Structure of cleavage steps on Si(111)

D. Haneman

School of Physics, University of New South Wales, P. O. Box 1, Kensington, Australia 2033
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The occurrences of (322)-type steps, as experimentally observed by scanning tunneling micros-copy (STM) on cleavage surfaces of Si, are shown to arise naturally on the three-bond-scission mod-el of Si surfaces. Two kinds of structure arise from this model and appear to be consistent with the two types observed by STM, providing a straightforward explanation of the data without complex reconstructions.

There have been several theoretical speculations and calculations about the structures of steps on (111) cleavage surfaces of Si,[1-3] and particular discussion has focused on the experimental observation[4-7] that steps are of the [$2\bar{1}\bar{1}$] type and not the opposite direction [$\bar{2}11$] type. Recently, excellent scanning tunneling microscopy (STM) data have been obtained for such steps,[8] showing that the experimental situation is rather different from those previously calculated. It features at least two kinds of steps that appear to be (332). Interpretation of the data was made in terms of the (111) surface having the Pandey-model (PM) structure,[9] based on cleavage proceeding through the single bond (111) plane, followed by subsurface bond breaking and substantial re-structuring of the surface. The structures that were pro-posed for the steps to fit the STM data were also com-plex,[8] and are subject to serious conceptual difficulties, as discussed below.

We recently introduced an alternative model for (111) cleaved surfaces based on the proposal that scission occurs through the three-bond (111) plane [the three-bond-scission (TBS) model], which possesses the experi-mentally necessary features of bonded chains in the [110] directions in the surface.[10,11] It also has the conceptual advantage of no bond breaking and little restructuring after cleavage. Other important advantages have been discussed recently.[12] It is therefore of interest to see whether this TBS model can account for the STM step data. We show that it does, and that it is only necessary to invoke simple lattice relaxations at the steps rather than postulate extensive restructuring.

The STM data of Feenstra and Stroscio[8] show that at least three kinds of step region occur: (1) disordered, (2) those showing an apparent double step (2S) in the transi-tion region that covers the drop of 3.14 Å from one (111) plane to the next, and (3) those showing an apparent tri-ple step (3S). Interestingly, the 2S and 3S regions were adjacent.

To understand the data, we first briefly discuss the ideal step situation. For the case of single bond cleavage, two possible ideal (shortest) steps are shown in Figs. 1(a) and 1(b) for the observed [$2\bar{1}\bar{1}$] direction, and a recon-struction of Fig. 1(b) proposed by Pandey[2] is shown in Fig. 1(c). This bending down of the bond to the edge atom obviously involves considerable angular strain, and

also bond-length strain according to calculations by Chadi,[3] who found the energy-minimized structure to have bond-length expansions as large at 5.7%. However, this effect is balanced overall by the removal of the dan-gling bond.

If the cleavage is initially as shown in Fig. 1(a), there is an ideal double sp^3 dangling bond. It has been calculat-ed[1] that this could rehybridize to a low-energy doubly occupied sp state and a high-energy empty p state, result-ing in significant lowering (from 2.35 to 0.4 eV) of the en-ergy required to create the extra dangling bond.
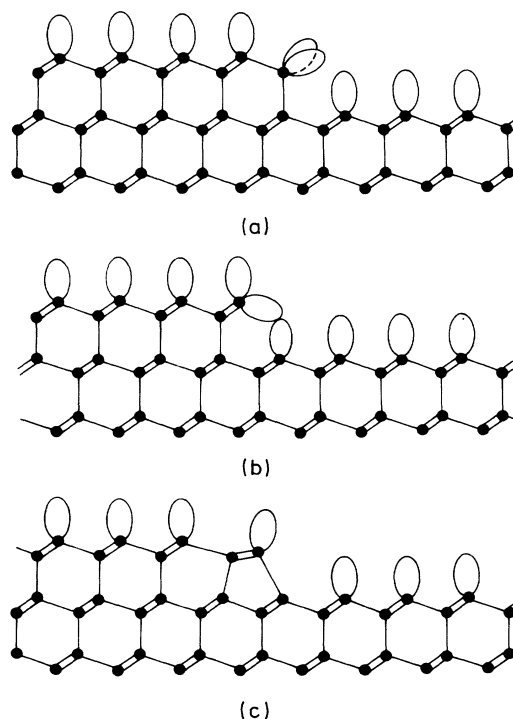

FIG. 1. Schematic view of the ideal (shortest) step along [$2\bar{1}\bar{1}$] direction. The step edge runs along the [$01\bar{1}$] direction. The single lines represent bonds in the [$01\bar{1}$] planes. The shorter double lines represent two bonds that are at an angle (ideally half the tetrahedral angle) to the [$01\bar{1}$] planes. (a) Case of two dangling bonds at the step. (b) Case of one dangling bond at the step. (c) Possible reconstruction of (b) according to Pandey (Ref. 2).

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In principle there are, in addition to Fig. 1, an infinite number of possible [$2\overline{1}\,\overline{1}$] step geometries. These depend on (a) whether the (111), horizontal, cleavage is through a single- or three-bond plane, (b) whether, in the former case, the vertically inclined portion of the cleavage is through a single- or two-bond plane [Figs. 1(b) or 1(a), respectively], and (c) the width of the step-edge reconstruction region. Defining the step orientation as that of a plane laid across the step to join the nearest edges of the prevailing (111) structure, calculations of step energies were carried out by Chadi[3] for (331) steps (propagating in the [$\overline{2}11$] direction, which is not seen in cleavage), and for (311) and for (211) steps. However, from the STM data, the step orientation turns out to be (322), so that the calculations are not directly applicable. It may be noted, however, that for the (211) step, Chadi's surface energy calculation showed that the Pandey-model surface structure was strongly inhibited. Here the terrace width is $2\frac{2}{3}c$ versus $4\frac{2}{3}c$ for a (322) step, where c is 3.32 Å. If the calculation has relevance to the (322) case, it suggests that the PM structure should not occur right at the step edge. However, such an occurrence was invoked to account for the STM data. Two models were proposed[8] for the three-step structure, which are shown in Fig. 2(a) and 2(b), and one for the two-step structure, which is shown in Fig. 2(c).

In assessing the models, the authors referred only to the dimensions that are shown on the diagrams in Fig. 2. The two rows observed in the step-edge region were reported to have a lateral separation of 4.5 ± 0.5 Å. The values for the models in Figs. 2(a) and 2(b) were 5.1 and 3.6 Å.

In order to test alternative models, we measured the x (lateral) and z (vertical) parameters of the STM contour plots, and first compared them with those of the atom centers in the proposed models in Fig. 2. While there are estimation errors of 0.1 to 0.2 Å in this procedure, and the STM contours reflect the positions of the outer portions of electron charge distributions and not atom centers, giving lateral errors[8] of 1 to 1.5 Å, nonetheless it is a guide that is often used in dealing with STM contours. The values are shown in Table I and do not show a strong match between the data and the models of Fig. 2. While appreciating that the significance of this procedure is limited, we need some form of guide to test the fit of al-
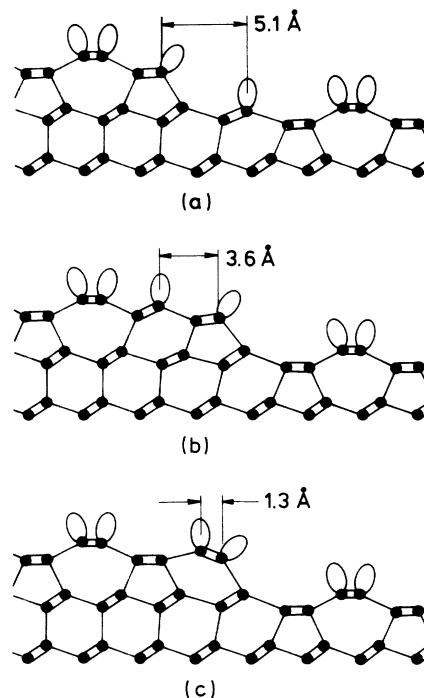

FIG. 2. Models of steps proposed by Feenstra and Stroscio (Ref. 8). (a) and (b) refer to case (3S) where three substeps are observed and were given as alternative possibilities. (c) Refers to the case (2S) of two substeps.

ternative models.

Apart from aspects of the fit above, there are conceptual difficulties with the models. At the instant of cleavage, the structure for single-bond cleavage is presumably as shown in Figs. 1(a) or 1(b). To achieve the structure of the models in Fig. 2, the surface portions must first undergo subsurface cleavage on every second bond, as discussed previously.[10] The extra energy that this appeared to require, not found experimentally,[13] was shown to be much less than supposed, by postulating a process in which new bonds formed before old ones were fully broken.[14] However, this scheme required very strong shear forces in the surface layer. It was shown that there was no conceivable origin for such forces,[10] and that the above calculation had succeeded in translating the prob-

TABLE I. Parameters (in Å) of step contours from STM data and from models. The incremental depth Δz is of the substep peak below the surface. For models, distances are between nuclei. Estimates are accurate to 0.1–0.2 Å. Total is theoretically 3.13 Å. The incremental distance Δx is of the substep peak from the prevailing surface edge atom peak in the [$2\overline{1}\,\overline{1}$] direction. For models, distances are between nuclei. Estimates are accurate to 0.1–0.2 Å. Total is theoretically 15.5 Å.

| | | Incremental depth Δz | | | | | Incremental distance Δx | | | |
| | | | Model FS | | | | | Model FS | | |
		Data	a	b	Model H		Data	a	b	Model H
3 substeps	Δz_1	~0.8	~0.9	~0.5	0.6	Δx_1	~5.4	~4.1	~4.1	7.0
	Δz_2	~1.8	~2.5	~1.0	2.4	Δx_2	~4.5	~5.1	~3.6	3.6
	Δz_3	~0.3	0	~1.8	0.1	Δx_3	~5.6	~6.3	~7.8	4.9
2 substeps	Δz_1	~1.3	~0.7		1.1	Δx_1	~6.9	~7.2		7.7
	Δz_2	~1.7	~2.4		2.0	Δx_2	~8.5	~8.3		7.8

lem of accounting for nonexistent energy into one of pos- tulating apparently nonexistent forces. In the case of the step, this problem is heightened, since subsurface bond- breaking reconstructions are supposed to occur right at the step edge. Here it is even harder to see how the re- quired shear forces could originate.

An additional problem is that the two-step and three- step structures are observed to occur contiguously. Hence one must suppose that both the structure in Fig. 2(a) or 2(b) is created, and also that one cell constant along the step, the structure in Fig. 2(c), is created.

We now consider the step problem from the TBS mod- el. The structure, in untilted form, has been shown to have a reasonable low-energy electron-diffraction fit fac- tor of 0.3 in recent calculations.[15] Figure 3(a) shows the ideal (shortest) cleavage, corresponding to Figs. 1(a) or 1(b). Note that for $[2\bar{1}\bar{1}]$ cleavage, there is now only one possible ideal structure, the vertically inclined portion of the cleavage passing through the double bond and leaving these two bonds dangling. However, the onset of the TBS surface structure allows for two further possibilities. The rows of singly bonded atoms pull together to form chains, with the row nearest to the edge pulling away from it as in Fig. 3(b), or towards it as in Fig. 3(c). Then immediately one has two kinds of (322) steps. In the second case the atoms would appear able to bond to the edge atoms, as depicted in Fig. 3(c). Note that this final configuration is the same as that assumed by Pandey for the step in Fig. 1(c), but it arises in a different way alto- gether.

These two structures presumably relax slightly. This is the main assumption necessary to match the STM data. For the case of Fig. 3(b), we assume that the rehybridiza- tion that must occur causes p-like bonding, forcing a reduction of the angle between the two lattice bonds to- wards 90°. This causes a relaxation as indicated, in which bond lengths have been approximately preserved but bond angles allowed to deform. Using a deformation minimization procedure, parameters of the step are shown in Table I. They show a fit somewhere between those of the two models of Feenstra of Stroscio. Note that the spacing between the step rows of 4.5±0.5 Å is not met by the separation of the nuclei in the model (3.6 Å). However, the STM measurement would be of the spacing between the centers of the upward-pointing lobes of charge on the upper row and the tops of those directed at about 45° in the second row, which would add about an angstrom to the expected measurement from our structure, and thus match the data. [This would also ap- ply, to a slightly lesser extent, to the Feenstra and Stros- cio model of Fig. 2(b) but not to model 2(a).]

The nature of the dangling double bond is not known at present. Dimerization along the step edge is not ex- pected on our model, nor was the doubling of periodicity to which such dimerization might lead observed.[8] Chadi and Chelikowsky[1] calculated a minimum-energy sp plus p configuration, although it should be pointed out that cleavage does not necessarily provide a minimum-energy structure.

The reconstruction that occurs for the case of Fig. 3(c) was determined from a similar bond-angle deformation
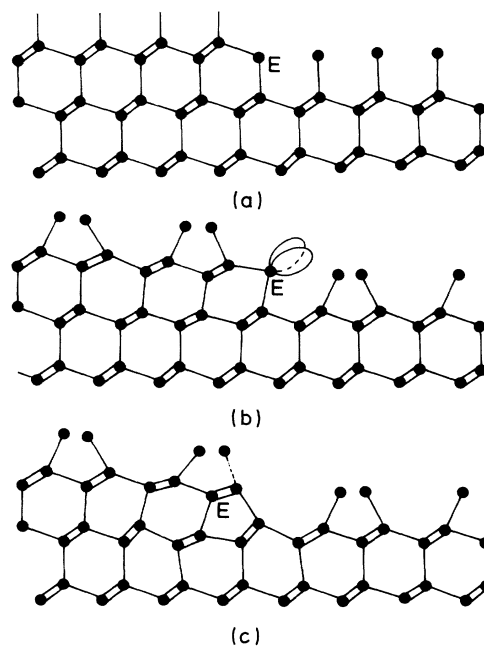

FIG. 3. Models of step based on three-bond-scission model (Refs. 10 and 11). (a) Ideal step, corresponding to Figs. 1(a) and 1(b). (b) Reconstruction with atom rows pairing away from step, giving the 3S case. (c) Reconstruction with the atom row tilting towards the edge atom row, giving the 2S case.

procedure as for Fig. 3(b). Ideally it does not have the atoms that are shown with a dashed bond line, present at the edge. However, there was some indication in the data of Feenstra and Stroscio that an atom-bonded chain oc- curred at the edge in the 2S case. This could be account- ed for by the presence of the atoms shown, which would come by transfer from the top edge of the other portion of the cleavage—during separation such edge atoms seem to be in a readily transferable condition. The corre- sponding opposite surface then has the edge atoms in Fig. 3(c) missing; the many reconstructions that are then pos- sible have not been pursued pending more extensive and quantitative data on these points. The fit shown in Table I is on average similar to that of the model of Feenstra and Stroscio. With present accuracy it is not possible to determine that either model has a better fit.

Note that the explanation for the fact that regions on the step edge which show two rows in the transition re- gion (3S) can be contiguous with regions showing one row (2S) is now understandable. The difference between them simply depends on the phase of the paired atom rows on the surface, which could be partly random. For the con- tiguous structures illustrated in Figs. 3(b) and 3(c), the la- teral separation between the first row of region 3S and the single row of region 2S is 0.7 Å, compared with about 1.5 Å read from the STM contour plots and 2.9 Å from the models of Feenstra and Stroscio. Again we cannot com- ment further about these parameters until their values are more precisely known, after which more detailed calcula- tions would be warranted.

Finally, we refer to the question of the cleavage prefer- ence for the $[2\bar{1}\bar{1}]$ rather than $[\bar{2}11]$ direction. The ex-

planation previously suggested by Pandey,[2] whereby the structure in Fig. 1(c) has the fewest broken bonds, would apply to the structure of Fig. 3(c). However, clearly more than one structure occurs experimentally. That of Fig. 3(b) has ideally more broken bond energy than the equivalent step in the opposite, $[\bar{2}11]$, direction, which could have only one broken bond per edge atom, so that simplistically the $[\bar{2}11]$ direction would be preferred. However, since the step, like the cleavage surface, is likely to be in a metastable condition, these bond-energy considerations alone are not sufficient for analyzing the processes. Both $[2\bar{1}\bar{1}]$ and $[\bar{2}11]$ steps are observed on heated surfaces[7,16] so the energy differences between them are presumably not very great. It is quite possible that step structures of minimum energy do not occur under the conditions of cleavage, which produce a metastable and not minimum-energy phase, as evidenced by the low transition temperatures of the surface.[17,18] It may well be that the dynamics of the cleavage process, which on the TBS theory involves bond reformation at the time of rupture, is complex, and is responsible for the preferred direction of the cleavage steps.

In conclusion, we have shown that the TBS model of cleaved surfaces can account for the STM data on steps, and is able to do so by invoking simple relaxation mechanisms, rather than complex restructuring. This is also the case with the model's explanation of the surface structure itself. It may be helpful to take STM data on other kinds of step to help make the structure solutions more definitive.

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