Reply to comment by D R Bowler et al,

Bi nanolines on Si(001): registry with the substrate

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Abstract

The registry of bismuth dimers, integral components of the bismuth nanoline on Si(001), is examined. In contrast to the currently accepted view, the bismuth dimers are found to be in registry with the two-dimensional lattice created by the silicon dimers. The consequences of this finding are briefly explored.

PACS numbers:
The authors of the previous Comment [1] are aware that we have generated some of the most compelling support for the Haiku Si(001)-Bi nanoline geometry [2–6], first proposed by Owen et al [7]. They have, for example, drawn upon our published work for a review article entitled *Self-assembled nanowires on semiconductor surfaces* that is to be published in the near future [8]. Briefly, we have (1) performed ab-inito theoretical studies of the Haiku nanoline geometry, compared it with other candidate geometries, and found it to have the lowest total energy [2, 4–6], (2) performed scanning tunneling microscopy (STM) studies of the nanoline, and produced: a line profile, a line width estimate and a determination of the Bi-dimer separation for the nanoline geometry on a Si(001) surface, without using H-termination [3, 5, 6], (3) performed theoretical simulations of the STM constant-current topographs and compared these with our experimental images [4–6].

However, in the Comment, Bowler et al. asperse a recent paper that we published in this journal that included a short review of the experimental evidence for/against the Haiku model. In particular, we discussed two experimental studies performed by other groups: an x-ray standing wave (XSW) study [9] and an x-ray photoelectron diffraction (XPD) study [10]. In the Comment, the authors criticize us for ‘failing to note various important experimental facts’. Some of these facts are found in a paper [11] that was published in Physical Review B on 26 September 2005, more than 6 months after our paper was received by Nanotechnology (17 March 2005). The paper [11] provides evidence that the amorphous cap used in the XSW study [9] destroys the nanoline structure.

The authors of the Comment also criticize us for failing to note that the results of the XPD study [10] were analysed using the Miki model. We are aware of this fact but believe that the XPD study is a valuable complement to STM studies of the nanoline geometry and, for reasons presented both here and also below, we suggest that the XPD study should not be disregarded. We have summarised the results of the XPD study and the results of our ab initio calculations in Table 1. The experimental estimates for the Bi dimer bond length and the Bi dimer lateral shift are in reasonable accord with our theoretical predictions; the lateral shift being reproduced most closely by the Haiku model. However, the vertical separation between the Bi dimer and the substrate layer is in poor agreement with our calculations, for both the Miki and the Haiku models. For example, to bring the experimental value for the Bi dimer-to-substrate spacing into agreement with the DFT prediction for the Miki model, the experimental value has to be shifted 1.75 times the quoted uncertainty. For the

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2
Haiku model, the experimental value has to be shifted a remarkable 5.5 times the quoted uncertainty. We had hoped, by drawing attention to this poor level of agreement, that it would encourage the authors of the XPD study to re-analyze their data using the Haiku model or motivate a new study of the nanolines using XPD, a technique that is ideally suited for this purpose. Perhaps the former could be done by K. Miki who is an author on both the comment and the XPD study?

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<th>DFT Miki</th>
<th>DFT Haiku</th>
<th>XPD</th>
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<tbody>
<tr>
<td>Bi dimer to substrate</td>
<td>0.65</td>
<td>1.40</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td>Bi dimer bond length</td>
<td>3.10</td>
<td>3.07</td>
<td>3.0 ± 0.3</td>
</tr>
<tr>
<td>Bi dimer lateral shift</td>
<td>0.47</td>
<td>0.63</td>
<td>0.7 ± 0.3</td>
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</table>

The authors of the Comment also criticize us for failing to notice that the Miki model has the wrong registry with the substrate. They claim that ‘every STM study which has measured the registry of the Bi nanoline, including those by the authors of the article, has concluded that it occupies the space of four substrate dimers with Bi dimers lying between the substrate dimers.’ The issue of registry is of fundamental importance. We have not addressed it explicitly before. We do so now.

In Fig.1 we have reproduced the results of our ab initio STM simulation using the Miki (Fig.1a and b) and the Haiku models (Fig.1c and d). In the lower two panels we have reproduced one of our experimental constant current topographs (e) with the associated linescan (f). Added to all panels are vertical lines coincident with the positions of the silicon dimers in the surface layer. The horizontal lines are baselines, defined to be the average height of the linescan on either side of the nanoline. It has been assumed that the local maxima can be attributed to silicon dimers when the linescan is taken along the dimer rows. We have shown previously [6] that for static dimers there is a doubling of the surface lattice constant and also a phase shift of \( \pi \) if the linescan is taken between rather than on dimer rows. Figure 1 demonstrates that the registry of our experimental line profile is reproduced by the Miki model but not by the Haiku model. The center of the experimental line is coincident with the lattice created by the silicon dimers in the surface layer.
Our STM studies were performed on surfaces that had not been exposed to hydrogen after nanoline growth. In contrast, most of the STM studies cited in the Comment, that address the subject of registry [7, 12, 13], were performed on surfaces that were exposed to hydrogen after nanoline growth. Our simulations [6] suggest that it should be possible to use H-terminated silicon surfaces for studies of line registry, as long as the STM line profiles are taken along the silicon dimer rows, on the clean surface, and along the rows of silicon atoms, on the H-terminated surface. However, it is the line structure on the clean silicon surface that is of primary interest. Consequently after growing bismuth nanolines, we did not expose our surfaces to hydrogen.

Regarding line width, we have stated before [6] that the measured width can’t be used to differentiate between the Miki and Haiku line geometries. To illustrate this we have added three shaded regions on Fig.1 that indicate the full width at half maximum (FWHM) measured relative to the baselines (b, d and f). Although our experiments indicate that the base-to-base width of the line equals four surface lattice constants, the FWHM are in much better accord with both the experimental and simulated topographs; all three FWHM are close to three surface lattice constants (3\(a_o\)), indicating that the measured nanoline width, however it is defined, can’t be used to distinguish between the Haiku and Miki geometries.

To conclude, in our paper we said that ‘The results of the total energy calculations support the stability of the Haiku model over the Miki model’ but that ‘the energetically less stable Miki model exhibits better agreement with experimental measurements for equilibrium geometry’. The results that we have reproduced here demonstrate that the registry of our lines is reproduced by the Miki model but not by the Haiku model. As the authors of the Comment argued, registry is the smoking gun that differentiates between the Miki and the Haiku models. Consequently the conclusions of our paper are strengthened, not weakened, by the consideration of registry. However, the Bi dimers in the nanolines that Owen et al. have grown [7] are clearly out-of-registry with the silicon dimers in the substrate. Consequently, either there are two different nanoline structures or H-passivation complicates the determination of registry. As we mentioned above, our simulations [6] suggest that the latter scenario is unlikely. How about the former? Is it possible that we have grown Miki lines whereas Owen et al [7] have grown Haiku lines? Although this explanation would provide a satisfying solution, it meets with the following objection. At comparable biases, STM line profiles that we have taken across bismuth nanolines have a similar apparent height to those
taken by Owen et al. [7]. However, the Miki and Haiku line structures should have different apparent heights [6]. Clearly further work is needed to bring clarity to these important issues.

FIG. 1: Simulated STM images, calculated for a bias of $V_{\text{sample}} = -1.72$ V (full states), and the corresponding simulated linescans are shown for the Miki (M) model in (a) and (b), and for the Haiku (H) model in (c) and (d), respectively. (e) Filled state STM image of the Bi lines for a bias $V_{\text{sample}} = -2.09$ V and (f) the corresponding linescan. The shaded regions indicate the full width half maximum line widths $\approx 3a_o$. In all panels, except (c) and (d), the center of the line is coincident with the position of the silicon dimers in the surface (vertical lines).