0.450	0.286	2.8625	B2	−0.875	−0.375	0.0
9	0.505	0.745	2.0	B3	−0.125	−0.125	0.0
10	0.745	0.505	2.0	B4	−0.375	0.125	0.0

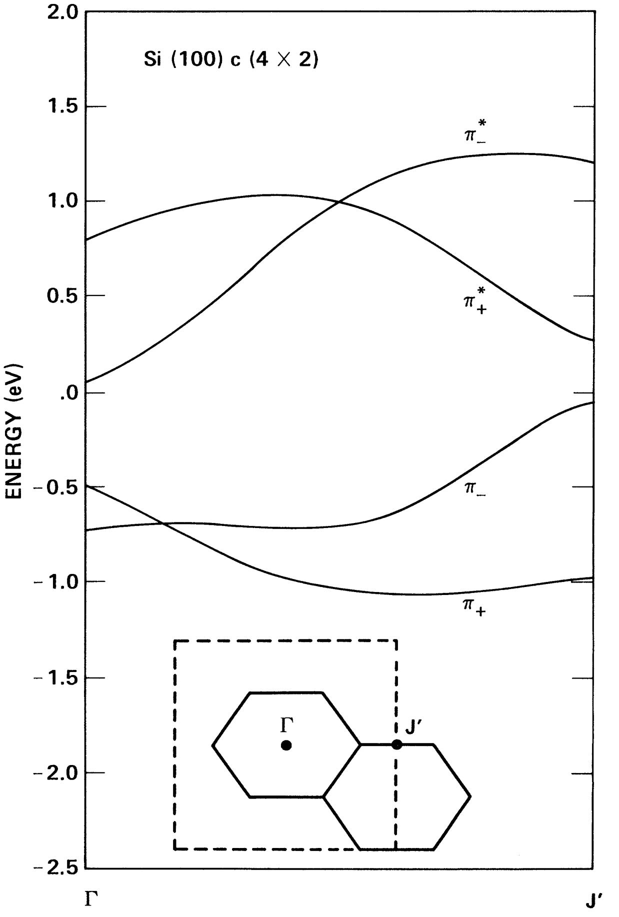

FIG. 3. Surface states for the $c(4\times 2)$ chain model calculated with the self-consistent pseudopotential method. Two occupied π and two empty π^* bands exist. The inset shows the $c(4\times 2)$ Brillouin zone (solid lines) and the (1×1) zone (dashed lines).

The essential features of the surface band structure can be understood within the framework of a model with one dangling-bond orbital per atom. With interaction matrix elements V_1 for *cis* bonds, and V_2 for *trans* bonds, the calculated dispersion is $E(\mathbf{k}) = \pm\{V_1^2 + V_2^2 \pm 2V_1V_2\cos(\mathbf{k}\cdot\mathbf{a})\}^{1/2}$, where $\mathbf{a}$ is a (1×1) lattice vector pointing along the chain. V_1 is larger than V_2 because of steric factors. This model, with $V_1 = 0.6$ eV and $V_2 = 0.3$ eV, agrees qualitatively with the band structure shown in Fig. 3. The difference arises in part from interchain coupling, which is neglected in the model calculation.

In the model calculation, the surface-state band gap is $2|V_1 - V_2|$ and the dispersion of the occupied (or empty) surface states is $2V_2$. For the values of V_1 and V_2 described above, the surface band structure is consistent with experiments. Namely, photoemission[19,20] reveals that the total width of the occupied surface states is 0.5 to 0.65 eV, and electron energy-loss[21] and differential reflectivity[22] experiments indicate that the surface-state band gap is ~ 0.6 eV. In addition, electron energy-loss experiments[21] suggest that an unoccupied surface state has an energy minimum at the Γ point. This, too, is consistent with the present model.

In summary, I have proposed a new model for the reconstruction of the Si(100) surface which has a lower total energy than the (2×1) asymmetric dimer model, and which is consistent with diffraction[2–4] and photoemission[19,20] experiments. This model should also be applicable to C(100) and Ge(100).

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