

## Self-Consistent Pseudopotential Calculations on Si(111) Unreconstructed and $(2 \times 1)$ Reconstructed Surfaces\*

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(Received 3 February 1975)

A recently developed method for the self-consistent calculation of localized configurations has been applied to the Si(111) surface. Results have been obtained for unreconstructed, relaxed, and  $(2 \times 1)$  reconstructed (buckled) surfaces. Densities of states and charge densities are presented and discussed. The salient experimental findings are reproduced.

In this Letter we report self-consistent pseudopotential calculations on Si(111) surfaces. Three different surface models have been studied and the resulting calculated density-of-states curves and electronic-charge-density distributions have been examined to extract the essential physical features of the various models. In each case the calculations were carried to self-consistency following a recently developed procedure<sup>1</sup> which is based on the pseudopotential scheme.

The three different models for the Si(111) surface studied are as follows:

(a) An unreconstructed, unreconstructed surface, in which all surface atoms remain at their exact "bulk" positions.

(b) A relaxed surface, in which the outermost atomic layer is rigidly relaxed inwards by an amount  $\Delta = 0.33 \text{ \AA}$ . These two models have been studied by Appelbaum and Hamann<sup>2</sup> in the only previously existing self-consistent<sup>2</sup> approach to the problem, and their results are basically confirmed by our calculations. In addition we find new types of surface states and are able to present density-of-states curves.

(c) A  $(2 \times 1)$  reconstructed surface, in which atoms of the outermost atomic layer are alternatively moved inward and outward to form a  $(2 \times 1)$  planar unit cell. This model has been refined in a second step as first proposed by Hane-man<sup>3</sup> by moving atoms of the second atomic layer slightly laterally, the effect of which was small compared to the effect of the "buckling" at the first step. The predominant result of this  $(2 \times 1)$  reconstruction is the splitting of the "dangling-bond" surface state in the gap into *two* peaks corresponding to *two* separate surface bands one of which is occupied. This essential feature is in good agreement with experiments<sup>4-6</sup> and is not obtained in the other two models.

The method used to obtain the electronic sur-

face structure in a self-consistent fashion has been discussed in detail in our recent  $\text{Si}_2$ -molecule calculation,<sup>1</sup> and therefore we only review the essential features in this paper. The local configuration in the present case is a twelve-layer slab of Si, simulating two *noninteracting* surfaces. The slab is placed in a periodic lattice sufficiently spaced to prevent interaction between the different slabs (or surfaces). This artifact has the enormous advantages that the system can now in principle be treated as any periodic crystal and that the pseudopotential method in its standard form can be applied. A self-consistent treatment, however, is necessary to achieve the correct screening of the atoms in the neighborhood ( $\sim 3-4$  atomic layers) of the surfaces.

As for the molecule case<sup>1</sup> the calculations are initiated with an empirical pseudopotential carried over from crystalline calculations. From the resulting total charge density, screening and exchange potentials are derived and added to an atomic  $\text{Si}^{+4}$ -ion potential.<sup>7</sup> New screening and exchange potentials are derived and the process is repeated until self-consistency (stability of the eigenvalues or stability of the input versus output potentials within 0.1 eV) is reached. Plane waves with a maximum reciprocal-lattice vector corresponding to an energy of 2.7 Ry were used in the basis set. This corresponds to about 180 plane waves for the twelve-layer  $(1 \times 1)$  structure. Another 340 plane waves up to an energy cutoff of 6 Ry were included by second-order perturbation theory. The potential was cut off at 3 inverse Bohr radii.

Density-of-states curves for the self-consistent results for the three surface models are presented in Fig. 1. Since these curves represent the total density of states for a twelve-layer slab, their overall features strongly resemble those of the Si bulk density of states. To locate

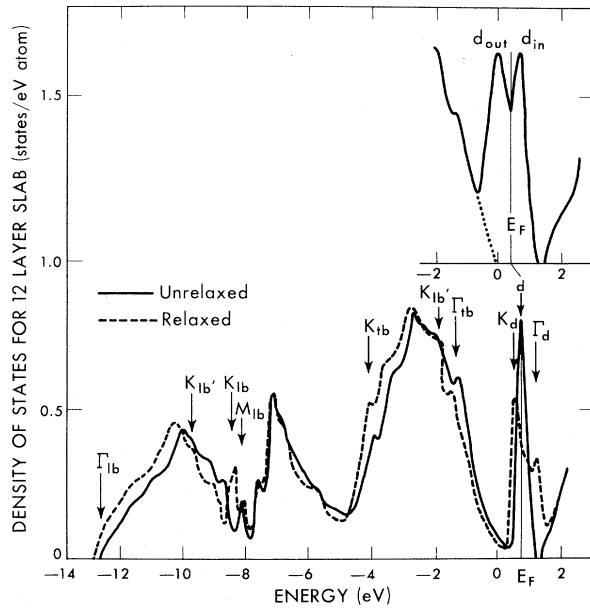


FIG. 1. Calculated density of states for a twelve-layer Si(111) slab. The results for the unrelaxed (full line) and relaxed surfaces are superimposed. The labeling of the various surface states refers to their locations in  $\vec{k}$  space and to the type of bond (transverse or longitudinal). Inset, result of a six-layer-slab calculation of the density of states for the dangling bond of the  $(2 \times 1)$  reconstructed surface.

structures associated with surface states (no distinction is made in the present case between bona-fide surface states and strong surface resonances) we investigated the charge-density distributions for small energy intervals scanning

the entire width of the valence bands.

The locations of some of the very apparent surface states (for the *relaxed* case) are indicated by arrows in Fig. 1. Their energies are compared in Table I with experimental data obtained from ultraviolet-photoemission-spectroscopy measurements<sup>4</sup> and with previous calculations<sup>2,8</sup> on Si(111) surfaces.

In particular we investigated the points  $\Gamma$  (center) and  $K$  (corner) of the two-dimensional hexagonal Brillouin zone.

Let us first discuss the results at  $\Gamma$ . Below the energy zero which was chosen to coincide with the bulk valence-band edge  $E_V$  we find (in agreement with Appelbaum and Hamann<sup>2</sup> and Pandey and Phillips<sup>8</sup>) three surface states. Two of them are degenerate and close to  $E_V$ , representing the transverse back bonds with charge localized between the first and second atomic layers. The third state is localized at the bottom of the valence bands and is predominantly  $s$ -like around the outermost atoms. With the dangling-bond state above  $E_V$ , which we shall discuss later, there are four surface states at  $\Gamma$ , which agrees with the classical tight-binding concept.<sup>8</sup> The situation, however, is different at  $K$ . We find only one "pure" transverse back bond  $K_{lb}$ , the remaining states  $K_{lb'}$  and  $K_{lb}$ , having more longitudinal or  $s$ -like character. The interesting feature is that some states  $K_{lb'}$  (at  $-2.0$  and  $-9.7$  eV) have most of their charge localized between the *second* and *third* layers in contrast to the state  $K_{lb}$  (at  $-8.5$  eV) which is a mixture of

TABLE I. Calculated energies of several surface states of the relaxed surface at  $\Gamma$  (center) and  $K$  (corner) of the two-dimensional Brillouin zone. Also indicated are experimental (ultraviolet photoemission spectroscopy) results for  $(2 \times 1)$  and  $(7 \times 7)$  reconstructed surfaces. The energy zero is taken at the bulk valence-band edge  $E_V$ .

	Present relaxed	AH <sup>a</sup>	PP <sup>b</sup>	Experiment	
				$(2 \times 1)$	$(7 \times 7)$
$\Gamma$	+1.2	+0.88	+1.04	...	...
	-1.4(2x)	-1.95(2x)	-1.71(2x)	...	-1.5 <sup>c</sup>
	-12.6	-12.87	-12.90	-11.7 <sup>c</sup>	-12.3 <sup>c</sup>
$K$	+0.5		+0.11	-0.5 <sup>c</sup>	+0.1 <sup>c</sup>
	[0 for $(2 \times 1)$ reconstructed]			-0.45 <sup>d</sup>	
	-2.0		...	-0.6 <sup>e</sup>	
	-4.2		-5.65		-3.6 <sup>c</sup>
	-8.5		-8.35		...
	-9.7		-9.60		-7.5 <sup>c</sup>

<sup>a</sup> Ref. 2.

<sup>b</sup> Ref. 8.

<sup>c</sup> Ref. 6.

<sup>d</sup> Ref. 4.

<sup>e</sup> Ref. 5.

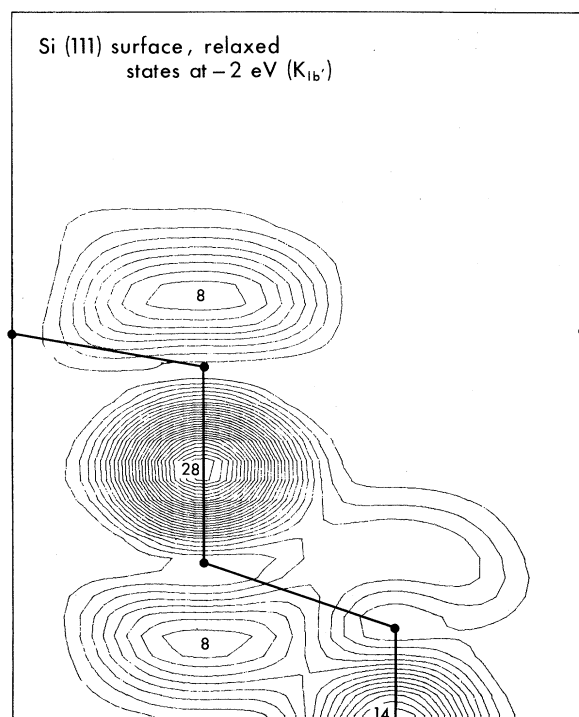


FIG. 2. Charge-density contours, in a (110) plane cutting the relaxed (111) surface, of the longitudinal back-bond state  $K_{1b}'$ .

*s*-like and *p*-like states at the outermost atoms giving rise to a charge distribution between the *first* and *second* layers. In Fig. 2 we show a contour map of the charge of the state  $K_{1b}'$  at  $-2.0$  eV. We would like to stress the fact that surface states apparently can "penetrate" into the second longitudinal bond, which puts some limitation on the position of a "matching plane"<sup>2</sup> separating the surface region from the bulk. The appearance of surface states at  $K$  in the second longitudinal bond increases the number of surface states from four to five, which has been predicted by model calculations<sup>9</sup> but which is in contrast to the findings of Pandey and Phillips.<sup>8</sup> At the point  $M$  the situation is expected to be similar but less pronounced, with some of the surface states merging into the bulk continuum.<sup>9</sup>

Let us now examine the surface states in the energy gap above  $E_V$ . As shown in Fig. 1 we find for the unrelaxed, unreconstructed surface *one* very flat surface band at about mid gap. This almost dispersionless band is half-occupied, placing the Fermi level right at the peak. The charge distribution of these (either occupied or empty) mid-gap surface states is very much dan-

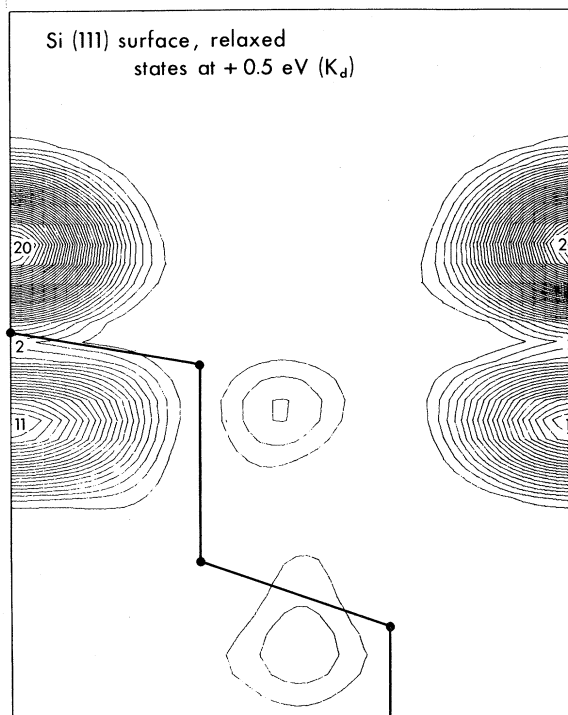


FIG. 3. Charge-density contours of the occupied part  $K_d$  of the dangling-bond states for the relaxed-surface model.

gling-bond-like, exhibiting a pronounced *p*-like charge centered at the outermost atoms. When the last atomic layer is relaxed inward, the back bonds get stronger, resulting in a mixing of the dangling-bond states with lower-lying back-bond states. This increases the interaction between the individual dangling bonds via the second atomic layer and the dispersion of the surface band increases. In fact, the resulting density of states exhibits the asymmetric shape of critical points expected for a planar triangular network of *s*- or  $\pi$ -like orbitals. The critical points are labeled  $K_d$  and  $\Gamma_d$  in Fig. 1, indicating their origin in  $\vec{k}$  space. A charge-density plot for the states  $K_d$  is shown in Fig. 3. It exhibits the very pronounced dangling-bond character. The unoccupied states  $\Gamma_d$  show a stronger mixing with back bonds. As for the unrelaxed case there is only *one* surface band which is half-occupied. This changes qualitatively when we consider the  $(2 \times 1)$  reconstructed surface. Enlarging the real-space unit cell in one dimension corresponds to folding back the Brillouin zone in certain directions. Thus *two* surface bands will appear separated by a gap resulting from the potential per-

turbation of the reconstruction. If this gap is smaller or comparable to the dispersion of the surface bands it might not lead to a vanishing density of states between the bands. This situation is found for the self-consistent result of a  $(2 \times 1)$  buckled surface (see Fig. 1) with atomic displacements of  $\Delta_{\text{in}} = 0.11 \text{ \AA}$  and  $\Delta_{\text{out}} = 0.18 \text{ \AA}$  as suggested by Haneman.<sup>3</sup> The two peaks in the density of states now correspond to *two* separate bands,<sup>10</sup> thus allowing, e.g., for an infrared surface absorption as observed by Chiarotti *et al.*<sup>11</sup> The states of the two peaks in Fig. 1 show very interesting real-space behavior. Electrons in states originating from the lower peak labeled  $d_{\text{out}}$  predominantly sit on those atoms which have been moved outward (with a charge distribution resembling the one given in Fig. 3) and avoid the atoms which have been moved inward. Conversely the wave functions for unoccupied states of the peak labeled  $d_{\text{in}}$  are mostly concentrated around those atoms which have been moved inward. The surface thus exhibits a  $(2 \times 1)$  pattern of twofold occupied dangling-bond states. Roughly speaking, the unpaired electron of every second surface atom (in) is transferred to its neighboring atom (out) where it pairs up with another electron.

In addition to the appearance of two split surface bands we observe an overall shift towards lower energies placing the occupied surface state at about  $E_V$ . This trend is compatible with all available experiments<sup>4</sup> which give a surface state at about 0.5 eV below  $E_V$ .

Our self-consistent calculations on the  $(2 \times 1)$  reconstructed-surface model<sup>11</sup> thus give results which for the first time agree with the salient features of the experimental findings, i.e., split surface states, possibility of infrared absorption, and lowering of the occupied surface band below  $E_V$ .

The authors would like to thank Dr. F. Yndurain, Professor L. Falicov, and Professor D. Ha-

neman for stimulating discussions. Part of this work was done under the auspices of the U. S. Energy Research and Development Administration.

*Note added.*—We have recently extended the  $(2 \times 1)$  reconstructed calculation to twelve layers. A gap opens at the Fermi energy. Also a detailed analysis of the back-bond states shows that these states are likely to be responsible for the angular photoemission spectrum seen by J. E. Rowe, M. Traum, and N. V. Smith [Phys. Rev. Lett. **33**, 1333 (1973)]. J. A. Appelbaum and D. R. Hamann (to be published) have also made a similar correspondence using studies based on stretched back bonds.

\*Work supported in part by the National Science Foundation under Grant No. DMR72-03206-A02.

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<sup>1</sup>M. L. Cohen, M. Schlüter, J. R. Chelikowsky, and S. G. Louie, to be published.

<sup>2</sup>J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. **31**, 106 (1973), and **32**, 1433 (1974). A self-consistent calculation for Li using methods similar to those used here was done by G. P. Alldredge and L. Kleinman, Phys. Rev. B **10**, 559 (1974).

<sup>3</sup>A. Taloni and D. Haneman, Surface Sci. **10**, 215 (1968); D. Haneman, Phys. Rev. **170**, 705 (1968).

<sup>4</sup>D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. **28**, 1378 (1972).

<sup>5</sup>L. F. Wagner and W. E. Spicer, Phys. Rev. Lett. **28**, 1381 (1972).

<sup>6</sup>J. E. Rowe and H. Ibach, Phys. Rev. Lett. **32**, 421 (1974).

<sup>7</sup>I. V. Abarenkov and V. Heine, Phil. Mag. **12**, 529 (1965).

<sup>8</sup>K. C. Pandey and J. C. Phillips, Phys. Rev. Lett. **32**, 1433 (1974).

<sup>9</sup>F. Yndurain and L. M. Falicov, to be published.

<sup>10</sup>G. P. Betteridge and V. Heine, Surface Sci. **43**, 417 (1974).

<sup>11</sup>G. Chiarotti, S. Nannarone, R. Pastore, and P. Chiaradia, Phys. Rev. B **4**, 3398 (1971).