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Surface stacking sequence and (7×7) reconstruction at Si(111) surfaces

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The (7×7) surface is considered to have a triangular checkerboard structure in which the layer stacking sequences $\cdots AaBbA$ and $\cdots AaCcA$ alternate in neighboring triangular subunits in conformity with ion-backscattering results. The topological requirements of joining double layers at the subunit boundaries lead to the prediction of arrays of dimers and of deep (6.3-Å) holes which are consistent with results of electron diffraction and of tunneling microscopy, respectively.

The structure of the Si(111)-(7×7) surface has long been a subject of speculation,[1–4] but all of the many structural models that have been proposed assume—apparently unnecessarily—that the diamond bulk stacking sequence $\cdots AaBbC$ prevails right up to the surface. Here, letters denote atom layers, so that, e.g., C denotes the outermost layer (assumed to consist of three-coordinated atoms), bC the outermost double-layer, and $\cdots$ denotes continued diamond stacking. Recently it was reported[5] that a greatly improved interpretation of He$^+$- or H$^+$-ion Rutherford backscattering results[6,7] could be obtained by assuming a stacking fault and surface wurtzite (hexagonal diamond) stacking sequences such as

$$\cdots AaBb|A\ , \tag{1a}$$

$$\cdots Aa|CcA \tag{1b}$$

(the vertical bar indicates the position of the stacking fault). The best fit to experiment was obtained with a 50-50 mixture of these stacking sequences.[8] The results suggest that the (7×7) surface has a triangular checkerboard structure in which the stacking sequences (1a) and (1b) alternate in neighboring triangular subunits as sketched in Fig. 1. This is the key to understanding the (7×7) reconstruction. It leads naturally and almost automatically to a model of the (7×7) surface that accounts for all experimental results that can be interpreted confidently in terms of structure.

All of the important features of the (7×7) structure follow from the topological requirements of joining double layers at the sides and apex of each triangular subunit in Fig. 1. Along the sides, the double layer $b|A$ must be joined to cA and aB to $a|C$ [cf. Eq. (1)]. This can only be done (without gross distortions of band angles and bond lengths) for the orientation shown in Fig. 1—i.e., where the outward normal to the (1a) subunit side is in a $[\bar{1}\bar{1}2]$ direction. The subunit side structure for that case is shown in Fig. 2(a). Similar remarks apply to the apex structure,

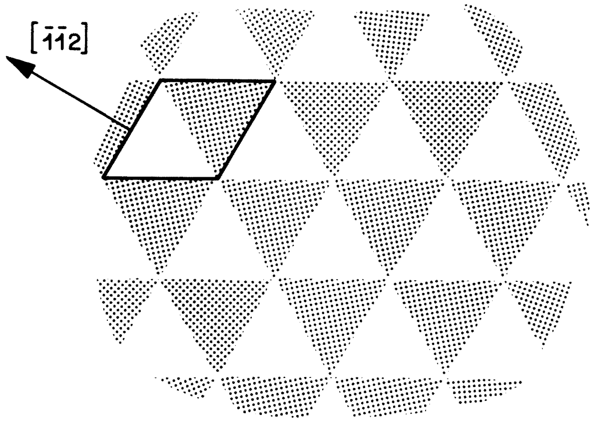

FIG. 1. Triangular checkerboard structure of Si(111)-(7×7) surface (plan view). Open and shaded triangles indicate subunits in which the surface stacking sequences are $\cdots AaBb|A$ and $\cdots Aa|CaA$, respectively. One unit mesh is outlined and the orientation required for joining double layers (see text) is indicated.

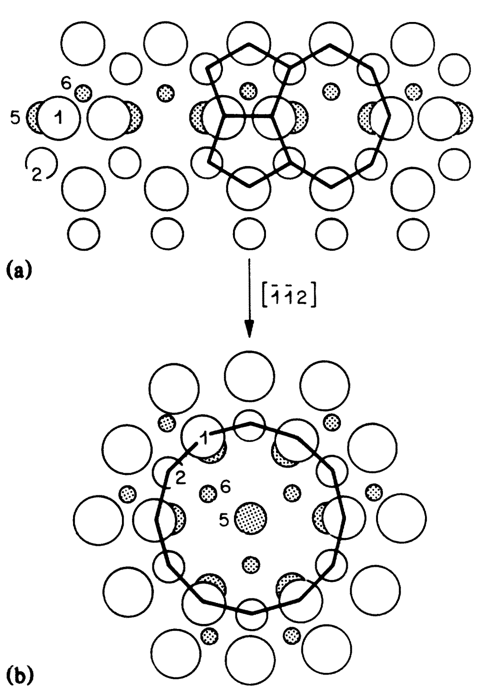

FIG. 2. Structures resulting from the joining of double layers at (a) the edge and (b) the apex of a triangular subunit (see Fig. 1). Atoms belonging to layers 1, 2, ... are represented by circles as indicated. Atoms in layers 3,4 are directly below atoms in layers 1,2 and so are not shown in this view. The visible edge structure (a) consists of pairs of five-membered rings alternating with eight-membered rings as outlined. The dimers (see text) are formed by pairing atoms common to each pair of five-membered rings. The visible apex structure (b) consists of a twelve-membered ring (outlined).

which is shown in Fig. 2(b). The resulting structure of the first two monolayers is shown in Fig. 3(a). Little bond strain is involved in forming this structure or fitting it on to the substrate.

In addition to the stacking fault, which explains the ion backscattering results, the model in Fig. 3(a) has certain structural features that have already been respectively inferred from low-energy electron diffraction (LEED) (Ref. 9) or apparently observed directly in tunneling microscopy[10] experiments of Si(111)-(7×7) surfaces. These features are indicated schematically in Fig. 3(b).

An analysis of LEED patterns[9] led to the conclusion that in each (7×7) unit mesh there are nine dimers formed by the pairing of atoms lying on the sides of each triangular subunit. In the model (Fig. 3) there are nine vertically separated *pairs* of dimers with that lateral arrangement. However, the same interpretation of the LEED patterns would go through unchanged because the relevant beam intensities were attributed to a forward scattering process and so would be insensitive to vertical atom displacements.

The conclusions based on LEED are strongly supported by observations of the Si(111)-(7×7) surface by 100-kV transmission electron diffraction.[11] The diffraction pattern can be described by kinematical theory[11] and is thus much easier to interpret than are LEED patterns. Figure 4 shows the observed pattern[11] together with the intensity distribution among the fractional-order beams as calculated kinematically for the model. The observed and calculated patterns agree to the extent that the intensities of any two neighboring beams are given in the same order. For example, along the line joining the (10) and (11) beams, both the calculated and observed intensities (m_1m_2) of the $(m_1/7\, m_2/7)$ beams are in the order $(71)>(72)<(73)>(74)$. The overall appearance of the pattern is also given correctly by the model. Almost all the fractional-order spots off the lines joining neighboring integer-order ones are very weak. This is a consequence of the shape transform of the triangular subunits of the model as has already been explained in the context of LEED.[12] The irregular variations of fractional-order intensity along the lines joining neighboring integer-order beams are characteristic of the specific arrangement of nine dimers (or dimer pairs) provided by the model. The extent of qualitative agreement is not particularly sensitive to the length of the dimer bonds; qualitatively similar calculated patterns are obtained for dimer bond lengths ranging from 2.3 to 2.7 Å.

Tunneling microscopy[10] has revealed a large round depression at the apex and six smaller oval depressions along the sides of each triangular subunit. The model (Fig. 3) accounts well for the lateral sizes and shapes as well as the positions of these depressions. The maximum observed excursion of the experimental scans (~ 3 Å) was smaller than the depths of the holes in the model (6.3 Å) but this would be expected and does not appear inconsistent with the ~ 3 Å lateral resolution of the experiment. The adatom structure proposed[10] to explain other details of the observations was not present on Si(111)-7×7 surfaces observed by transmission electron diffraction.[11] The features attributed to adatoms are at the positions of certain first-layer atoms in the model (Fig. 3); the possibility of assigning the observed features to variation of electronic factors in tunneling to inequivalently situated surface atoms should not be overlooked.

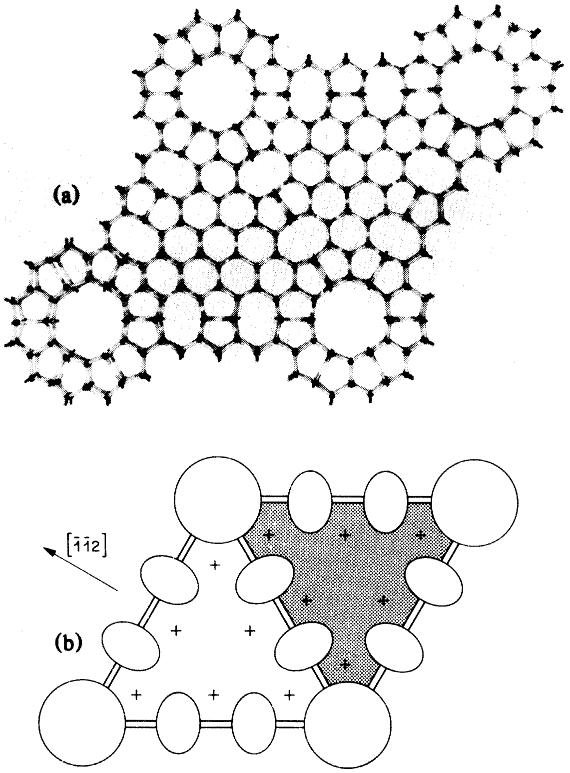

FIG. 3. Content of the outermost two double layers of the (7×7) unit mesh. (a) Ball-and-stick model. (b) Schematic indication of structural features, namely dimers (double lines), oval holes bounded by eight-membered rings (outlined) and round apex holes bounded by twelve-membered rings (outlined). The holes are two double layers (6.3 Å) deep. Crosses indicate first-layer atoms referred to in the text. The open and shaded areas have the same meaning as in Fig. 1.

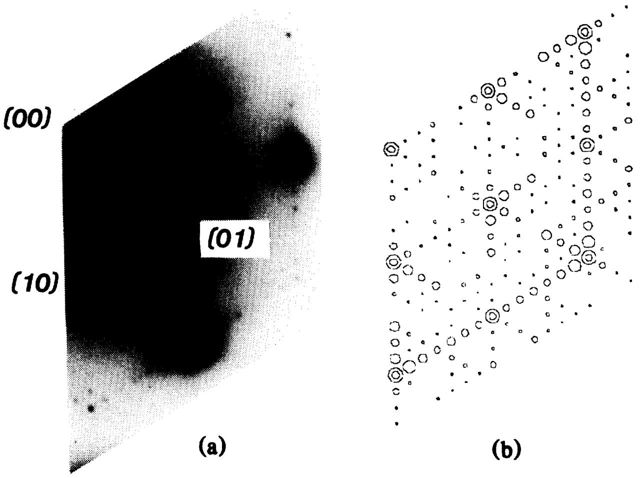

FIG. 4. (a) Diffraction pattern observed in transmission of 100-kV electrons through Si crystal. The pattern has approximate six-fold symmetry. Only one-third of the observed pattern is shown (courtesy of Spence and Takayanagi, Ref. 11). (b) Diffraction pattern calculated by kinematical theory for the model shown in Fig. 3(a). Double circles indicate the positions of integer-order beams. The areas of the other circles are proportional to the calculated intensities of the corresponding fractional-order beams.

The model proposed in this paper (Fig. 3) might at first sight appear very complicated, but it can be rationalized by a single stabilizing interaction, namely, the backbonding of surface atoms to atoms directly beneath them. This can be important only for wurzitelike surface stacking sequence.

When an atom takes part in backbonding, the lengths of the bonds between it and neighboring atoms in the same double layer are not importantly affected. Therefore, backbonding inevitably causes compressional stress of the outermost two double layers. The (7×7) reconstruction may be viewed as the mechanism whereby this compressional stress is relieved.[13]

The model provides 30 surface atoms per (7×7) unit mesh that are favorably situated to form back bonds. These comprise the 15 surface atoms in each triangular subunit. The stability of the (7×7) surface results from the energy benefit of backbonding less the strain energy cost of the lateral expansion of the outermost two double layers in each subunit.

In $N\times N$ analogs of the model (N odd, $N\geqslant3$), both the backbonding energy benefit and the strain energy cost per unit area increase as N increases. The backbonding energy benefit increases approximately as the number of back bonds per unit area increases—i.e., as $(N-1)(N-2)N^{-2}$. The strain energy per unit area is very small for $N=3$ and increases approximately as $N(N-3)$.[14] The shapes of these variations depend on the $N\times N$ model geometry and guarantee that the net energy has a minimum for a finite value of N. Thus the occurrence of a (7×7) unit mesh may be interpreted as a minimum of the net energy for $N=7$.

A satisfactory account of the (7×7) reconstruction requires that the postulated backbonding be sufficiently strong to account for the observed stability of the (7×7) relative to the (2×1) surface observed on cleaved Si surfaces.[15] In order for the energy lowering per (1×1) unit mesh area to equal the value for the 2×1 surface (0.2 eV) (Ref. 16) it would be necessary for the energy benefit per back bond to exceed $\frac{49}{30}$ times this value—i.e., ~0.4 eV. This is a plausible backbonding energy. Recent molecular cluster calculations[17] have shown that both silyl (SiH_3) cation and silyl anion form stable linear three-center bonds with disilane (Si_2H_6). The bond energies are about 0.4 eV in both cases.[17] However, the neutral silyl radical was found to bond comparatively weakly to disilane. It is not known to what extent these results are transferable to Si surfaces.

A fuller account of several topics touched on in this paper is planned for publication elsewhere.[18]

ACKNOWLEDGMENTS

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[8] The statement that the best fit to ion backscattering results is obtained with a 50-50 mixture of stacking sequences (1a) and (1b) (see text) is based on inspection of Table I of Ref. 5 together with rough estimates of the additional surface peak contributions due to atom displacement away from bulk (diamond or wurzite) positions. However, it is not possible on this basis to rule out other possibilities including 100% (1b) stacking (Ref. 5). This possibility can be accounted for by a checkerboard structure such as that of Fig. 1 where the open areas indicate double-layer islands [E. G. McRae (unpublished)]. The edge and apex structures are, however, identical to those arrived at for the case considered in the present paper [E. G. McRae (unpublished)]. Recent tunneling microscopy results [G. Binnig, H. Rohrer, C. H. Gerber, and E. Weibel, Phys. Rev. Lett. 50, 120 (1983)] deny the existence of double-layer islands, in apparent conflict with earlier experimental findings [M. J. Cardillo, Phys. Rev. B 23, 4279 (1981); E. G. McRae and C. W. Caldwell, Phys. Rev. Lett. 46, 1632 (1981)].

[9] E. G. McRae, Surface Sci. 124, 106 (1983).

[10] Binnig, Rohrer, Gerber, and Weibel, Ref. 8.

[11] J. C. H. Spence and K. Takayanagi, *Ultramicroscopy* (in press).

[12] McRae and Caldwell, Ref. 8.

[13] The idea that the (7×7) reconstruction involves the relief of compressional stress was introduced by J. C. Phillips [Phys. Rev. Lett. 45, 905 (1980)] in the context of his double-layer island model.

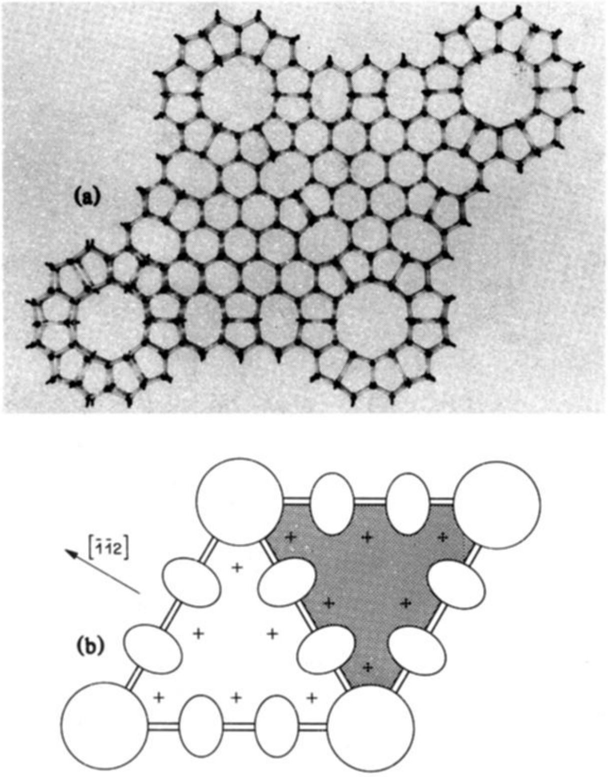
[14] The strain energy has a major contribution from the bending of bonds between the fourth and fifth atom layers. This contribution has the indicated dependence of N. However, there are other important contributions having a slower dependence on N (McRae, Ref. 8).

[15] The (7×7) surface is more stable than any other surface on Si(111) at temperatures up to 1040 K. In particular, the (2×1) reconstruction of Si(111) surfaces formed by cleaving reverts to (7×7) on mild annealing (Refs. 1 and 2).

[16] The value cited is relative to the relaxed (1×1) surface (diamond stacking). The energy lowering relative to unrelaxed (1×1) has been estimated as 0.35 eV [K. C. Pandey, Phys. Rev. Lett. 49, 223 (1982)] of which 0.15 eV is attributable to relaxation.

[17] L. C. Snyder (unpublished).

[18] McRae, Ref. 8.



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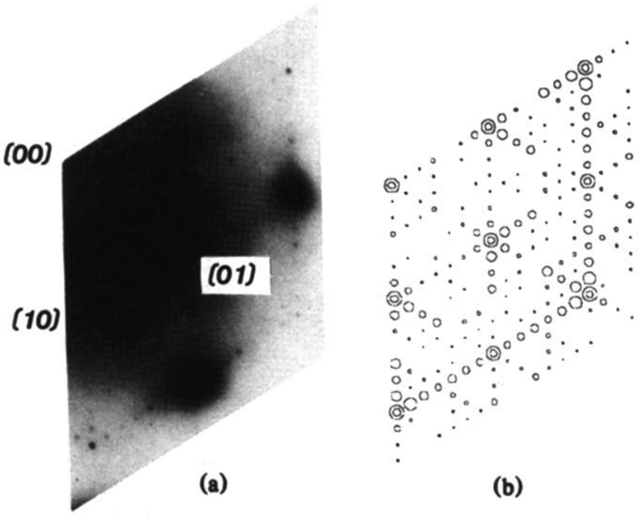

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