First Principles Calculation of the Structure and Energy of Si(113)

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(Received 17 August 1992)

Results of an *ab initio* pseudopotential total energy calculation of the atomic structure and surface energy of the 3×2 reconstruction of the (113) surface of Si are presented. Despite many reports in the literature that (113) is a particularly low energy surface of Si, the calculated surface energy of 0.138 eV Å^{-2} is *not* small in comparison with similar calculations of the surface energy of Si(111) and Si(100). This discrepancy is discussed with reference to the role of carbon contamination in stabilizing the (113) surface.

PACS numbers: 68.35.Bs, 68.35.Md, 71.45.Nt, 73.20.−r

There has been a long history of interest in the (113) surface of Si. This is largely based on the frequent observation of faceting along {113} in thermal etching and vacuum annealing experiments [1], and the potential of the (113) surface as a substrate for epitaxial growth [2]. As one of the most striking examples of {113} faceting, Gibson, McDonald, and Unterwald [3] annealed thin {110}-oriented specimens *in situ* in a UHV electron microscope and observed extensive areas of flat {113} surface, in addition to the low-index surfaces {111}, {100}, and {110}. These observations of {113} faceting have been interpreted in terms of the (113) surface having a particularly low surface energy, if not the *lowest* energy of any surface plane [3,4]. At first sight this conclusion is surprising because high-index surfaces would normally be expected to have a higher surface energy than their low-index counterparts. For example, Chadi [5], using an empirical tight-binding model, calculated the surface energies of a number of high-index surfaces of Si and found that all had a considerably higher surface energy than the 2×1 reconstruction of Si(111), with the (113) surface energy being particularly *high.* There is a clear need for a first principles calculation of the surface energy of Si(113) in order to determine whether or not it does have a low energy in comparison with the low-index surfaces.

More recently, there has been considerable controversy about the stable reconstruction on Si(113), with both 3×1 and 3×2 reconstructions being reported [6-11]. The recent scanning tunneling microscopy (STM) studies of Knall *et al.* [11] have confirmed the 3×2 reconstruction, and they explain the observation of a 3×1 reconstruction in terms of a high density of boundaries between 3×2 domains which will tend to diminish LEED reflections related to the 3×2 reconstruction while retaining the 3×1 reflections. Ranke [10] has proposed a number of possible structures for Si(113), based on the simple chemical ideas that no surface atom will have more than one dangling bond, dangling bond density will be reduced by dimerization or by adatoms, bond stretching by more than about 5% is unfavorable while bond-angle deviations are softer, and rehybridization away from tetrahedral sp^3 towards a planar (sp^2-like) or rectangular (p-like) configuration may be energetically favorable. Only one of Ranke's structures is consistent with the recent STM studies [11,12], and we take this as the starting point for our study. Knall *et al.* [11] also emphasize the significance of rehybridization in stabilizing Si(113), pointing out the high density of atoms that have the freedom to rehybridize towards sp^2. In this Letter we present the results of an *ab initio* pseudopotential total energy calculation of the structure and energy of Si(113). The aim is to confirm the stability of the experimentally determined structure, to determine its structural parameters to look for evidence of rehybridization, and, more importantly, to compare the surface energy with similar calculations on the (100) [13,14] and (111) [15,16] surfaces.

The pseudopotential calculations were carried out on 32 nodes of a Meiko i860 Computing Surface using a parallel total energy code (CETEP) specifically designed for this type of machine [15,17]. The method is based on Car and Parrinello's *ab initio* molecular dynamics scheme [18], with the electron states being expanded in a plane-wave basis and the energy minimization with respect to the plane-wave coefficients being carried out using the conjugate-gradients technique developed by Teter, Payne, and Allen [19]. We use Perdew and Zunger's [20] parametrization of the exchange-correlation energy and a Kerker [21] pseudopotential for Si applied in a Kleinman-Bylander [22] form. The s-wave potential is taken as local and the p and d nonlocal potentials are treated in real space, using the method proposed by King-Smith, Payne, and Lin [23].

The starting structure for the calculation comes from a model based on Ranke's 3×2 reconstruction [10] which is consistent with the STM data [11,12]. The structure was initially relaxed using the empirical Stillinger-Weber (SW) potential [24]. The slab we use has inversion symmetry about its center and consists of ten double layers in the [113] direction, with each double layer containing 12 atoms. The Ranke structure has 5 additional atoms on

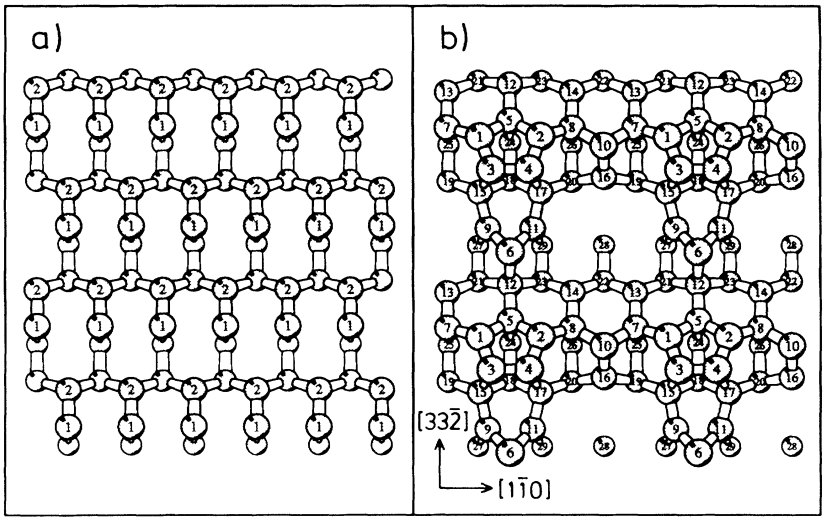

FIG. 1. Ball-and-stick plan view models of the Si(113) surface. (a) The bulk-terminated structure. (b) The 3×2 reconstruction. The relationship between the structures may be seen by superimposing the figures. See text for details.

each surface, making 130 atoms in total. The slab thickness is approximately 18 Å, with about 10 Å of vacuum gap in the periodically repeated cell. The 3×2 cell in the surface plane has basis vectors $\frac{1}{2}[33\bar{2}]$ and $\frac{3}{2}[1\bar{1}0]$, and so with a cubic lattice parameter of 5.43 Å the dimension of the unit cell of the calculation is 12.73 Å×11.52 Å×27.83 Å. For comparison, the energy of a bulk-terminated (113) slab was also calculated in the same sized cell. In this case the slab comprises ten double layers in the [113] direction and includes 120 atoms. A single k point (at Γ) is used in these large cells for Brillouin zone averaging. To calculate the surface energy for both bulk-terminated and reconstructed surfaces we have also calculated the total energy of bulk silicon in an equivalent geometry and with an equivalent k-point density. In all calculations the plane-wave cutoff energy is 120 eV, for which structures and energy differences are well converged [25]. For the large unit cell, this cutoff gives 12207 plane waves. In relaxing the 120- and 130-atom slabs the two innermost double layers are held fixed and all other atoms are allowed to move until forces are less than 0.1 eV/Å.

TABLE I. Bond lengths (in Å) for the (113) surface.

Bond	Length	Bond	Length
1-3,2-4	2.20	9-27,11-29	2.30
1-5,2-5	2.28	10-7,10-8	2.31
1-7,2-8	2.29	10-16	2.22
3-4	2.29	13-7,14-8	2.32
3-15,4-17	2.30	16-19,16-20	2.31
5-12	2.37	28-22	2.33
6-9,6-11	2.30	24-5	2.49
6-12	2.46	24-18	2.42
9-15,11-17	2.36		

The bulk-terminated (113) surface is shown in Fig. 1(a). Surface atoms 1 and 2 have 2 and 1 broken bonds, respectively. When this surface is allowed to relax (without reconstruction) atoms 1 and 2 form a dimer with bond length 2.25 Å. The backbonds from these atoms contract to 2.34 Å (atom 1) and 2.30 Å (atom 2), and the dimer tilts to give bond angles of 93° for atom 1 and 113° and 2×121° for atom 2. This is exactly what would be expected from a rehybridization argument, with atom 2 adopting an sp^2 configuration while the bonding of atom 1 becomes more p-like. The relaxed structure of the 3×2 reconstruction is shown in Fig. 1(b), and some of the key structural parameters are given in Tables I and II [26]. The main features of the structure are the tetramer consisting of atoms 1 to 4; the adatom 6 with its neighbors 9, 11, and 12; the dimer formed by atoms 10 and 16; and the remaining atoms with dangling bonds 13, 14, and 28. The surface is highly corrugated, with a deep hollow whose surface is defined by atoms 9, 11, 13, 14, 16, and 28. The height difference between the highest (3,4) and lowest (28) atoms in the surface is 3.3 Å. Figure 2 shows the charge density along the $(1\bar{1}0)$ mirror planes in the surface, and it is clear that the general height of the surface is considerably higher in Fig. 2(a) than in Fig. 2(b). Table I shows that the tetramer is very strongly bonded, with the 3-4 and 1-3 bond lengths being 2.29 and 2.20 Å, respectively. The backbonds into the surface are also considerably shortened with respect to the bulk value of 2.35 Å, with the bond length from atoms 3 and 4 being

TABLE II. Sum of bond angles for surface atoms (degrees).

Atom	1,2	3,4	6	9,11	10	13,14	16	28
Sum	342	331	289	357	332	338	336	328

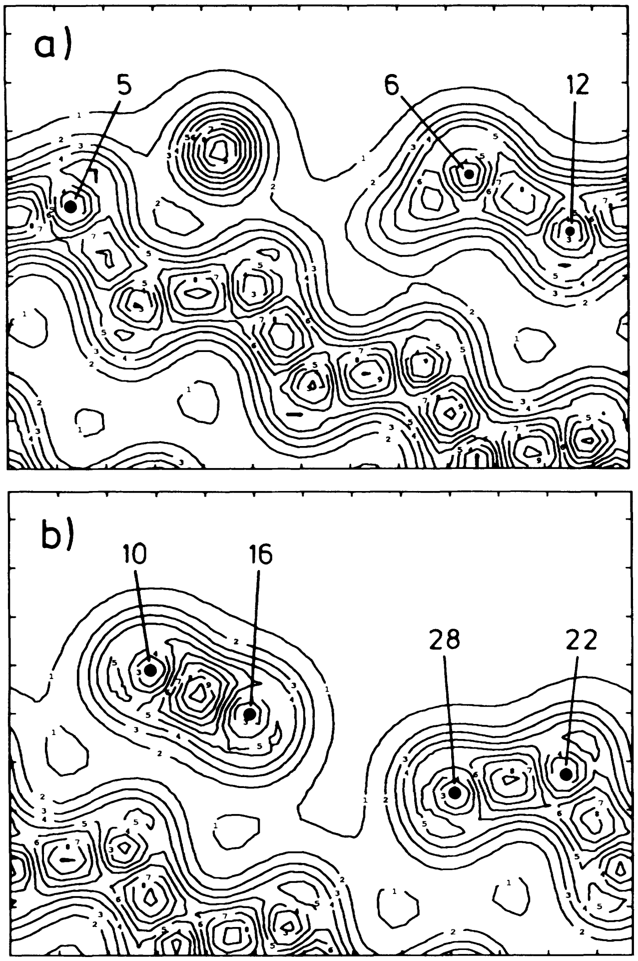

FIG. 2. Contour plots of the charge density along $(1\bar{1}0)$ mirror planes through atoms (a) 5, 6, 12 and (b) 10, 16, 28, 22 in Fig. 1(b). The spacing of the tick marks is 1 Å.

2.30 Å, and those from atoms 1 and 2 being 2.28 Å (to the shared atom 5) and 2.29 Å. The 6-9 and 6-11 bond lengths are similarly compressed at 2.30 Å, but the 6-12 bond is 4.5% stretched at 2.46 Å. The dimer formed by atoms 10 and 16 has a bond length of 2.22 Å, while the backbonds from these atoms are again compressed at 2.31 Å. All other bond lengths vary from about 2% compression to 1.5% stretch. The only exception is that the atom under the tetramer (atom 24) has two considerably stretched bonds at 2.42 and 2.49 Å (to atoms 18 and 5, respectively).

To investigate rehybridization we look at the sum of the three bond angles subtended at the atoms which have a dangling bond. In an ideal sp^3 configuration this sum would be 328.4°, changing to 360° and towards 270° for sp^2- and p-like bonding, respectively. The results are listed in Table II. It can be seen that considerable bond-angle deviations do occur, with atoms 1, 2, 9, 11, 13, 14, and 16 all moving towards a planar configuration, this being particularly marked for atoms 9 and 11. Atoms 3, 4, 10, and 28 do not move far from sp^3, while atom 6 has a considerably reduced sum of bond angles. Within these sums there is some degree of variation between the individual bond angles, but except for the group comprising atoms 6, 9, and 11 this is not very marked. For this group the bond angles subtended at atom 6 are 74° and $2\times 107.5°$ while those subtended at atoms 9 and 11 are 141°, 104°, and 112°. This group of atoms appears to have the most interesting rebonding behavior, with atoms 9 and 11 coming considerably closer together than in the starting SW structure. In fact, the final separation of these atoms is only 2.75 Å, indicating that the p-like dangling bonds from the planar-configured atoms 9 and 11 are overlapping to form an extra weak bond. Some evidence for this may be seen in Fig. 2(a), where the charge cloud from atom 6 is seen to extend into the region between atoms 9 and 11. Other than this, the charge density plots in Figs. 2(a) and 2(b) show the expected features, given the bond lengths discussed above. In Fig. 2(a) we see a perpendicular cross section through the strong 3-4 dimer bond, together with the relative weakening of the elongated 6-12 and 5-24 bonds. Figure 2(b) shows the strong 10-16 dimer bond, the dangling bond on atom 28, and the deep hollow in the structure between the two.

We now turn to the calculated surface energies. The bulk-terminated surface has an energy relative to the bulk of 0.177 eV Å^{-2}. When this surface is allowed to relax, as described above, the energy reduces to 0.159 eV Å^{-2}. The SW starting structure for the 3×2 reconstruction has an energy of about 0.16 eV Å^{-2} (this value is uncertain because in this case the ions were allowed to start relaxing before the electronic states were fully converged). Upon relaxation, this value reduces to 0.138 eV Å^{-2}. It is interesting to compare these results with those from similar calculations on the (100) and (111) surfaces. Northrup [13] quotes a value for the (100) surface energy of 1.45 eV per 1×1 cell, which is equivalent to 0.098 eV Å^{-2}. Roberts and Needs [14] do not give an absolute surface energy for (100), but they find, for their lowest energy surface, an energy saving (relative to the bulk-terminated surface) of 2.11 eV per dimer, which corresponds to 0.071 eV Å^{-2}. This is considerably more than the 0.039 eV Å^{-2} we find for the (113) surface, but this is not surprising since every atom in the bulk-terminated (100) surface has two broken bonds. Stich *et al.* [15] and Brommer *et al.* [16] give the absolute surface energy of the 7×7 reconstruction of Si(111) as 1.153 and 1.179 eV per surface atom, respectively, which translate to 0.090 and 0.092 eV Å^{-2}. Our calculations therefore clearly indicate that the (113) surface energy is considerably higher than those of (100) and (111). It is important to note that absolute surface energies are obtained by subtracting two large energies and are therefore subject to error. However, the excess energy of this (113) surface is too large to be explained by inaccuracies in the calculation. For example, based on calculations for bulk Si and similar calculations on other surfaces [15], we estimate that the error due to inadequate **k**-point sampling cannot be more than about 0.1 eV per surface atom (≈ 0.01 eV Å^{-2}), which is not enough to reduce the calculated value of 0.138 eV Å^{-2} to the (100) and (111) values.

The significance of these surface energies is best seen by considering the stability of the (113) surface against faceting into (111) and (100). The Wulff-Herring construction [27] leads to the following criterion for (113) to be stable:

$$\sigma_{(113)} < 0.522\sigma_{(111)} + 0.603\sigma_{(100)} , \qquad (1)$$

where $\sigma_{(hkl)}$ is the energy of the (hkl) surface. The values for $\sigma_{(100)}$ and $\sigma_{(111)}$ given in Refs. [13], [15], and [16] therefore imply that, for stability, $\sigma_{(113)} < 0.107$ eV Å^{-2}. Although we again stress that we would not want to push the accuracy of these calculations too far, the clear indication is that (113) does *not* have a particularly low surface energy, and may well be on the brink of being unstable against faceting into (111) and (100).

How can we reconcile this result with the experimental observation that (113) is a low energy surface? We have considered two possibilities here. First, the experimentally determined structure may not be correct and an alternative, lower energy structure may exist. Although Wilson *et al.* [12] found some difficulty in obtaining an exact match between their model of the (113) surface (which is topologically the same as ours, but details of bond lengths, etc., differ) and their STM images, there seems to be little doubt that the basic structural elements of the 3×2 reconstruction are as determined. On the basis of our total energy calculations we have no alternative structure to propose which is likely to have a significantly lower energy. Second, the work of Yang and Williams [6] may be particularly relevant here. They showed that carbon contamination plays a crucial role in the faceting of several Si surfaces, including (100), (111), and (112). Although it is difficult to be quantitative, they found a "direct relationship between carbon concentration and the extent of faceting." They found the (112) surface to be most sensitive to carbon, but even here faceting can be prevented with careful cleaning. Yang and Williams go on to conclude that the small quantity of carbon required to initiate faceting can explain all of the previous annealing studies. This is consistent with our finding that *the clean Si(113) surface does not have an anomalously low surface energy*. Finally, we may use our calculated structure to speculate on why carbon might be effective in reducing the (113) surface energy. Carbon has a considerably larger *s*-*p* promotion energy than Si, which tends to favor sp^2 hybridization over sp^3. It is therefore possible that, for example, in a rehydridized dimer, energy can be gained by substituting the atom which tends towards an sp^2 configuration with C, while leaving the more *p*-like atom as Si. As discussed above, a particular feature of the (113) surface is the substantial dimerization and rehybridization which is present.

The calculations were performed within the "Grand Challenge" collaborative project funded by the United Kingdom Science and Engineering Research Council under Grant No. GR/G32779. We thank Professor D. J. Tildesley for coordinating this project.

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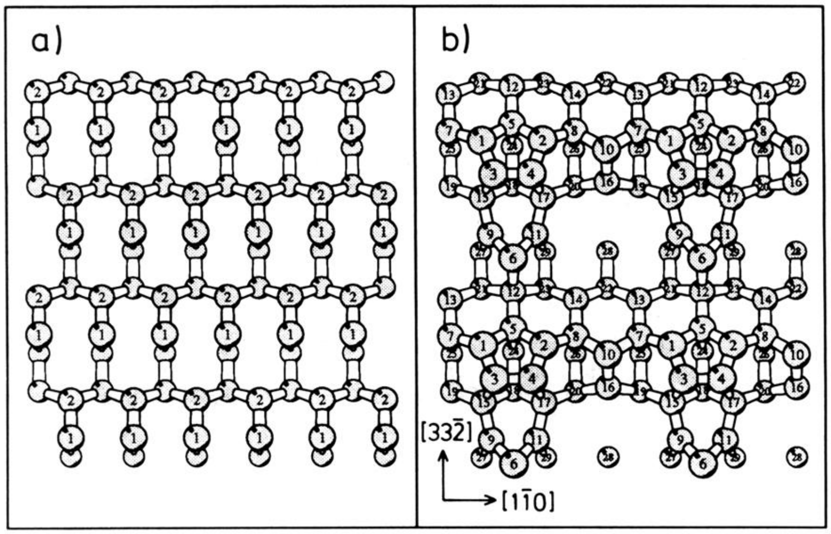

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