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## Analysis of the Si(111)5 × 5–2 × 1 phase boundary

D Haneman

School of Physics, University of New South Wales, POB 1, Kensington, 2033 Australia

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**Abstract.** Experimental scanning tunnelling microscopy data for the Si(111)5 × 5–2 × 1 phase boundary are analysed with reference to the structure of the 2 × 1 surface. The height change data are subject to significant correction factors, making interpretation difficult due to the small theoretical differences involved. The theoretical lateral differences are much larger, being 3.3 Å, and these are analysed.

### 1. Introduction

Recently, scanning tunnelling microscopy (STM) measurements were reported for the boundary between the Si(111)2 × 1 structure and a derivative obtained from it by annealing to about 330 °C for 15 minutes, namely Si(111)5 × 5 [1]. The boundary appeared to be sharp, and is of particular interest because its theoretical profiles differ significantly depending on the model used for the Si(111)2 × 1 structure. The authors interpreted their data to favour the Pandey chain (PC) model [2] over the three-bond scission (TBS) model [3,4]. In this analysis we show that the situation is not this clear cut, and indeed one might come to the opposite conclusion.

Figure 1 reproduces a height scan from [1] through the long diagonal of the Si(111)5 × 5 cell, in the [211] direction, crossing orthogonally over the [110] oriented chains of atoms of the 2 × 1 structure. Figure 2(a) shows a top view of the scan, with the dimer–adatom–stacking–fault (DAS) model [5,6] used for the 5 × 5 structure. The 5 × 5 surface is defined as the layer on which the adatoms sit. Figure 2(b) shows a side view of the boundary using the unbuckled PC model for the 2 × 1 structure [1]. The TBS structure is, to a first approximation, simply the PC structure with the top layer of pi-bonded chains of atoms removed. The chains then occur in the new surface layers. Quite clearly there are significant differences: (a) The surface of the (2 × 1) structure of the PC model is at about the same level as the surface of the 5 × 5 structure; (b) for the TBS structure, the surface is at approximately 0.9 Å below that of the 5 × 5.

A glance at the profile in figure 1 shows immediately that the 2 × 1 surface is indeed below that of the 5 × 5, apparently favouring the TBS model. However Feenstra and Lutz [1] made the assumption that the average height of the STM scan of the 5 × 5 structure was not that of the majority surface but of the adatoms. In that way they argued that the observed height difference of  $1.1 \pm 0.2$  Å favoured the PC structure. (The authors interpreted the higher section of 5 × 5 structure they observed at the boundary as due to some electronic enhancement.)

We now examine the question of the STM height difference. Figure 1 shows that the depth resolution of the tip that was used was not the best. Looking at the 5 × 5 surface,

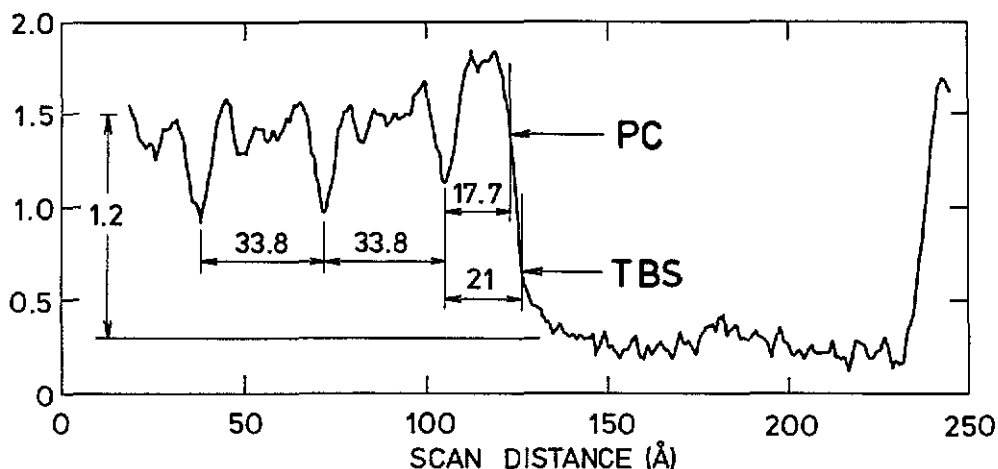
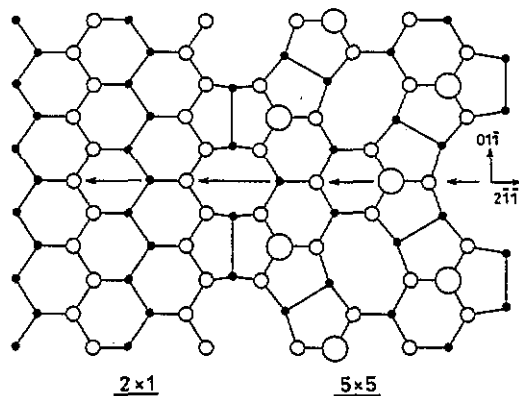


Figure 1. STM scan of profile across  $5 \times 5 - 2 \times 1$  boundary on Si(111), from Feenstra and Lutz [1]. The scan line is shown by arrows in figure 2(a). The LHS in this figure is  $5 \times 5$  phase. Distances and heights are in Å. Theoretical onsets of Pandey chain (PC) and three-bond scission (TBS) models are shown.

(a) TOP VIEW



(b) SIDE VIEW

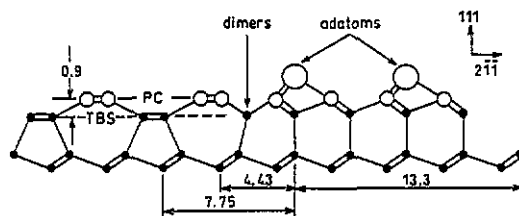


Figure 2. (a) Top view of ideal atom structure across boundary of  $5 \times 5$  (RHS) and  $2 \times 1$  phases on Si(111) surface. Large open circles are adatoms, small open circles are surface atoms. Very small solid circles are atoms in layer beneath surface layer. The  $2 \times 1$  phase shows the PC model. If the small open circles are removed, it shows the TBS model. (b) Side view of boundary. Distances are in Å. Surfaces of PC and TBS models of  $2 \times 1$  structure are indicated.

the height difference between the bottom of the corner hole and the adatoms on either side is only 0.6 Å, against a theoretical value of over 4 Å. In other STM studies of the  $5 \times 5$  structure [7] scans along the long diagonal produced a height difference from hole to adatom of about 2.4 Å. The height difference from surface to adatom was about 1 Å whereas in figure 1 it is only 0.2 Å. A similar reduction occurs for the  $2 \times 1$  surface corrugations.

It must be noted that a blunt tip interacts with not only the nearest atom, but also with adjoining atoms. Of course all tips are blunt to some extent and it is a matter of degree, significant in the present case. The result is that for a given tip current, the tip is at a different height from the surface than a perfect atomic tip since it exchanges current with more atoms. This 'interaction correction height'  $DZ$  depends on the surface structure, i.e. positions and number of surrounding surface atoms with which the tip interacts.

This and other related effects do not matter if the surface structures of the upper and lower levels of a step are the same, since  $DZ$  is the same for both. However, when the arrangements of atoms are very different, as for the  $5 \times 5$  and the  $2 \times 1$  phases, then  $DZ$  for the two can differ significantly. A quantitative estimate is difficult to extract, but a small fraction of an ångström is quite possible.

This is not the only source of correction. The tip samples the outer charge densities of the surface atoms. The height of a given charge density above its nucleus may well differ significantly for different structures. This is particularly so for the  $5 \times 5$  structure with its adatoms and the  $2 \times 1$  structure with its pi-bonded chains. For the latter case, a charge density contour calculation using the PC model in buckled form gave numerical values [8]. From these, one observes that the charge density was a maximum midway along the bond between a surface and second layer atom, with a value of 291 electrons/(3376 au<sup>3</sup>). It appears to have reduced to only half this value at a height of 1.1 Å above the upper surface atom nucleus, and to about 18% of it at a height of 2.0 Å. This suggests that the orbitals extend well upward from the surface nuclei.

In the case of the  $5 \times 5$  structure, there have been two recent calculations of charge density contours [9, 10]. They agree that the heights of the adatoms are different on the faulted and unfaulted halves of the unit cell, the difference between particular adatoms being as large as 0.3 Å, and on average 0.17 Å [10]. This appears to occur in the scan shown in [7], but cannot be reliably discerned in the data of [1]. The significant point is that the higher adatoms have more s-like orbitals, whereas the lower ones have more p-like orbitals. The charge contours are displayed in the calculations of [9], but without absolute units. Although a meaningful comparison between charge contours obtained by different authors on different surfaces should be treated with caution, there is nevertheless a clear indication that the charge contours from the pi-orbitals on the  $2 \times 1$  surface may extend significantly higher than the more s-like orbitals on the adatoms on the  $5 \times 5$  structure. The key question is the magnitude of this difference. Although a reliable quantitative answer is not possible, the above results show that a good fraction of an ångström might be possible.

Finally on this aspect, the discussion by Feenstra and Lutz [1] did not consider the possibility of buckling on the  $2 \times 1$  surface. In the case of the PC model, buckling of around 0.3 Å is required in order to fit ion scattering data [11]. Amounts of 0.35 or 0.38 Å were needed in exhaustive attempts to fit low energy electron diffraction data [12, 13], although a definitive fit could not be obtained.

All the above correction factors operate to reduce the STM height difference from its true value. Thus the difference in height between the  $2 \times 1$  surface and the  $5 \times 5$  layer of adatoms is subject to underestimation even by a sharp tunnelling tip due to the higher charge contours expected from the  $2 \times 1$  surface. In addition, the density of adatoms on the  $5 \times 5$  surface is lower than that of the atoms on the  $2 \times 1$  surface. Hence the  $DZ$  correction

factor would also cause the tip to sit lower on the  $5 \times 5$  surface than on the  $2 \times 1$  surface. The amount is difficult to quantify, but increases with tip bluntness. Finally if there is significant buckling on the  $2 \times 1$  surface, the difference in heights will be reduced again.

From this we conclude that the height difference of  $1.1 \pm 0.2$  Å reported by the STM measurement of Feenstra and Lutz [1] could well conceal a much larger true difference. The theoretical height difference from the adatoms on the  $5 \times 5$  surface to the TBS surface structure is about  $2.2 \pm 0.2$  Å. The quoted error arises from the fact that there is no quantitative structure determination of the  $5 \times 5$  surface. The figure is reduced by about 0.3 Å if buckling is taken into account. Given all the above uncertainties, the two figures can certainly not be declared as incompatible.

There is another difference between the theoretical profiles across the boundary. The  $2 \times 1$  average surface is established closer to the  $5 \times 5$  structure boundary for the PC model, figure 2(b) than for the TBS model. The difference is approximately 3.3 Å, and one could expect to be able to detect this difference. To test this, one needs to establish a clear origin on the  $5 \times 5$  surface. The electronically enhanced edge might be unreliable. However the deepest points of the corner holes are clearly defined. For the three shown in figure 1, the distances scaled from the graph are 33.8 Å, in excellent agreement with the theoretical 33.3 Å. (All parameters are given to three significant figures only.) Therefore we take the last corner hole before the boundary as the origin. From the models, the first  $2 \times 1$  row should start at 17.7 Å for the PC structure, and distinctly further out, at 21 Å for the TBS structure. The start is measured at the axis of the first line of atoms of the new structure.

These distances are marked on figure 1. Clearly, the theoretical onset of the PC structure does not agree with the data at all. However the TBS onset occurs correctly near the base of the profile step.

To critically assess this point, one must check the magnitude of any edge effects that could distort the data. An estimate of these is possible. The corner hole in the  $5 \times 5$  structure represents a relatively broad feature. It is a pit of depth 4 Å from the adatom level, and the width between the adatoms is a theoretical 13.3 Å. Hence if there is an edge broadening effect, the edges of this pit would be displaced inward, giving a smaller width. From the STM scans, the width of the pit between the adatoms measures approximately 13.5 Å, in excellent agreement with the theoretical 13.3 Å. This clearly shows that any edge broadening was only a small fraction of an ångström, and certainly not capable of explaining away a lateral discrepancy of over 3 Å.

It is still possible to try to rescue the PC model by arguing that the tip has a shape such that although it registers the edge of the corner hole, it gives an incorrect profile. It is difficult to quantify this point. A simplistic argument is to assume that the profile of the tip corresponds to the profile registered for the corner hole. However this assumes perfect rotational symmetry for the tip, and more importantly, does not take into account the role of other atoms on the tip as it enters the hole (assuming the constant current mode), and causes interaction with the edges. However one may look at examples of tips scanning edges shown in the literature. Thus the profile of the step between a  $9 \times 9$  and  $7 \times 7$  Si surface showed the full complement of atoms in the unit cell on the 2 levels, although the drop was 3.1 Å [7]. If the profile had missed some of the structure on the lower level, then some of the cell would have been missing, but this was not the case. This tip was sharper in that it showed a corner hole depth of 1.6 Å, but the drop was much greater, 3.1 Å instead of a nominal 1.2 Å in the case we are discussing. In another example, a 1.3 Å step was shown in profile between two levels of  $2 \times 1$  surface on a Si(100) surface [14]. Here the theoretical corrugation of about 2 Å on the (100) surface appeared as only 0.3 Å on the STM scan. Nevertheless the 1.3 Å step appeared quite clearly with no part of the lower

terrace missing. Therefore in the data shown by Feenstra and Lutz [1], there is an *a priori* possibility that the profile correctly shows the step between the two levels of charge density, and one has to note the discrepancy with the PC model, but fit with the TBS model.

The above discussion has assumed that the atomic boundary is as shown in figure 2. This model is straightforward and consistent with that for the two steps discussed above. There does not appear to be any other way of constructing a boundary so as to bring the PC model further out by the necessary 3–4 Å.

An argument introduced by Feenstra and Lutz refers to the atom densities in the 5 × 5 and PC 2 × 1 surfaces. They used the fact that the top bilayer contains the same numbers of atoms per unit cell for the two models, as a significant factor. However the two structures are totally different. Indeed, it is not even understandable how the very stable PC structure could be affected at all by an annealing temperature of only 330 °C. On the other hand, the TBS structure is less stable [15], and it has been shown in detail how it can convert to a DAS structure at temperatures in the mid-300 °C [16]. Sources of diffusing atoms were required, and these were postulated to be antiphase boundaries [16]. Clear evidence for these has been shown in recent STM studies of cleaved Si surfaces [17]. Although not previously considered in detail, additional sources of diffusing atoms would include kink corners. Diffusion distances of 0.1 μm are readily possible for the times and temperatures used by Feenstra and Lutz, as they themselves demonstrated [1]. Hence there are clear mechanisms for atom supply and diffusion at the temperatures used to form the first DAS structure. The usual principles of energy reduction would appear to be the overriding factors involved in determining the structures formed after heat treatment, with conservation of atom concentration only a component.

Although it is not the purpose of this paper to discuss other aspects of surface models, it may be noted that in the above mechanism for conversion of the TBS model to the 5 × 5 surface, the areas stripped of atoms would be ideally 1 × 1 with one dangling bond per atom. In principle one might therefore expect to see such regions, although the atom stripping may render them disordered. The evidence from low energy electron diffraction is equivocal on the existence of 1 × 1 regions [16]. However at the elevated temperatures and in the presence of atom diffusion, it is likely that atoms from kink corners and elsewhere accrete onto at least some of these initial 1 × 1 regions so as to form the 5 × 5 structure. Therefore it may be difficult to find any ordered 1 × 1 regions in limited area STM surveys of heated 2 × 1 surfaces.

In conclusion, STM profile scans across the Si(111)5 × 5 to 2 × 1 surface phase boundary should provide a differentiator between the PC and TBS models. However the theoretical height difference is only about 0.9 Å, and this is small enough to be affected by various factors discussed above, so as to render a definitive conclusion difficult. The lateral difference is much larger, 3.3 Å, and this should lead to a clearer result. However this data also is subject to tip effects. One concludes that the categorical conclusions of Feenstra and Lutz cannot be supported, to say the least.

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