

π -bonded molecular and chain models for the Si(111) surface

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The cleaved Si(111)-(2 × 1) surface is proposed to have *two* distinct structures with chainlike and molecular types of π bonding, respectively. The two structures give rise to similar five- and sevenfold rings of atoms at the surface. The occurrence in varying proportions of both bonding configurations provides a natural explanation for the well-known cleavage-dependent properties of the Si(111) surface.

The Si(111) surface has been studied more extensively than almost any other semiconductor surface. Recent theoretical¹⁻³ and experimental⁴⁻⁶ developments, however, have generated a new interest in the atomic and electronic properties of this surface. Accurate total energy calculations^{1,2} have shown that the buckling distortion long associated with the (2 × 1) reconstruction of the surface⁷ is unstable with respect to the nonbuckled, *relaxed* (1 × 1) surface. The calculations effectively rule out the buckling model as a satisfactory description for the cleaved surface.

The novel π -bonded chain structure recently proposed by Pandey provides an explanation^{1,2} for the stability of the Si(111)-(2 × 1) surface. In this model the surface dangling bonds interact via first-neighbor instead of second-neighbor interactions, resulting in an appreciable lowering of the total energy which stabilizes the surface. A simple way of obtaining the π -bonded structure from the ideal (1 × 1) surface has been demonstrated by Northrup and Cohen.³ The energy barrier between the buckled and π -bonded geometries is found to be surprisingly small (≈ 0.03 eV/atom) indicating that the chain structure can be easily obtained during cleavage. Additional evidence in favor of this model is provided by the highly dispersive dangling-bond state seen in the angle-resolved photoemission measurements of Uhrberg *et al.*⁵ and the remarkable agreement with the theoretical results³ for the chain model.

Despite the attractive features of the π -bonded chain model a number of problems remain unresolved. The most important of these is the cleavage dependence or irreproducibility of experimental data.^{4-6,8,9} The presence of domains at the surface greatly contributes to the complexity of analysis. But domain effects alone do not appear to be the sole cause of the problems. This can be seen, for example, from an examination of the recent three angle-resolved photoemission measurements.⁴⁻⁶

(i) Himpfel, Heimann, and Eastman⁴ find evidence for *two* surface dangling-bond bands. The upper state appears to be dispersive with a positive Γ - J (Fig. 1)

dispersion; the lower state is nearly dispersionless. Significantly, the two bands exhibit very different sensitivities to hydrogen with the lower state disappearing more rapidly with exposure than the upper one.

(ii) Uhrberg *et al.*⁵ observe *only* a dispersive ≈ 0.8 -eV-wide band along Γ - J which is consistent with the upper band seen in the previous experiment. They suggest that the two bands seen by Himpfel, Heimann, and Eastman⁴ are a result of a two-domain surface. This assumption brings the two sets of data into good agreement for states near J , but the different sensitivities of the two bands to hydrogen⁴ and the absence of a two-domain pattern in the electron-diffraction data remain unexplained.

(iii) Petroff *et al.*⁶ find *only* a dispersionless band between Γ and J for some samples, consistent with the lower band seen in the first experiment.⁴ It would be difficult to reconcile the flat and dispersive bands by invoking domain arguments.

The conflicting experimental results discussed above raise the question of the uniqueness of the surface atomic structure on cleaved "one-domain" Si(111) surfaces. The π -bonded chain model provides an excellent description of the dispersive state³ but not of the dispersionless state seen in the photoemission measurements. To resolve this problem it is proposed that the Si(111) surface contains two in-

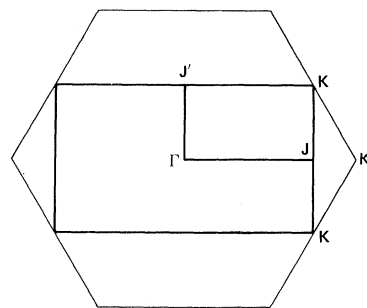


FIG. 1. The hexagonal (1 × 1) and rectangular (2 × 1) surface Brillouin zones for the Si(111) surface are shown.

equivalent structures consisting of Pandey's chain model together with a new "molecular" structure. The two surface geometries described below have interesting structural similarities but very different electronic properties. Together they provide a natural explanation for the cleavage dependence of experimental results.^{4-6,8,9}

The top view of the π -bonded chain model is shown in Fig. 2(a). The side view is given in Fig. 2(b) for comparison to that of the ideal surface [Fig. 2(c)]. The numbering of atoms is designed to show the changes in atomic positions resulting from surface reconstruction. Figures 2(b) and 2(c) show that the displacements involve primarily the first double layer of surface atoms (i.e., atoms 1-4). Northrup and Cohen³ have demonstrated that the chain structure can be obtained in a simple way from the ideal structure by applying a low-energy shear distortion to the top double layer of atoms, breaking the bond between atoms 1 and 5 [Fig. 2(c)]; and forming a new bond between atoms 4 and 5 [Fig. 2(b)]. The displacements preserve the underlying bulk mirror-reflection symmetry.

The top and side views of the new "molecular" structure proposed in this paper are shown in Figs. 3(a) and 3(b), respectively. The side view of the ideal surface is shown in Fig. 3(c). The substrate

atoms (atoms 5-8 and beyond) are in nearly the same positions as in Fig. 2. The atomic displacements and rebonding leading to the new structure are very similar to those for the π -bonded chain model except for one essential difference. Starting from the ideal surface, the shear distortion of the first double layer of atoms occurs at 120° with respect to the long axis of the unit cell instead of parallel to it as in the chain model. The reconstruction results in replacing the bond between atoms 1 and 5 [Fig. 3(c)] by one between atoms 4 and 5 [Fig. 3(b)]. The resulting structure breaks the underlying mirror-reflection symmetry. There are, therefore, two such geometries related by mirror reflection.

The new model (Fig. 3) gives rise to pairs of threefold coordinated atoms that are separated from other pairs by $\approx 3.85 \text{ \AA}$. Five- and sevenfold rings of atoms and bond-angle distributions very similar to those of the π -bonded model^{1,3} are also obtained. The occurrence of such rings at the surface is remarkably similar to those observed at the grain boundary between (111) planes in Ge. Very-high-resolution electron microscopy studies¹⁰ have provided direct evidence for the presence of alternating five-

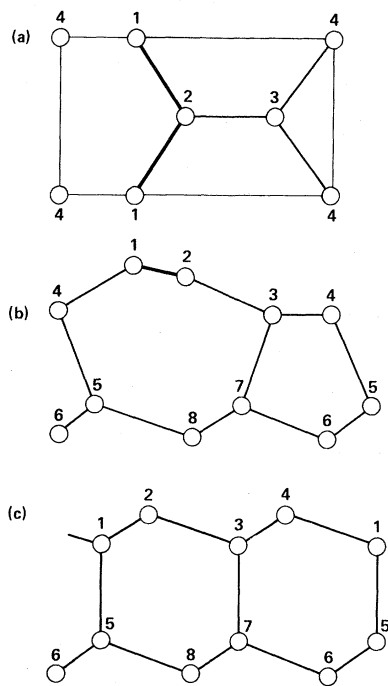


FIG. 2. Top and side views of the π -bonded chain structure are shown in (a) and (b), respectively. The side view of the ideal (1×1) surface is shown in (c). The numbering on the atoms is to facilitate a comparison of the atomic positions in the ideal and reconstructed structures.

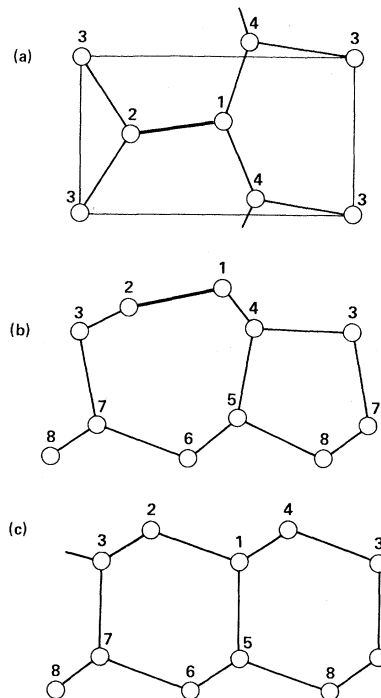


FIG. 3. Top and side views of the π -bonded molecular structure proposed in this paper are shown in (a) and (b), respectively. The side view of the ideal (1×1) surface is shown in (c). Atoms 5-8 and all substrate atoms (not shown) have nearly the same positions as in Fig. 2. The only change from Fig. 2(c) to Fig. 3(c) is the interchange of surface atoms 2 and 4. The two reconstructions involve primarily the first double layer of atoms at the surface.

and sevenfold rings at the boundary which (unlike the case of the surface) result in the elimination of all dangling bonds.

The surface electronic structure for the new model is dominated by the strongly correlated π -bond between nearest-neighbor dangling-bond electrons and by the large separation between surface atoms in adjacent unit cells. The nearly zero dispersion of the surface band for this model is a result of the small second-neighbor hopping matrix elements. Photoemission from the dispersive state for the case of normal emission is a particular interest because of polarization selection rules. The two possible final states for the remaining electron on the molecule have symmetric $(\phi_1 + \phi_2)/\sqrt{2}$ and antisymmetric $(\phi_1 - \phi_2)/\sqrt{2}$ character where ϕ_1 and ϕ_2 are the two dangling-bond orbitals of the molecule. The energy difference between these two states is about $2V \approx 1$ eV, where V is the nearest-neighbor hopping matrix element. Normal emission leading to the symmetric case is allowed only for p -polarized light (i.e., electric field vector normal to the surface). The antisymmetric state can be excited only s -polarized light with the electric field vector pointing along the molecular axis. Photoemission measurements^{4,11} show that emission at Γ from the flat band at 0.7 eV below the valence-band maximum occurs only for p -polarized light. States corresponding to the excitation of the antisymmetric final state are apparently not seen in the experiments. For the chain model the character of the wave function at Γ indicates that the matrix elements should be nonzero for both s - and p -polarized light. The different sensitivities of the dispersive and flat bands to hydrogen chemisorption⁴ would indicate, within the context of the proposed models for the surface structure, a larger sticking coefficient on molecular sites than on chain sites.

The question of the relative stabilities of the π -bonded chain and molecular structures in an important one. A calculation of the energies using the self-consistent pseudopotential approach is in progress.¹² The similarities in bond-angle and bond-length distributions for the two models suggest that the difference in total energies is determined primarily by the differences in surface dangle-bond energies. In the following the results of simple calculations employing the Hubbard model for the dangling-bond electrons are discussed.

For the chain model self-consistent unrestricted Hartree-Fock calculations¹² give a nonmagnetic ground state with a small charge transfer between surface atoms. The energy-band dispersion is approximated well by

$$E(k) = \text{const} - [\epsilon_0^2 + (2V \cos \pi k)^2]^{1/2}, \quad (1)$$

where k is the projection of the wave vector along the Γ - J direction of the Brillouin zone [with J given by $k = 0.5$ in Eq. (1)], V is the nearest-neighbor hopping

matrix element between dangling bonds, and $\pm\epsilon_0$ are the dangling-bond self-energies in the unit cell. The total energy per unit cell is given, to a good approximation, by

$$E_{\text{chain}} = U/2 - 8V/\pi, \quad (2)$$

where U is the intraatomic repulsive Coulomb energy for placing two electrons on the same site. The term involving V in Eq. (2) comes from averaging $E(k)$ over the Brillouin zone and neglecting terms of order $\epsilon_0^2/2V$. The value of ϵ_0 determines the optical gap; a value of $\epsilon_0 \approx 0.22$ eV gives a gap of ≈ 0.45 eV in agreement with the experimental results of Chiaradia *et al.*¹³ The measured⁵ and calculated³ bandwidths of close to 1 eV for the chain structure indicate a π -bonding interaction V of nearly 0.5 eV at the surface, nearly half the bulk value.¹⁴ The magnitude of the parameter U in the bulk obtained from theoretical¹⁵ and experimental^{16,17} work is in the range (0.25 ± 0.05) to (0.35 ± 0.1) eV. The lower screening at the surface is expected to increase U .

For the molecular structure the three singlet configurations with real-space basis functions

$$\begin{aligned} \psi_1 &= \phi_1(r_1)\phi_1(r_2), \quad \psi_2 = \phi_2(r_1)\phi_2(r_2), \\ \psi_3 &= [\phi_1(r_1)\phi_2(r_2) + \phi_2(r_1)\phi_1(r_2)]/\sqrt{2}, \end{aligned}$$

where ϕ_1 and ϕ_2 are the two dangling-bond orbitals in the unit cell, can be used to solve for the "exact" (i.e., non-Hartree-Fock) total energy. The energies for the ionic configurations ψ_1 and ψ_2 are higher than for the covalent configuration ψ_3 by the amount $U' = (U - E_M)$, where E_M is the screened nearest-neighbor Madelung energy. The energy of the molecular structure can be obtained from solving a 3×3 matrix. In the limit where the two dangling bonds are equal in energy ($\epsilon_0 = 0$) the total energy is given by

$$E_{\text{molecule}} = U'/2 - [U'^2/4 + 4V^2]^{1/2}, \quad (3)$$

which neglecting terms of order $U'^2/16V$ reduces to

$$E_{\text{molecule}} = U'/2 - 2V = (U - E_M)/2 - 2V. \quad (4)$$

Assuming that the V 's and U 's in Eqs. (2) and (3) are equal, the energy difference between the two structures is given by

$$\Delta E \equiv E_{\text{chain}} - E_{\text{molecule}} \approx E_M - 0.55V. \quad (5)$$

It is interesting that ΔE involves E_M but not U . This results from the similarity of the charge distributions on the surface atoms of the chain and molecular structures for the case $\epsilon_0 = 0$. The appearance of E_M in Eq. (5) reflects the importance of the two ionic configurations ψ_1 and ψ_2 for the molecular case. Assuming a surface dielectric constant of 6.5 (approximately half the bulk value) the screened Madelung energy E_M for pointlike charge distributions is about

0.94 eV. The actual value of E_M is probably somewhat lower. The above considerations suggest that the two different π -bonded structures should have comparable total energies.

The occurrence in different proportions of the two π -bonded geometries at the surface provides an explanation for the strong cleavage dependence of the experimental results. The expected nearly equal barrier heights for creating the two structures from the relaxed (1×1) surface implies that both geometries can be produced with equal ease during cleavage. Results from photoemission,^{4-6,8} surface photovoltage,⁹ and electron-diffraction⁹ measurements are consistent with this picture. The latter experiments⁹ reveal an "inhomogeneous" surface after cleavage with large local variations in properties which cannot all be correlated with steps. The surface becomes uniform [and remains (2×1)] after annealing to 500 K for 10 min. Changes in the surface state absorption spectrum and the I - V profiles of electron-diffraction spots are observed as a result of the anneal.

It is interesting to speculate whether the two different π -bonded structures occur on other Si(111) surfaces. On the laser-annealed surface, core-shift studies indicate the presence of four types of surface atoms.¹⁸ These probably correspond to the surface atoms in disordered chain and molecular structures. The (1×1) structure seen^{19,20} on the Ge(111) sur-

face cleaved at liquid-He temperatures may, on the other hand correspond to an ordered (1×1) lattice stabilized by spin-polarization effects.^{2,21-24} The π -bonded structures most probably also occur on the (7×7) surface.¹ The appreciable energy gain (≈ 1 eV) resulting from π -bonding on the (2×1) surface is largely dissipated in overcoming the large angular distortions that occur in the substrate. The (7×7) structure presumably takes much better advantage of the energy reduction resulting from π -bonding.

In summary, it is proposed that the cleavage dependence of the Si(111) surface properties is a result of the nonuniqueness of the surface atomic structure. Two distinct structures with chainlike and molecular atomic arrangements are suggested to occur at the surface. The observation in photoemission measurements of dispersive or dispersionless dangling-bond bands implies that surfaces consisting of predominantly one type of structure can be prepared.

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¹K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981); **49**, 223 (1982).

²J. E. Northrup, J. Ihm, and M. L. Cohen, Phys. Rev. Lett. **47**, 1910 (1981).

³J. E. Northrup and M. L. Cohen, J. Vac. Sci. Technol. **21**, 333 (1982); and (unpublished).

⁴F. J. Himpsel, P. Heimann, and D. E. Eastman, Phys. Rev. B **24**, 2003 (1981).

⁵R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, and S. A. Flodstrom, Phys. Rev. Lett. **48**, 1032 (1982).

⁶F. Houzay, G. M. Guichar, R. Pinchaux, G. Jezequel, and Y. Petroff (unpublished); and F. Solal *et al.* (unpublished).

⁷D. Haneman, Phys. Rev. **121**, 1093 (1961); D. J. Chadi, Phys. Rev. Lett. **41**, 1062 (1979).

⁸A. W. Parke, A. McKinley, and R. H. Williams, J. Phys. C **11**, L993 (1978).

⁹J. Assman and W. Mönch, Surf. Sci. **92**, 34 (1980).

¹⁰O. L. Krivanek, S. Isoda, and K. Kobayashi, Philos. Mag. **36**, 931 (1977).

¹¹F. Houzay, G. M. Guichar, R. Pinchaux, and Y. Petroff, J. Vac. Sci. Technol. **18**, 860 (1981).

¹²O. H. Nielsen, R. M. Martin, K. Kunc, and D. J. Chadi (unpublished).

¹³P. Chiaradia, G. Chiarotti, S. Nannarone, and P. Sassaroli,

Solid State Commun. **26**, 513 (1978); G. Chiarotti *et al.*, Phys. Rev. B **4**, 3398 (1971).

¹⁴D. J. Chadi and R. M. Martin, Solid State Commun. **19**, 643 (1976). The sign of V is taken to be positive in Eqs. (2)–(5) to avoid the use of absolute values. The reduction of the π interaction at the surface arises from the less than optimal orientation of the nearest-neighbor dangling bonds.

¹⁵G. A. Baraff, E. O. Kane, and M. Schluter, Phys. Rev. Lett. **43**, 956 (1979).

¹⁶H. Dersch, J. Stuke, and J. Beichler, Phys. Status Solidi (b) **105**, 265 (1981).

¹⁷W. B. Jackson, Solid State Commun. (in press).

¹⁸F. J. Himpsel, D. E. Eastman, P. Heimann, B. Reihl, C. W. White, and D. M. Zehner, Phys. Rev. B **24**, 1120 (1981).

¹⁹D. Haneman and R. Z. Bachrach (unpublished).

²⁰V. Yu. Aristov *et al.* (unpublished).

²¹R. Del Sole and D. J. Chadi, Phys. Rev. B **24**, 7431 (1981); D. J. Chadi and R. Del Sole, J. Vac. Sci. Technol. **21**, 319 (1982).

²²A. Redondo, W. A. Goddard, and T. C. McGill, J. Vac. Sci. Technol. **21**, 649, 328 (1982).

²³M. Lanoo and G. Allan, Surf. Sci. **115**, L137 (1982).

²⁴C. B. Duke and W. K. Ford, Surf. Sci. **111**, L165 (1981).