PHYSICAL REVIEW B VOLUME 41, NUMBER 8 15 MARCH 1990-I

Atomic structure of the Si(001)-(2 × 1) surface

Inder P. Batra
IBM Research Division, Almaden Research Center (K35/801), 650 Harry Road, San Jose, California 95120-6099

(Received 2 August 1989; revised manuscript received 9 November 1989)

We have performed an extensive set of first-principles self-consistent-field (SCF) pseudopotential total-energy and force calculations for Si(001)-(2×2) and -(2×1) surfaces to arrive at an optimized model for the 2×1 surface. We started with the symmetric dimer model proposed by Abraham and Batra (AB) based on the Stillinger-Weber potential as well as the Yin-Cohen (YC) asymmetric dimer model to carry out the optimization procedure. We confirm the short dimer bond length obtained by YC, unlike in the AB model. However, a symmetric dimer model with a substantial (0.45 Å) inward relaxation of the top layer is found to be lower in energy than the AB model and is highly competitive with a slightly modified YC model. This supports the use of the symmetric model by Pandey in the construction of the extended defect model and also in the recent spin-unrestricted model calculations. From the 2×2 cell calculations we conclude that in the small-buckling limit, some energy gain is possible, provided that the dimers are tilted in opposite directions. We also establish that there is no barrier associated with the surface dimer formation but twisting of the dimers is energetically unfavorable. A detailed account of the Hellmann-Feynman forces is given for various structures.

I. INTRODUCTION

There is currently a great deal of interest[1] in understanding the growth of metals like Ga on Si(001). The driving force behind this is the potential for optoelectronic devices based on GaAs/Si(001) epitaxy.[2] An essential prerequisite for a proper understanding of the growth[3] of materials on Si(001) is the correct atomic information about the substrate itself. Only when the atomic structure of the substrate is firmly known can one speak about its modification upon adsorption of foreign species. For example, it is believed[4] that upon adsorption of some metals, the surface reconstruction is lifted and the metal symmetric dimers appear in the overlayer. However, it still remains an open question as to whether the Si dimers of the 2×1 reconstructed Si(001) substrate itself are symmetric or asymmetric. A large number of studies have been devoted to the 2×1 Si(001) surface and have been reviewed[5] in several articles.

It is by now generally accepted that the Si atoms on the (001) surface dimerize along the [110] direction, thereby doubling the repeat length along this direction. The pairing of atoms reduces the number of dangling bonds and hence the system achieves a lower-energy configuration. Starting with this basic dimerization notion, many detailed models have been obtained by improving the theoretical comparison with the low-energy electron diffraction (LEED),[6–10] photoemission,[11–13] ion scattering,[14] by doing empirical modeling,[15] and total-energy minimization,[16–19] as well as electronic-structure calculations using cluster models.[20–22] Although a (2×1) reconstruction is the strongest feature in most LEED studies,[6–10] higher-order periodicities have also been considered.[23–26] However, in the present work we shall mainly focus on the (2×1) reconstruction and give a detailed structural model by fully optimizing the atomic coordinates of the top four layers of Si(001).

As mentioned above, one of the nagging issues for the 2×1 reconstruction model of Si(001) has been the actual configuration of the surface dimers. In an early pioneering total-energy calculation by Yin and Cohen[19] (YC), the dimers were found to be asymmetric as well as buckled. These models contained a nice feature, namely they produced a surface with semiconducting properties in agreement with the experimental findings.[27] Within the one-electron picture, the validity of the highly buckled dimer model for Si(001)-(2×1) was questioned in a conference presentation paper by Pandey[25] in 1984. He went on to propose[25] a π-bonded defect model based on symmetric dimers to explain various observed periodicities. Shortly thereafter, Abraham and Batra[28] (AB) presented the results of their molecular-dynamic computer simulations using Stillinger-Weber[29] empirical Si-Si potential. This potential led to a symmetric dimer reconstruction with some areas of the surface which were devoid of dimers altogether. Recent scanning tunneling microscopy[30] (STM) experiments have revealed symmetric dimers at least in the regions away from the extended defects.

One main objection against the symmetric dimer model has been that within the one-electron picture it leads to a metallic surface. This is in disagreement with the experimental data.[27] A way out of this difficulty has been proposed by invoking the spin degree of freedom in the cluster-model calculations.[22,31] In 1982, Redondo and Goddard[22] found a correlated singlet of the symmetric dimer configuration to be the ground state of the system. More recently, Artacho and Yndurain[31] found that an antiferromagnetic spin arrangement within the symmetric-dimer-model arrangement lowers the total energy and opens up a gap in the surface-state bands. It therefore becomes essential to reevaluate the atomic structure of the Si(001)-(2×1) surface.

In what follows, we present optimized structural models based on total-energy and force calculations. We establish that there is no barrier associated with the surface dimer formation. There may be some barrier to buckling but the depths of local minima for a highly buckled asymmetric model and symmetric model are shown to be comparable. The electron and hole Fermi surfaces for our optimized symmetric dimer model are also sketched. The calculations are based on a state-of-the-art self-consistent-field pseudopotential method.[32,33] These calculations are spin restricted in nature. However, for a nonmagnetic material such as Si one does not expect[34] bond lengths to depend much on the spin polarization. We also give an account of Hellmann-Feynman forces as utilized here in reaching the optimized configurations. We hope that the detailed atomic coordinates presented here shall be useful to those carrying out adsorption and growth studies on Si.

II. METHODOLOGY AND COMPUTATIONAL DETAILS

We performed SCF pseudopotential calculations[32,33] within the framework of the Hohenberg-Kohn-Sham local-density-functional theory applied in momentum space.[35] We used nonlocal, norm-conserving ionic pseudopotentials given by Bachelet *et al.*[36] and Ceperly-Alder exchange and correlation potential[37] as parametrized by Perdew and Zunger.[38] The calculations were done for the Si(001) surface using a repeating-slab geometry. The vacuum spacing between slabs is taken to be 14 a.u. The silicon substrate with the (001)-(2×1) reconstructed surface is simulated by a slab consisting of 8 Si atomic layers (containing 16 Si atoms and 4 saturating H atoms in the slab unit cell). We chose Si atoms dimerization direction ([110]) along the x axis. Only the top surface is allowed to reconstruct; the dangling bonds on the bottom surface were saturated by hydrogen atoms. There is some question[9] as to whether the dimers also suffer some twisting motion (along the y direction). To resolve this issue and also to study dimers tilted in the opposite directions we performed a number of calculations with a 2×2 unit cell which has twice the area of the conventional 2×1 surface cell. This represents a major computational effort since it contains 40 atoms (32 Si atoms and 8 saturating H atoms) per unit cell coupled with the fact that a large number of structures are to be explored. We also check the sensitivity of our results to the input calculational parameters.

To arrive at optimized structures we started with the atomic positions of the Si atoms as given in a symmetric dimer-bond model proposed by Abraham and Batra.[28] We also did several calculations starting with the ideal structure as well as with the Yin-Cohen[19] asymmetric dimer model. For each structure, we computed Hellmann-Feynman forces on all atoms and used these as a guide to generate the next structure. Total-energy value dictated if the structure was more optimum because some moves led to a redistribution of forces without significantly affecting the total energy.

For the majority of the calculations, the electronic states were represented by ~730 plane waves for a 2×1 cell and ~1470 plane waves for a 2×2 cell corresponding to an energy cutoff of 5.5 Ry. During the self-consistency iterations the charge density was sampled at 15 and 9 **k** points, respectively, for the two cells placed uniformly in the surface Brillouin zone. This calculational parameter set (to be referred to as set $S1$) is adequate for optimizing atomic coordinates but may not lead to absolutely converged forces or formation enthalpies. This conclusion was arrived at by systematically increasing the energy cutoff to 7.5 Ry and 32 **k** points in the 2×1 cell. The final optimized structures were obtained with this extended set. We used a strict self-consistent field (SCF) convergence criterion (rms deviation in potential $\sim 10^{-7}$) because of the demands[39] of the calculations of the forces.

III. RESULTS AND DISCUSSION

Before delving into the results of our calculations, it is worthwhile to briefly describe various dimerization models[40] in the interest of establishing a common terminology. In Fig. 1 (see inset) we have shown a side view of the Si(001) surface in the x-z plane. Here x [110] is the dimerization direction and z is normal to the surface along the [001] direction. Four planes of atoms are shown and are labeled 1–8. Atoms 1 and 2 have two dangling bonds each for an ideal bulk truncated structure. A simple dimer model is obtained by only moving the surface atoms (atoms labeled 1 and 2 in Fig. 1) by equal and opposite amounts (Δx) along the x direction. A displacement $\Delta x = 0.75$ Å places atoms 1 and 2 at their ideal bulk bond length (2.35 Å). A relaxed simple dimer model is one where other layers of atoms are allowed to rearrange to minimize the total energy. A model of this type was first obtained by Appelbaum and Hamann[16] using the Keating

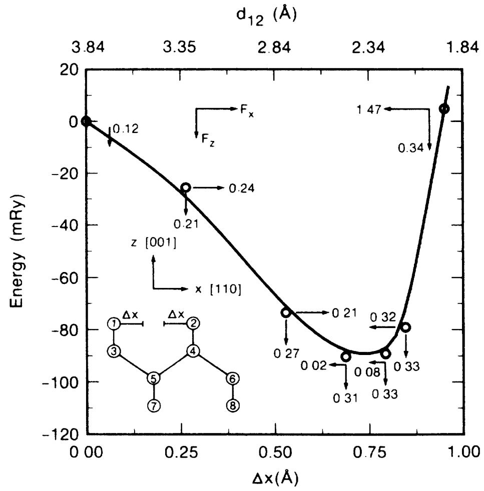

FIG. 1. Total energy of a simple symmetric dimer model for Si(001)-(2×1) as a function displacement (Δx) of surface atoms as well as the dimer bond length (d_{12}). Total energy of the ideal bulk truncated surface is taken to be zero. Also shown are the forces F_x and F_z (in units of 10^{-8} N) on surface atoms. The inset shows a side view of Si(001). Atoms labeled 1–8 specify the top four layers and their coordinates are given in Table I.

potential. An asymmetric dimer model is one where the surface atoms move by unequal amounts. In particular, if the surface atoms have unequal z displacements then the dimer is asymmetric as well as buckled. Models of this type were first proposed by Chadi[17,18] and Yin and Cohen[19] and have been quite successful in explaining many observations. Finally, if one permits a motion of the dimer along the $\pm y$ $[1\bar{1}0]$ direction one obtains a twisted dimer model. Such a model was proposed by Yang, Jona, and Marcus[9] based on a LEED analysis. A subsequent LEED study by Holland, Duke, and Paton[10] indicates that one can get a similarly good fit without invoking the y twist.

We started with the calculational set $S1$ and only moved the two surface atoms in a 2×1 unit cell to examine if there is any barrier to the dimer formation. This is what we have called a simple symmetric dimer model above. Results presented in Fig. 1 readily establish qualitatively that there is no barrier associated with the simple dimer formation. The energy decreases monotonically as the surface atoms 1 and 2 are moved towards each other by an amount $\Delta x \le 0.75$ Å. Note that as Δx increases the dimer bond length, d_{12}, decreases. The minimum is found around $\Delta x \simeq 0.75$ Å leading to a dimer bond length, $d_{12} \simeq 2.34$ Å. The net lowering of energy is ~ 0.6 eV per surface atom when all the other atoms are held rigidly in their ideal bulk truncated positions. The energy rises very sharply when we compress the dimer atoms together by more than 0.2 Å beyond the optimum bond length. The shape of the well around the minimum is seen to be nonsymmetric.

It is instructive to examine the forces acting on the surface dimer atoms as a function of Δx. Thus in Fig. 1 we have also shown the calculated Hellmann-Feynman forces F_x and F_z (in units of 10^{-8} N$\simeq$0.25 Ry/a.u.) acting on the dimer atoms. Since the parameter set $S1$ is used, only the qualitative aspects are significant. The x components of the forces were always equal and opposite and z components were always directed inwards. Atoms did not experience any forces along the y direction. Near (metastable) equilibrium we observe that while the x components of the forces have indeed become small, the dimer atoms are experiencing strong z forces demanding an inward relaxation. Such relaxations shall be carried out during the complete optimization to be discussed below. Incidentally, we note that forces of magnitude in the range $(0.02-0.08)\times10^{-8}$ N are to be considered small for the calculational parameters at hand (these being the residual F_x forces acting on atoms around the minimum of the total-energy curve). Thus during the complete optimization we shall strive to obtain forces on all atoms to be $\le 0.05\times10^{-8}$ N.

To arrive at an optimized structural model we started with the AB (Ref. 28) model in a 2×1 unit cell and moved the atoms in the direction of forces to obtain a lower-energy structure. After performing about 20 structural calculations with the set $S1$ we arrived at the model described in Table I. For comparison, we have also given the original YC and AB models. The dimer bond length obtained by us is in good agreement with a short dimer bond length of 2.25 Å predicted by YC many years earlier. This is to be contrasted with the AB model which essentially gets a normal bulk single-bond length (2.35 Å). The subsurface relaxations obtained by us are also qualitatively similar to those obtained by YC. A point of departure is that our dimers are symmetric and nonbuckled, in agreement with the AB model. Another essential ingredient of our model is that the back bonds between the first and second layer atoms are considerably strengthened (all bond lengths are 2.29 Å). A small amount of buckling (~ 0.03 Å) raised the total energy suggestive of a barrier to buckling. A further comparison of the original YC and the present symmetric dimer model is given in Fig. 2.

To keep ourselves from being trapped in a local minimum, we performed a number of calculations starting with an ideal structure but in a 2×2 unit cell. These calculations used the set $S1$ and serve as a check on the convergence of our results. The final coordinates differed from those obtained from a 2×1 cell calculation by $<\pm0.01$ a.u. Another important reason for doing the 2×2 calculations was to examine some relative orientations of the dimers. We found that whenever we attempted to twist the dimers by making any y displacements with respect to the ideal y positions, serious F_y forces developed opposing that move. For example, displacing one dimer by giving its atoms a ±0.1 a.u. displacement led to the development of large $\sim 0.1\times10^{-8}$ N restoring

TABLE I. Ideal bulk truncated atomic positions (in Å) for the top four surface layers of the Si(001) 2×1 lattice and the relative displacements required for the Yin-Cohen (Ref. 19) (YC), Abraham-Batra (Ref. 28) (AB), and the present optimized model. The coordinates x,y,z refer to the [110], $[1\bar{1}0]$, and [001] directions, respectively (see inset in Fig. 1). No y displacements ($\Delta y = 0$) are present for these models. These calculations were performed with the parameter set $S1$.

	Ideal lattice			YC model		AB model		Optimized	
N	x	y	z	Δx	Δz	Δx	Δz	Δx	Δz
1	−1.92	0.0	0.0	0.57	−0.16	0.72	−0.10	0.83	−0.45
2	1.92	0.0	0.0	−1.04	−0.47	−0.72	−0.10	−0.83	−0.45
3	−1.92	1.92	−1.36	0.09	−0.05	0.11	0.02	0.09	−0.09
4	1.92	1.92	−1.36	−0.12	0.02	−0.11	0.02	−0.09	−0.09
5	0.0	1.92	−2.72	−0.01	−0.19	0.0	−0.09	0.0	−0.20
6	3.84	1.92	−2.72	−0.03	0.13	0.0	0.09	0.0	0.04
7	0.0	0.0	−4.08	0.06	−0.14	0.0	−0.05	0.0	−0.10
8	3.84	0.0	−4.08	−0.06	0.10	0.0	0.05	0.0	0.04

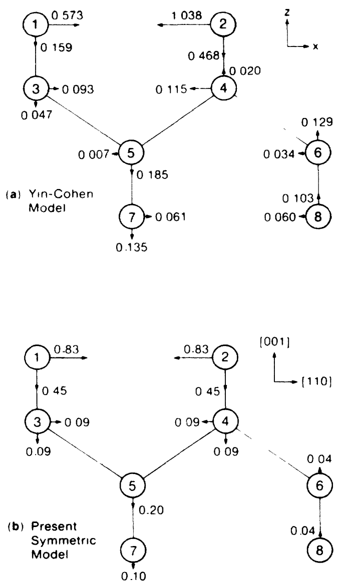

FIG. 2. Atomic displacements (in Å) from the ideal bulk positions to generate (a) the original YC model of Si(001)-(2×1) and (b) the present optimized model.

forces. More importantly, the energy increased by 1 mRy per atom, which led to the conclusion that the dimers are not twisted, contrary to the assertion of one of the LEED-derived models.[9]

Another aspect we explored in the 2×2 cell was the stability of dimers to small buckling in the opposite directions. In a 2×1 cell all dimers by construction must have the same tilt. In a 2×2 cell, we found that even some small buckling can be tolerated provided adjacent dimers are tilted in the opposite directions. For example, our calculations showed that in the 2×2 cell a buckling of 0.15 a.u. lowers the energy by 0.02 mRy per atom provided the two dimers in the unit cell are oppositely tilted.[30] Although this energy change is below the accuracy we are willing to claim, the resultant forces on the atoms were also suggestive that this may be an acceptable configuration. This so called p-(2×2) model, discussed by Chadi,[24] has a different periodicity than the 2×1 model and shall not be pursued here.

The formation enthalpies obtained in our calculations place a simple dimer model (using the set $S1$) at about 0.6 eV per atom lower energy than the ideal structure. We did not fully optimize the dimer bond in a simple dimer model because this is an intermediate metastable structure. The completely optimized structure generated by us is ε_a $(=1.17)$ eV per atom lower in energy than the ideal structure. The major lowering in energy here arises due to strong inward relaxation (~ 0.45 Å) of all surface atoms which strengthens all back bonds. For comparison, we also recomputed the total energy of the original YC model in our slab geometry using the atomic displacements given by YC for the top four Si layers. According to our calculations, the YC model has 1.11 eV per atom lower energy (more stable) than the ideal structure. It is only slightly less stable (0.06 eV/atom) than the symmetric dimer model obtained by us. The AB model is fairly unstable (0.34 eV/atom) with respect to the present symmetric dimer model.

In computing formation enthalpies, we have used the energy of the ideal Si(001) surface (which tends to converge slowly) as a reference. As the energy cutoff is systematically increased from 5.5 to 6.5 and finally to 7.5 Ry (with 32 **k** points in the Brillouin zone), ε_a becomes 1.17, 1.03, and 0.93 eV/atom, respectively. The reason is that the total energy of the ideal surface is preferentially lowered upon increasing the cutoff due to slow convergence. This changes the reference energy, making our symmetric dimer model less stable in the absolute sense, with only a minor effect on the relative stability. The value 1.03 eV obtained by us at 6.5 Ry cutoff is in agreement with the value obtained by Pandey.[25] A comparison of this with the value of 0.85 eV quoted by YC led to the suggestion[25] that the highly buckled YC model is energetically unfavorable.[40] Such a conclusion is probably not warranted, since, as shall be seen below, a slightly modified YC model can yield stability values similar to ours if identical calculational parameters and supercell geometries are used.

In Table II we compare the resultant forces on atoms in the original YC and our optimized model both calcu-

TABLE II. Forces on the top four layer atoms (in units of 10^{-8} N) for the Si(001) 2×1 lattice for the original YC model and the present optimized model. No y forces ($F_y=0$) are present for these models. The last two columns give residual forces on optimized atoms computed using the 2×2 cell. The parameter set $S1$ is used for calculations.

	YC model		Optimized		Optimized (2×2)	
N	F_x	F_z	F_x	F_z	F_x	F_z
1	0.084	−0.105	−0.014	−0.033	−0.031	−0.025
2	−0.054	−0.049	0.014	−0.033	0.031	−0.025
3	0.049	0.019	0.021	−0.008	0.018	−0.028
4	−0.047	−0.020	−0.021	−0.008	−0.018	−0.028
5	−0.027	0.010	0.0	0.002	0.0	−0.030
6	−0.006	−0.003	0.0	0.027	0.0	0.018
7	−0.151	0.091	0.0	−0.019	0.0	−0.048
8	0.069	−0.053	0.0	−0.026	0.0	−0.011

TABLE III. Atomic coordinates (in a.u.) for the top four surface layers for the Si(001)-(2×1) symmetric dimer model and a slightly modified YC (Ref. 19) asymmetric buckled dimer model obtained in the present optimization. All calculations were done using 7.5 Ry energy cutoff and 32 **k** points in the Brillouin zone.

	Symmetric dimer model			(Modified) YC Asymmetric model		
N	*x*	*y*	*z*	*x*	*y*	*z*
1	−2.10	0.0	−0.84	−2.50	0.0	−0.35
2	2.10	0.0	−0.84	1.60	0.0	−0.95
3	−3.45	3.63	−2.73	−3.45	3.63	−2.65
4	3.45	3.63	−2.73	3.41	3.63	−2.52
5	0.0	3.63	−5.48	−0.01	3.63	−5.48
6	7.26	3.63	−5.01	7.21	3.63	−4.89
7	0.0	0.0	−7.89	0.0	0.0	−7.89
8	7.26	0.0	−7.63	7.26	0.0	−7.63

lated in our slab geometry using the parameter set *S*1. The forces on atoms obtained from calculations in the 2×2 cell are also given in the last two columns. As explained earlier, the optimization was carried out until all forces on all atoms dropped below 0.05×10^{-8} N. For our model, we have reached a point where we can lower forces on some atoms at the expense of increasing forces on some other atoms with a ±0.02 mRy/atom change in total energy. For example, reducing the dimer bond length by 0.01 a.u. and at the same time moving the dimers outwards by 0.005 a.u. causes x components of the forces to increase on atoms 1 and 2 from 0.014×10^{-8} to 0.032×10^{-8} N. This is accompanied by a reduction in the z components of the forces on these atoms from 0.033×10^{-8} to 0.020×10^{-8} N. The x components of the forces also increase on atoms 3 and 4 from 0.021×10^{-8} to 0.042×10^{-8} N but the total energy is only raised by 0.09 mRy/atom. This change is just about at the limit of the accuracy of the calculations, which is estimated to be ±0.1 mRy/atom.

A small buckling of the dimer atoms by ±0.05 a.u. raised the energy by only 0.03 mRy/atom. At that point forces on atoms suggested that a further tilt is in fact desirable. As soon as we increased the tilt to ±0.1 a.u. the energy increased by 0.5 mRy/atom. Since a large buckling contained in the YC model has a local minimum (comparable to our symmetric dimer model) we conclude that there is probably a barrier associated with buckling. The atomic coordinates optimized by us may have a noise of $<\pm0.05$ a.u.

The forces on atoms in the original YC model as computed in our slab geometry (see Table II) indicate that the surface atoms are under the influence of large x- and z-directed forces. When we actually attempted to move the atoms, the forces developed to suggest further buckling. Other significant forces are to be found on the fourth layer atoms. However, this is not alarming because YC impose an artificial inversion symmetry in their supercell geometry. Our slab consists of 8 Si layers with saturating H atoms on the bottom surface.

Finally, in Table III we give the actual atomic coordinates for the symmetric dimer model obtained as a result of our optimization using the extended parameter set. Values differ only slightly from those given in Table I. Also given are the atomic positions for the strongly buckled YC type of model optimized in our supercell geometry using identical parameters. The symmetric and modified YC models are found to be 0.93 and 0.92 eV/atom, respectively, more stable than the ideal structure. The value quoted by YC is 0.85 eV/atom. The small deviation may well arise from different calculational parameters and minor differences in atomic positions. The important point is that the symmetric dimer model is only 0.01 eV/atom more stable than the asymmetric buckled model when calculations are done under identical conditions. Thus the two models have local-energy minima of nearly equal depth which seems to be borne out by the STM results.[30] Our atomic coordinates should facilitate any future optimization efforts and should also make it easier for others to use the optimized symmetric dimer model in adsorption and growth studies on Si. With that in mind, the coordinates are given in atomic

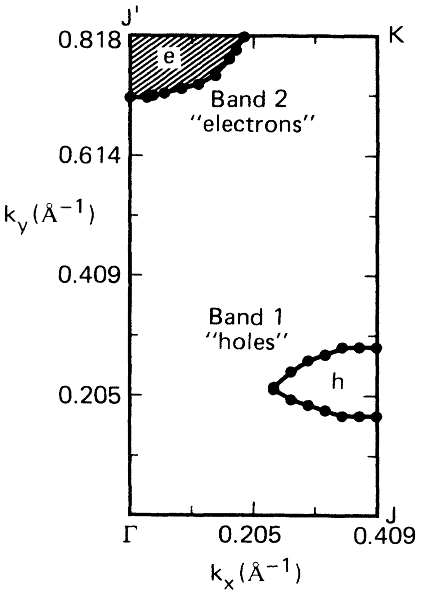

FIG. 3. The constant energy contour $E=E_F$, shown by solid dots, in one quadrant of the surface Brillouin zone for our Si(001)-(2×1) symmetric dimer model. The enclosed electron (hatched) and hole pockets are denoted by *e* and *h*, respectively.

units (as opposed to angstroms) since many calculations so require.

As noted in the Introduction, a symmetric dimer model leads to a metallic surface. It is therefore instructive to sketch the "Fermi surface." The computed constant-energy contour ($E=E_F$) in one quadrant of the surface Brillouin zone is displayed in Fig. 3 by solid dots. A fine mesh in **k** space was employed for these calculations. The metallicity in the present model is due to the Fermi line crossing two (dangling-bond) bands. The hole pocket, denoted by h, shows states in band 1 which are unoccupied at $T=0$ K. Actually, these states are enclosed by a closed contour if the Fermi line in the second quadrant (not shown) is translated by a reciprocal lattice vector. There are two such hole pockets in zone 1 centered around $(0.41\ \text{Å}^{-1}, \pm 0.24\ \text{Å}^{-1})$. The shaded region in Fig. 3 indicates states which are occupied in (dangling-bond) band 2 at $T=0$ K. The electron pocket also forms a closed contour around J' if pieces from other quadrants are translated by appropriate reciprocal lattice vectors. Only one such closed contour belongs to a unit cell. There are two electrons per 2×1 unit cell which are just enough to completely fill the states in one Brillouin zone. Hence the number of electron states per unit cell in band 2 is equal to the number of hole states in band 1. The symmetric dimer model is then an example of a "compensated" metal.

It is concluded that a symmetric dimer model reconstruction for the Si(001)-(2×1) surface is highly competitive with a strongly buckled YC type of model. There is probably a barrier associated with buckling but no barrier is present for symmetric dimerization of the Si(001) surface.

ACKNOWLEDGMENTS

I wish to acknowledge useful discussions with Dr. F. F. Abraham, and in particular for asking me often about the barrier (or lack of it) to symmetric dimer formation.

---

[1] See, for example, B. Bourguignon, K. L. Carleton, and S. R. Leone, Surf. Sci. **204**, 455 (1988).

[2] J. E. Northrup, Phys. Rev. Lett. **62**, 2487 (1989); E. Kaxiras, O. L. Alerhand, J. D. Joannopoulos, and G. W. Turner, *ibid.* **62**, 2484 (1989).

[3] D. Srivastava, B. J. Garrison, and B. W. Brenner, Phys. Rev. Lett. **63**, 302 (1989).

[4] R. I. G. Uhrberg, R. D. Bringans, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. Lett. **56**, 520 (1986); I. P. Batra, *ibid.* **63**, 1704 (1989).

[5] D. Haneman, Rep. Prog. Phys. **50**, 1045 (1987); A. Kahn, Surf. Sci. Rep. **3**, 193 (1983); D. J. Chadi, Vacuum **33**, 613 (1983); D. Haneman, Adv. Phys. **31**, 165 (1982); D. E. Eastman, J. Vac. Sci. Technol. **17**, 492 (1980); G. P. Kerker, S. G. Louie, and M. L. Cohen, Phys. Rev. B **17**, 706 (1978).

[6] R. E. Schlier and H. E. Farnsworth, J. Chem. Phys. **30**, 917 (1959); F. Jona, IBM J. Res. Dev. **9**, 375 (1965); T. D. Poppendieck, T. C. Ngoc, and M. W. Webb, Surf. Sci. **75**, 287 (1978); also see T. Ichikawa and S. Ino, *ibid.* **85**, 221 (1979).

[7] F. Jona, H. D. Shih, D. W. Jepsen, and P. M. Marcus, J. Phys. C **12**, L455 (1979); S. Y. Tong and A. L. Maldondo, Surf. Sci. **78**, 459 (1978); W. S. Yang, F. Jona, and P. M. Marcus, Solid State Commun. **43**, 847 (1982).

[8] G. J. R. Jones and B. W. Holland, Solid State Commun. **46**, 651 (1983).

[9] W. S. Yang, F. Jona, and P. M. Marcus, Phys. Rev. B **28**, 2049 (1983).

[10] B. W. Holland, C. B. Duke, and A. Paton, in *Proceedings of the 17th International Conference on the Physics of Semiconductors,* edited by D. J. Chadi and W. A. Harrison (Springer, Berlin, 1984), p. 59.

[11] J. E. Rowe and H. Ibach, Phys. Rev. Lett. **32**, 421 (1974).

[12] W. Gudat and D. E. Eastman, J. Vac. Sci. Technol. **13**, 831 (1976).

[13] F. J. Himpsel and D. E. Eastman, J. Vac. Sci. Technol. **16**, 1297 (1979); R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, and S. A. Flodström, Phys. Rev. B **24**, 4684 (1981).

[14] R. M. Tromp, R. G. Smeenk, and F. W. Saris, Phys. Rev. Lett. **46**, 9392 (1981); Solid State Commun. **39**, 755 (1981); M. Aono, Y. Hou, C. Oshima, and Y. Ishizawa, Phys. Rev. Lett. **49**, 567 (1982).

[15] R. Seiwatz, Surf. Sci. **2**, 473 (1964); J. C. Phillips, *ibid.* **40**, 459 (1973); W. A. Harrison, *ibid.* **55**, 1 (1976).

[16] J. A. Appelbaum, G. A. Baraff, and D. R. Hamann, Phys. Rev. B **14**, 588 (1976); J. A. Appelbaum and D. R. Hamann, Surf. Sci. **74**, 21 (1978).

[17] D. J. Chadi, Phys. Rev. Lett. **43**, 43 (1979); also see P. Krüger and J. Pollmann, Phys. Rev. B **38**, 10 578 (1988).

[18] J. Ihm, M. L. Cohen, and D. J. Chadi, Phys. Rev. B **21**, 4592 (1980).

[19] M. T. Yin and M. L. Cohen, Phys. Rev. B **24**, 2303 (1981).

[20] I. P. Batra and S. Ciraci, Phys. Rev. Lett. **36**, 170 (1976); I. P. Batra, S. Ciraci, and I. B. Ortenburger, Solid State Commun. **18**, 563 (1976).

[21] W. S. Verwoerd, Surf. Sci. **103**, 404 (1981).

[22] A. Redondo and W. A. Goddard, J. Vac. Sci. Technol. **21**, 344 (1982).

[23] J. J. Lander and J. Morrison, J. Appl. Phys. **33**, 2089 (1962).

[24] M. J. Cardillo and G. E. Becker, Phys. Rev. Lett. **40**, 1148 (1978); Phys. Rev. B **21**, 1497 (1980); D. J. Chadi, Appl. Opt. **19**, 3971 (1980).

[25] K. C. Pandey, in *Proceedings of the 17th International Conference on the Physics of Semiconductors,* edited by D. J. Chadi and W. A. Harrison (Springer, Berlin, 1984), p. 55.

[26] J. E. Northrup, Phys. Rev. Lett. **54**, 815 (1985).

[27] F. J. Himpsel and Th. Fauster, J. Vac. Sci. Technol. A **2**, 815 (1983).

[28] F. F. Abraham and I. P. Batra, Surf. Sci. **163**, L752 (1985).

[29] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1984).

[30] R. M. Tromp, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **55**, 1303 (1985); R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **24**, 5343 (1986).

[31] E. Artacho and F. Yndurain, Phys. Rev. Lett. **62**, 2491 (1989).

[32] M. Schlüter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B **12**, 4200 (1975).

[33] K. C. Pandey, Phys. Rev. Lett. **49**, 223 (1982); I. P. Batra, S. Ciraci, G. P. Srivastava, J. S. Nelson, and C. Y. Fong, Phys.

Rev. B **34**, 8246 (1986).

[34] S. C. Hong, A. J. Freeman, and C. L. Fu, Phys. Rev. B **39**, 5719 (1989).

[35] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[36] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[37] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[38] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[39] P. Bendt and Z. Zunger, Phys. Rev. Lett. **50**, 1684 (1983).

[40] F. Bechstedt and D. Reichardt, Surf. Sci. **202**, 83 (1988).