

The Si (100) surface—further studies of the pairing model

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The potential, charge density, spectrum, and surface density of states is calculated self-consistently for the pairing-model reconstruction of the Si 2×1 (100) surface. This calculation differs from our earlier study in two ways. First, the pair bond has been contracted by 0.13 Å, keeping the back bonds equal to the bulk bonds (2.35 Å) in length. This change allows us to study how the pair bond spectrum and charge density depend on bond length and to discuss the forces driving and opposing the bond tightening. Secondly, the matching plane (behind which the potential is equal to the bulk potential) has been moved two atomic planes further into the crystal. There is little effect on the charge density in the back region, which allows us to verify that the thinner surface region used in the earlier calculation was sufficiently thick. The present study further strengthens our conclusion that the (100) silicon surface reconstructs to the 2×1 form by pairing.

I. INTRODUCTION AND SUMMARY

This paper is an addendum to our recent study¹ of the 2×1 reconstruction of the Si (100) surface. In that paper, we described two of the models which have been proposed for the reconstructed form and carried out self-consistent calculations of the electronic potential, charge density, Fermi energy, and surface density of states for both. On the basis of arguments related to the internal consistency of the two models, on the basis of comparisons between the calculated and measured Fermi energy,² and on the basis of comparisons between the calculated and the measured occupied surface density of states,³ we concluded that one model, the pairing model,⁴ was a more probable description of reconstruction than was the other, the vacancy model.⁵

The pairing model we studied was the Levine⁶ elaboration of the Schlier-Farnsworth proposal. Levine suggested that pairs of surface atoms would move toward each other (maintaining a spacing of 2.35 Å from their nearest neighbors) until their distance from each other was also 2.35 Å, the bulk nearest-neighbor distance. In the present work, we report self-consistent calculations of the pairing model in which the two atoms on the surface are brought even closer together, to a separation of 2.22 Å. This allows us to study the effect of changes in the pair bond length in much the same spirit as we earlier studied the effect of changes in the normal coordinate of the outer layer of atoms.⁷

We choose to shorten rather than expand the pair bond for the following reasons: Our calculations¹ had shown that there is charge in π bonding states which gives the pair bond more strength than a single bond. Bond lengths usually shorten when this occurs.⁸ Moreover, the band structure we

had calculated¹ for the gap surface states predicted two bands of states whose separation, roughly constant and equal to 0.5 eV throughout the surface Brillouin zone, was insufficient to remove their overlap in energy, resulting in a metallic surface band structure. A metallic surface band structure we believed to be energetically unsatisfactory, and we anticipated that shortening the dimer bond would reduce if not entirely remove the metallic occupancy of the surface-state bands.

The shortening chosen goes about halfway towards what one would estimate for the length of a double bond.⁹ There are bond-bending forces which oppose the creation and tightening of the pair bond. It is therefore certain that the pair bond will not be as tight as a full double bond. Hence, shortening of the bond by 0.13 Å is a physically reasonable estimate. Unfortunately, we cannot compute the total energy with sufficient accuracy to predict the equilibrium pair bond length *a priori*.

It turns out that this shortening does considerably reduce, but does not remove the overlap in energy. The band structure we find, like the one we calculated earlier, is metallic and potentially unstable with respect to charge-density-wave^{10,11} formation.

There is a second feature of this calculation which differs from what we had presented earlier, namely, the position of the matching plane. As has been explained elsewhere,^{1,12} the matching plane plays two roles in these calculations. One role is to define the region over which the local density of states is integrated to produce what we called the "surface density of states," a quantity which is compared to the density of states as measured in photoemission. For this purpose, the optimum position of the matching plane is towards the rear of that volume of the solid from which photoelectrons can reach the surface. The other

role of the matching plane is to define a surface interior to which the potential is the same as the bulk potential. Operationally, this sets the limits over which the Schrödinger equation must be integrated for each new surface potential. For this purpose, the optimum position of the matching plane is as close to the surface as possible so as to minimize computational effort.

The calculations presented here have been carried out with the matching plane located midway between the fourth and fifth planes of atoms, two layers further from the vacuum than we used earlier. By comparing with our earlier calculation we have verified that there was no significant error caused by the earlier choice of matching-plane position.

After moving the matching plane, the new region included in the "surface-density-of-states" integration contains more undisturbed bulk region. Although our results do not differ dramatically from what we had found earlier, the slight changes in the spectrum associated with tightening the bridge and more importantly, the change in the depth of the surface region, do improve the fit between the calculated photoemission spectrum and the measured one. This strengthens our earlier conclusion about the essential validity of the pairing reconstruction.

II. RESULTS AND DISCUSSION

Let us now compare in detail the results of the new calculations in which the surface pair bond has a length of 2.22 Å, with the earlier calculations in which the length of the pair bond is 2.35 Å. Figure 1 consists of two contour plots, one for each calculation, of the charge density on a plane normal to the surface, passing through the two atoms involved in the surface pair bond. Locations of atoms in this plane are indicated by dots in Figs. 1(a) and 1(b). The matching plane in the tighter bridge calculation lies along the bottom edge of Fig. 1. In the looser bridge, its position is marked by the symbol MP at the side margins of Fig. 1.

The most pronounced difference in charge density occurs in the center of the pair bond. At this position, the potential is more attractive than it was before the bond was tightened and one expects the charge density to rise in this region. That rise is clearly seen in Fig. 1. The total charge in the bonding region also rises. A numerical integration of the charge between the atoms indicates that, interior to the contour marked 50, the tighter bond contains about 33% more charge. A more detailed comparison of the two contour plots shows that the extra charge has been drawn from

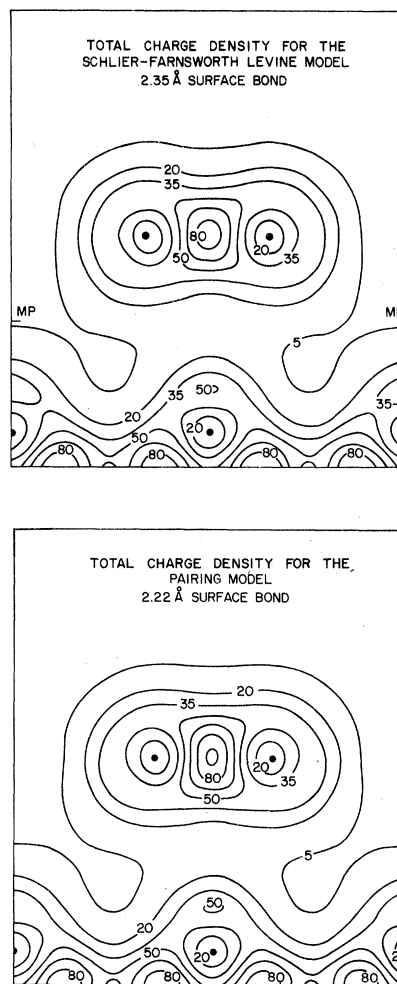


FIG. 1. Charge-density contours on a plane normal to the surface passing through the paired surface atoms and fourth-layer atoms (shown by dots). Second and third layer atoms lie out of this plane. Density is in 10^{-3} a.u. (a) Pair-bond length 2.35 Å, matching plane (MP) between atom layers 2 and 3. (b) Pair-bond length 2.22 Å, matching plane between atom layers 4 and 5.

the upper outer regions of the bond, roughly along the rays where, on a ball and stick model, the broken bonds would be located. This transfer of charge from regions of higher potential (towards the vacuum) to regions of more attractive potential (in the bond) is, as was explained in Refs. 1 and 13, the mechanism favoring the formation and tightening of the bond.

Note the similarity of charge density in the lower regions of Figs. 1(a) and 1(b). In Fig. 1(a), this lower region is behind the matching plane and thus the potential in the region is the self-consistent potential of the bulk. In Fig. 1(b), this same lower

TABLE I. Surface-state energies.

	Γ	J	K	J'
Upper state	0.63	0.83	-0.01	-0.17
Lower state	0.10	0.16	-0.46	-0.55
Bond length 2.35 Å		$E_F = 0.04$ eV		
	Γ	J	K	J'
Upper state	0.89	1.09	0.31	0.14
Lower state	0.19	0.30	-0.32	-0.41
Bond length 2.22 Å		$E_F = 0.13$ eV		

region is above the matching plane, and thus the potential in the region is one that was allowed to respond self-consistently to the surface. The similarity of the charge density in the lower regions of the two calculations provides evidence that the potentials were also the same there. It confirms that only a negligible error was introduced by having the matching plane in the higher position.

The second item to be compared is the spectrum of gap surface states. Table I gives the energy in eV, relative to the top of the valence band, of the two gap surface states at the four symmetry points of the surface Brillouin zone. It also gives the Fermi energy required to populate these bands with exactly two electrons. This gap surface state spectrum was used to calculate the surface state contribution to the g -dependent surface polarizability in our discussion of secondary reconstruction on the Si (100) surface.¹¹ We believe that this reconstruction, rather than a further tightening of the bond, acts to produce the gap in surface-state density at the Fermi energy.

Tightening the bridge does increase the splitting between the bands. It does so by causing the upper band to rise in energy roughly three times as much as the lower band, not by sending the lower band down and the upper band up. The charge density of the states involved is shown in Figs. 11 and 12 of Ref. 1. From those figures, one can see that neither state is able to benefit much from the lowered potential in the surface pair bond region although the lower energy state (Fig. 11, Ref. 1) is able to lower its potential energy slightly more than is the other. This is one factor that adds to the splitting. Kinetic energy increases associated with the reduced spatial region for the states will move states upward; they will move a state with more nodes (e.g., the higher-energy antibonding state of Fig. 12, Ref. 1) more than one with fewer nodes. This too increases the splitting. The increase in Fermi energy of 0.09 eV on tightening the bridge comes about because both states have

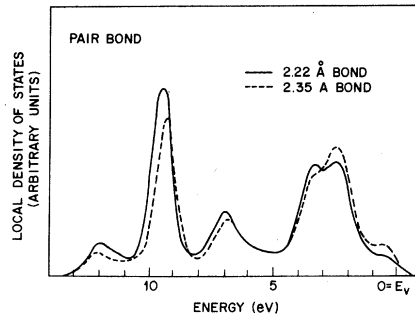


FIG. 2. Local density of states evaluated at the center of the pair bond.

moved upward in energy. The Fermi level positions for both geometries are consistent with the experimentally determined position within the experimental uncertainty.²

In Fig. 2, we consider the local density of states

$$\rho(r, E) = \sum_n |\psi_n(r)|^2 \sigma(E_n - E),$$

evaluated at the center of the pair bond, a point at which the total potential acting on an electron has dropped by 2.7 eV in tightening the bridge. The spectrum calculated for the tighter bridge has some of its weight shifted towards lower energies compared to that calculated for the looser bridge. Increased amplitude in the peak at -9.7 eV and decreased amplitude in the peaks near -3.5 eV are caused by tightening the bridge. The surface states which are well concentrated in the pair bond region, such as that shown in Fig. 10 of Ref. 1, drop in energy, but do so by only no more than 0.15 eV, approximately 5% of the maximum potential energy change. This reflects the fact that surface states are closely tied to the bulk band structure, and not free to move as one might expect from first-order perturbation theory. The wave functions do respond by changing their shape, however. The increase in weight in the -9.7-eV peak, associated with primarily s -like pair-bond states, occurs because even a small shift in a surface state further below the band minimum from which it is split can have a significant effect in reducing the range of its exponentially decaying tail of evanescent Bloch waves, thereby shifting more weight into the pair bond. The states in the -3.5-eV peak, being primarily p -like, undergo a greater increase in kinetic energy on tightening of the bridge, which apparently more than compensates for the change in potential, and moves these states in such a manner that they have longer tails, and thus less weight in the surface region.

In Fig. 3, we consider the local density of states evaluated at the center of a back bond joining a

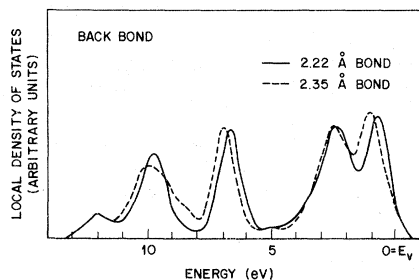


FIG. 3. Local density of states evaluated at the center of a back bond.

surface atom to one of its two nearest neighbors in the bulk. Tightening the surface pair bond raises the energy of each of the peaks in the local density of states, raising the local single-particle energies. This is an important contribution to the bond-bending forces which act to increase the energy of the system as the back bond angle, already some 16° less than the ideal 109° , is reduced still further.

Figure 4 shows the integrated density of states for the earlier calculation, the measured photoemission spectrum, and the integrated density of states calculated for the tighter bridge, all three aligned by equating their Fermi energy. The main difference between the two theoretical curves is that in the lower curve (tighter bridge and deeper matching plane) the peak near -1.0 eV is suppressed relative to its size in the top curve. This peak arises from the lower energy gap surface state, which is a state well localized in front of the matching plane so that its total contribution to both curves is substantially the same. Its relative contribution in the lower trace is reduced, however, because, with more bulklike region included, there are more electrons contributing to that curve. The other peaks are somewhat shifted in energy either because of their inherent shift relative to the bulk band structure (down for pair bonds, up for back bonds) or because of the shift in Fermi energy along which the curves are aligned. The fit between the experimental photoemission data and both of the two theoretical curves is reasonable but is somewhat better with the lower one. As we have pointed out previously, the suppression of the photoemission from the *s*-band region (below -8 eV) is common to all surfaces and is a matrix-element effect.

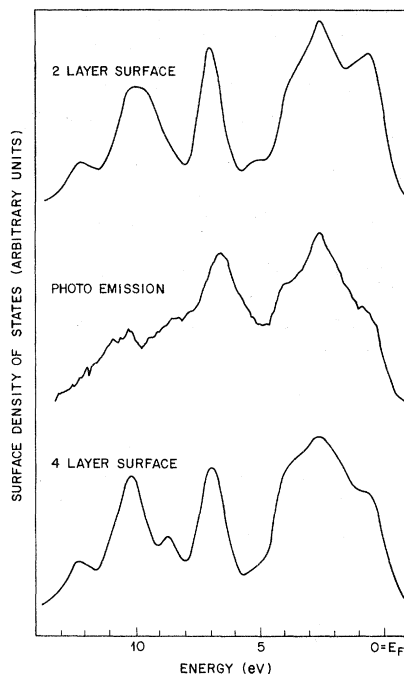


FIG. 4. Calculated surface-region density of states compared to $\hbar\omega = 21.1$ -eV photoelectron energy distribution from Ref. 3 with estimated secondaries subtracted.

III. CONCLUSIONS

We have found that the spectrum of the dimerized surface changes little with dimer bond length, compared to the changes we found between the dimer and vacancy models studied previously by us.

The somewhat improved agreement we obtain between the surface-region density of states and the photoemission spectrum is believed due primarily to the inclusion of more bulklike layers in the volume over which this quantity is integrated in the present calculation. These yield a better approximation to the escape-depth weighting of bulk and surface contributions. The actual changes in the spectrum are not sufficient to let us decide upon the bond length on the basis of this comparison. This relative spectral insensitivity also applied to the region of the Fermi surface. For both geometries, metallic Fermi surfaces were found that exhibited a strong tendency toward charge-density-wave formation. This insensitivity we take as additional evidence favoring a charge density wave instability as the explanation for the secondary reconstruction seen on Si(100).¹⁴

- ¹Joel A. Appelbaum, G. A. Baraff, and D. R. Hamann, Phys. Rev. Lett. 35, 729 (1976); and Phys. Rev. B 14, 588 (1976).
- ²J. E. Rowe, Phys. Lett. A 46, 400 (1974).
- ³J. E. Rowe and H. Ibach, Phys. Rev. Lett. 32, 421 (1974).
- ⁴R. E. Schlier and H. E. Farnsworth, J. Chem. Phys. 30, 917 (1959).
- ⁵J. C. Phillips, Surf. Sci. 40, 459 (1973).
- ⁶J. Levine, Surf. Sci. 34, 90 (1973).
- ⁷Joel A. Appelbaum, G. A. Baraff, and D. R. Hamann, Phys. Rev. B 12, 5749 (1975).
- ⁸See, for example, J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973), p. 20.
- ⁹L. Pauling, *The Nature of the Chemical Bond* (Cornell U. P., Ithaca, N.Y., 1960), Sec. 7.6.
- ¹⁰E. Tosatti and P. W. Anderson, Solid State Commun. 14, 773 (1974).
- ¹¹Joel A. Appelbaum, G. A. Baraff, and D. R. Hamann, Phys. Rev. Lett. 36, 450 (1976).
- ¹²Joel A. Appelbaum and D. R. Hamann, Phys. Rev. B 6, 2166 (1972).
- ¹³Joel A. Appelbaum, G. A. Baraff, and D. R. Hamann, Phys. Rev. B 11, 3822 (1975).
- ¹⁴M. B. Webb (private communication).