

## 1D semiconducting atomic chain of In and Bi on Si(001)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 L241

(<http://iopscience.iop.org/0953-8984/18/19/L03>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 10:38

Please note that [terms and conditions apply](#).

## LETTER TO THE EDITOR

**1D semiconducting atomic chain of In and Bi on Si(001)****D R Bowler<sup>1,2</sup>, C F Bird<sup>1</sup> and J H G Owen<sup>2</sup>**<sup>1</sup> Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK<sup>2</sup> International Center for Young Scientists (ICYS) and Nanomaterials Laboratory (NML), National Institute for Materials Science (NIMS) 1-1 Namiki, Tsukuba, Ibaraki 305-0044, JapanE-mail: [david.bowler@ucl.ac.uk](mailto:david.bowler@ucl.ac.uk) and [james.owen@nims.go.jp](mailto:james.owen@nims.go.jp)

Received 11 April 2006

Published 25 April 2006

Online at [stacks.iop.org/JPhysCM/18/L241](http://stacks.iop.org/JPhysCM/18/L241)**Abstract**

Deposition of In onto a Bi nanoline template on the Si(001) surface at a very low flux produces long, flat islands with a zigzag appearance. We show that these islands result from the intermixing of the In and the Bi dimer atoms in the nanoline, and comprise an In–Bi atomic chain structure along each half of the nanoline in which the In and Bi atoms can take up favoured hybridizations— $sp^2$  (with empty p orbital) and  $p^3$  (with filled s orbital) respectively. There are six different possible isomers of the double-zigzag structure, resulting from different arrangements of the chains on the two sides of the nanolines. Tight-binding and density functional theory (DFT) simulations of the different candidates find that three of these structures have a higher energy than the other three as a result of a repulsive Bi–Bi Coulomb interaction. The two lowest-energy isomers will both match the appearance of the double zigzag in filled-state STM images.

(Some figures in this article are in colour only in the electronic version)

In recent years there has been intense effort applied to the problem of fabricating materials on the nanoscale. The area of nanowires [1], and particularly atomic-scale nanowires, has attracted considerable attention for various reasons: the novel physics which can emerge at these length-scales; the potential use in electronics; and the growth mechanisms which yield these features. On semiconducting surfaces, 1D atomic chains can be formed by several different methods, including epitaxial growth of metals [2], STM lithography [3], adsorption at step edges on vicinal surfaces [4], and high-temperature annealing of deposited metal on a flat surface [5]. However, these techniques give little control over the location or coordination of the deposited metal.

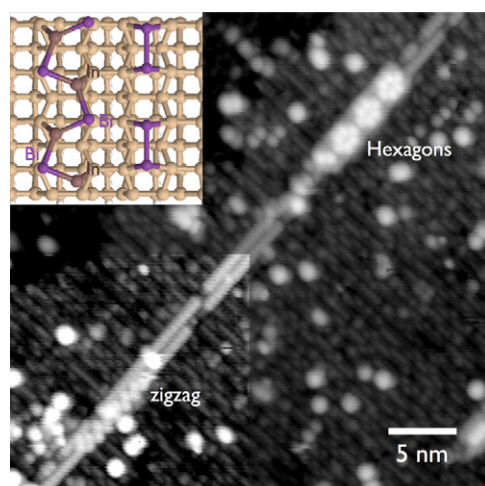
It has recently been shown [6] that the self-assembled Bi nanolines which form on Si(001) [7, 8] can be used as a template for the deposition of atomic-scale wires of metal, with

the structure of the resulting wire dependent on the metal deposited. The nanoscale template is achieved by deposition of hydrogen or ammonia *after* growth of the Bi lines, which passivates the substrate Si without reacting with the Bi [9] and leaves the Bi nanoline as a preferential adsorption site. Unlike the noble metals, which have been found to form nanoclusters along the template [10], In reacts with the Bi dimers of the nanolines, resulting in a one-dimensional III–V semiconducting nanowire. In this work, we investigate the physical and electronic properties of this atomic chain system, and explore the influence of the environment (i.e. the substrate and the two halves of the nanowire) on its electronic and atomic structure.

The experiments described here were performed in a JEOL 4500XT UHV-STM. The formation of the Bi nanoline template is described in detail elsewhere [6]; briefly, Bi nanolines are formed by deposition of Bi onto a clean Si(001) surface at 570 °C. A typical exposure of Bi was given by evaporation from a K-cell at a temperature of 450 °C for 20 min. After deposition, the surface was annealed at the same temperature for 20–30 min under STM observation until the nanolines were the only species visible on the surface, and then the substrate was cooled quickly to room temperature. The background Si was masked off using ammonia, which decomposes on the substrate Si dimers to H and NH<sub>2</sub> [11]. A 4 L exposure of ammonia is sufficient to saturate the Si dimers. We note that, for the deposition of In, there is no practical difference between ammonia passivation and hydrogen passivation. In was deposited onto the substrate at room temperature from an electron-beam evaporator, quantified using the flux monitor. The flux used was roughly 0.005 ML min<sup>-1</sup>. The STM tip was withdrawn during the In exposures, and the surface was examined in between each dose.

For the initial atomic relaxations, we performed tight-binding simulations [12] using a linear scaling technique (where the computational effort scales linearly with the number of atoms, not with its cube as is true for traditional techniques [13]), to test many possible structures rapidly [14]. Specifically, we used an implementation of the density matrix method (DMM) [15]. We used tight-binding parametrizations for Si–Si bonds developed specifically for Si(001) [16] and Bi on Si(001) [17]; In–Si and In–Bi parameters were developed for this work. The unit cells were one dimer row wide (using the  $p(2 \times 2)$  reconstruction), 10 dimers long and 10 layers deep, with the bottom two layers constrained to lie in bulk-like positions, and terminated in hydrogen. The DFT calculations were performed in the generalized gradient approximation (GGA) [18] using the VASP code [19], with ultrasoft pseudopotentials, a plane wave cut-off of 200 eV (sufficient for energy difference and force convergence) and a Monkhorst–Pack  $k$ -point mesh with  $4 \times 2 \times 1$  points. The same unit cells were used as for the tight-binding calculations.

In previous work [6], In deposition onto a Bi nanoline template was found to lead to the formation of elongated In islands on top of the Bi nanoline templates, with two distinct levels. An example is shown in figure 1. The substrate Si dimer rows are terminated by NH<sub>2</sub> and H groups, which have different contrasts [11]. Other features are background Bi dimers (due to the self-assembly process used to create the Bi nanoline template, some density of Bi dimers embedded in the background is inevitable) and double-dot features, which are thought to result from dopant segregation to the surface during the long anneal. Bright dots in the background indicate sites where In atoms have adsorbed onto background Bi dimers. In will not adsorb on a hydrogen-terminated Si(001) substrate [20] and thus it will adsorb either on the nanoline or on these background dimers. The In islands which have formed on the Bi nanoline templates have two different heights: the single-layer islands have a zigzag appearance, either on one side of the nanoline or on both sides, while double-layer islands have bright oval or hexagonal features in the upper layer. The structure of the latter hexagonal features, which are two and a half dimer rows wide, is still under investigation. In this work, we concentrate on the structure of the single-layer islands.



**Figure 1.** 35 nm  $\times$  35 nm STM image of a small coverage of In on a Bi nanoline. No adsorption onto the  $\text{NH}_2\text{-H}$  dimers has occurred. A few small In clusters have formed on background Bi sites. Two distinct layers can be seen in the In islands. The lower layer has a zigzag structure, while the higher layer (which appears white) takes a variety of features, from ovals aligned along the nanoline, to hexagonal features.

We now consider the atomic structure of the zigzag islands. The bright dots in the zigzag structure are measured to be about 1 Å higher than the Bi dimers in the unreacted nanoline, which suggests that they reside in the same layer as the original Bi dimer atoms. The fact that these are filled-state STM images suggests that they are produced by Bi atoms which have reacted with In atoms and been displaced from their original locations. Based on these observations, we developed a structural model for this zigzag feature. A ball-and-stick model is shown in the inset to figure 1. In this model, a chain of alternating In and Bi atoms runs along the nanoline substructure. The STM data indicates that the Bi atoms on the outside of the nanoline are aligned with a substrate Si dimer atom, so that the In–Bi bond on the outside of the nanoline is in phase with the Si dimer row, as shown here.

After relaxing the structure in DFT, we have found that the bond angles of the In are close to  $120^\circ$ , while the bond angles of the Bi are close to  $90^\circ$ , as might be expected from a consideration of the electronic structure of these atoms. We conclude that both species have been able to take up an energetically favourable hybridization—In forming  $sp^2$  hybrids with an empty p dangling bond, and Bi bonding with  $p^3$  symmetry, with an s-orbital lone pair [17]. While the hybridization of In atoms is consistent with normal III–V bonding, as seen on GaAs(110) or InAs(110) surfaces, the Bi hybridization is atypical for III–V bonding—arsenic, for instance, would be expected to take up an  $sp^3$  hybridization. The unusual hybridization found here results from the large atomic number of bismuth, which increases the s–p separation and makes it energetically unfavourable to form any s–p hybrid orbitals. The DFT simulations in this work do not incorporate any relativistic effects beyond those included in the pseudopotentials, though a recent all-electron calculation suggests that the correction might shift the 6s orbital of Bi down by as much as 2.5 eV relative to the 6p [21]. The tight-binding parametrization used was fitted to just such a fully relativistic calculation, and produces bond angles in Bi which are slightly closer to  $90^\circ$ . The DFT structure of the In–Bi atomic wires is consistent with the filled-state STM images, assuming that the visible dots of the zigzag are Bi atoms (which is consistent with the normal appearance of Bi atoms in STM). This would

suggest that, in empty-state images, the empty orbital on the In atoms would be imaged, leading to a phase shift<sup>3</sup>. This assignment is strengthened by considering the difference in physical height between the Bi atoms in the zigzag and the Bi atoms in the nanoline, 0.9 Å, in excellent agreement with the height difference measured in STM.

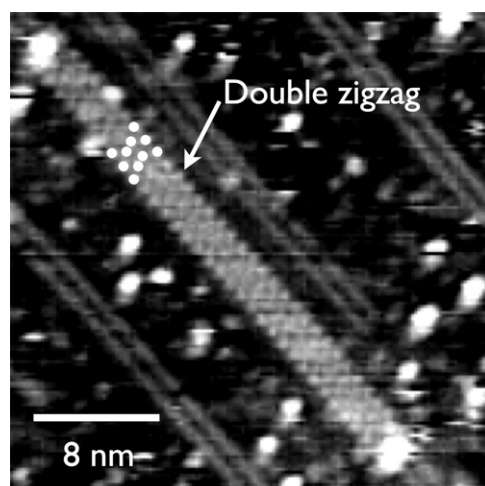
The structure taken for the Bi nanolines is the Haiku structure [8], which places the Bi dimers between the Si substrate dimers, and involves an extensive sub-surface reconstruction. We note that there have been recent suggestions that the Bi nanolines have the structure known as the ‘Miki’ model (where the Bi dimers are in line with the underlying Si substrate dimers, and are separated by a missing surface dimer) [22]. As shown in recent papers [23, 24], we believe that this assignment is contradicted by virtually all the evidence available; nevertheless, small islands of ‘Miki’ structure can remain in the substrate after preparation of a nanoline template [23], so we have modelled the effects of adding In to this structure. We find that it is at least 0.1 eV per pair of In atoms less stable than adding In to the Haiku structure. In experiments, In is not observed to adsorb on the background Bi (i.e. small islands of ‘Miki’ structure) until relatively high coverages of In have been deposited, and no examples of zigzags on the background Bi have been observed. We believe that this results both from the higher energy of In on this structure, and also from the defective nature of this structure, which will introduce large numbers of kinks and terminations, all of which will drive up the energy of In on these Bi dimers. For these reasons, we do not consider the ‘Miki’ model as a substrate for In deposition further.

Under the experimental conditions shown in figure 1, most zigzags seen have formed only on one side of the Bi nanoline: any double zigzags (i.e. zigzags on both sides of one Bi nanoline) have been covered in a second layer of In. However, using a lower In flux, it was possible to grow long, flat islands across the whole width of the nanoline, sometimes up to 50 nm in length. One example is shown in figure 2. The outer Bi atoms are well resolved, but the inner Bi atoms are not well resolved. Two unit cells of the zigzag are marked with white dots as a guide to the eye.

Given a single zigzag structure on one side of a nanoline, several different isomers of double zigzags can be formed. First, a double zigzag can be formed simply by translation of this structure to the other side of the Bi nanoline, producing structure (1) in figure 3. Structure (2) is produced from this by translating the right-hand zigzag along the nanoline by half a cell. Structure (3) is formed from structure (1) by reflecting the right-hand side in a plane perpendicular to the nanoline (i.e. lying along the dimer row), and structure (4) is again produced from this by translating the right-hand zigzag half a cell along the nanoline. Four more structures can be produced from these basic four by moving the entire double zigzag half a unit cell along the nanoline. However, this only produces two new structures: (2b) and (3b); (1b) and (4b) are equivalent to (1) and (4) respectively. On the clean Si(001) surface other isomers could be formed given different arrangements of the buckled Si dimers on either side of the nanoline, but these were not considered as the differences were expected to be small, and in practice all of these isomers form on an H-terminated Si(001) surface, where the substrate dimers are symmetric. The total energies of all these structures were first calculated using a tight-binding simulation, and then further relaxed using DFT, and are shown in table 1. There is good agreement in the ordering of the different structures between the two techniques, although the energy differences are larger in DFT, for reasons to be explored below.

The STM images of the double zigzag may be compared to the real-space electronic morphology of the different structures, as shown by an electron localization function (ELF) plot [25, 26] in figure 4. The identification of the bright dots in STM as Bi atoms is confirmed

<sup>3</sup> We note that it has not yet been possible to achieve high-resolution empty-state images on this surface.



**Figure 2.** A example of a single-layer double-zigzag island. The outer Bi atoms are well resolved and are out of phase with each other. However, the inner Bi atoms are not, but there is some indication that the dots are not evenly spaced. These features rule out isomers 2 and 4, but cannot give definitive identification of the structure between isomers 1 and 3.

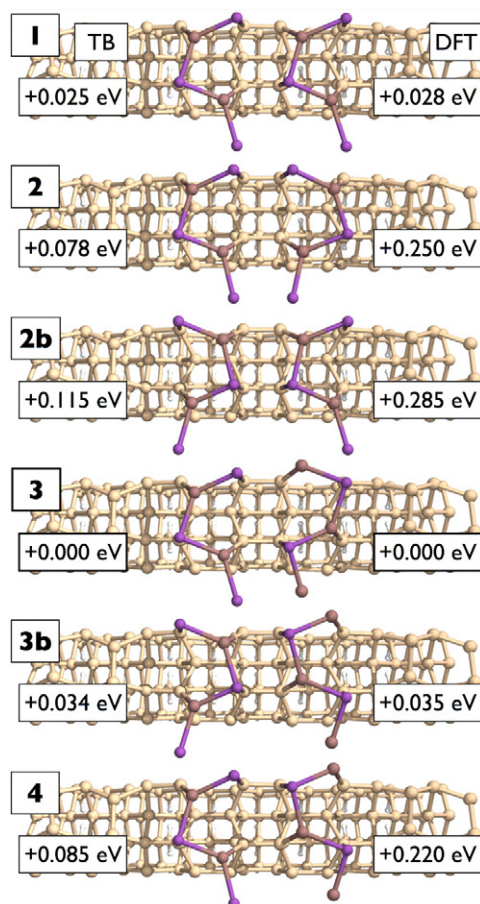
**Table 1.** The relative energies of the different double-zigzag isomers, as shown in figure 3, as calculated by tight-binding and by DFT on a clean Si(001) surface. Structures (2) and (4) are significantly higher in energy than (1) and (3), suggesting a repulsive interaction between adjacent Bi atoms. The second pair of columns gives the energies of these structures on an H-terminated surface.

Structure	TB (eV)	DFT (eV)	H TB (eV)	H DFT (eV)
1	+0.025	+0.028	+0.020	+0.020
2	+0.078	+0.250	+0.070	+0.236
2b	+0.115	+0.285	+0.103	+0.255
3	+0.000	+0.000	+0.000	+0.000
3b	+0.035	+0.035	+0.034	+0.060
4	+0.085	+0.220	+0.078	+0.200

by the ELF plots of all three isomers, where the electron density is localized around the Bi lone pairs. Moreover, the ELF plots can be used to identify the experimentally observed isomer. In the double zigzag shown in figure 2, the bright dots on the outside of the nanoline are out of phase with each other, which rules out structures (2) and (4), in good agreement with the predictions of their stability in DFT simulations. Filled-state STM data cannot distinguish easily between structures (1) and (3), as the main difference is the position of the In atoms, and the sideways shift of the middle Bi atom is very small. In (1) the middle Bi atoms are evenly spaced, while in (3) the spacings are 4.5 and 5.4 Å. The double zigzag shown in figure 2 suggests that it is the lowest-energy isomer, structure (3), which is observed, as the inner Bi atoms are not evenly spaced. However, a clearer image, or better still good empty-state images, would be required to make a definitive identification, and to determine if the other low-energy isomers, (1) and (3b), are ever observed.

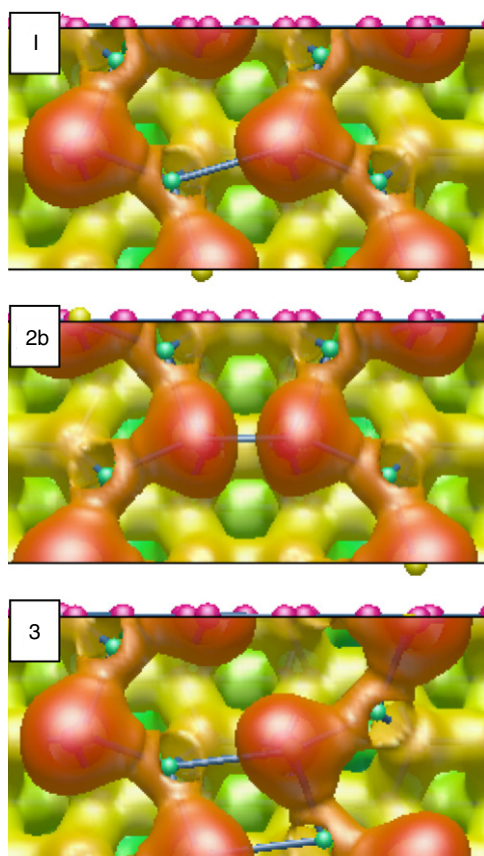
We now turn to the electronic structure of the In–Bi zigzag, in particular the source of the energy difference between isomers 2 and 4, and isomers 1 and 3. This difference is thought to arise from an electrostatic repulsion between the two central Bi atoms, which will cause





**Figure 3.** Ball-and-stick models of the six different arrangements of In–Bi zigzags on both sides of the nanoline. The relative energies given by the simulations are given for each structure, relative to the lowest-energy isomer, structure 3. Edge atoms have been wrapped around; there are only four atoms in each unit cell.

localized strain in the Bi–In and Bi–Si bonds. This strain may be detected from its effect on the electronic structure, as has been seen experimentally in STM in the case of missing-dimer defects on the Si(001) surface [27, 28], and in the case of the clean Bi nanoline [29]. Reduced bonding–antibonding splitting in the strained bonds leads to localization of the states closest to the Fermi level. Thus real-space maps of the HOMO (or equivalently, low-voltage STM imaging) will reveal the degree of localized strain in a system. Contour plots of the highest occupied band from DFT are shown for three isomers in figure 5. Comparing the dimensions and the electronic morphology of the different structures reveals that there are several sources of interaction between the two halves of the zigzag, and between the zigzag and the underlying Si lattice, which can account for their different energies. The strongest interaction is an electrostatic repulsion between Bi atoms. In structures (2) and (4), the inner two Bi atoms are closer to each other than in the other structures (3.5 Å rather than 4.5 Å). The electron density of structure (2b) is significantly distorted compared to that of structures (1) and (3), particularly on the two Bi atoms on the inside of the nanoline. Furthermore, the electron density of the HOMO is localized onto these two Bi atoms, and the In–Bi bonds

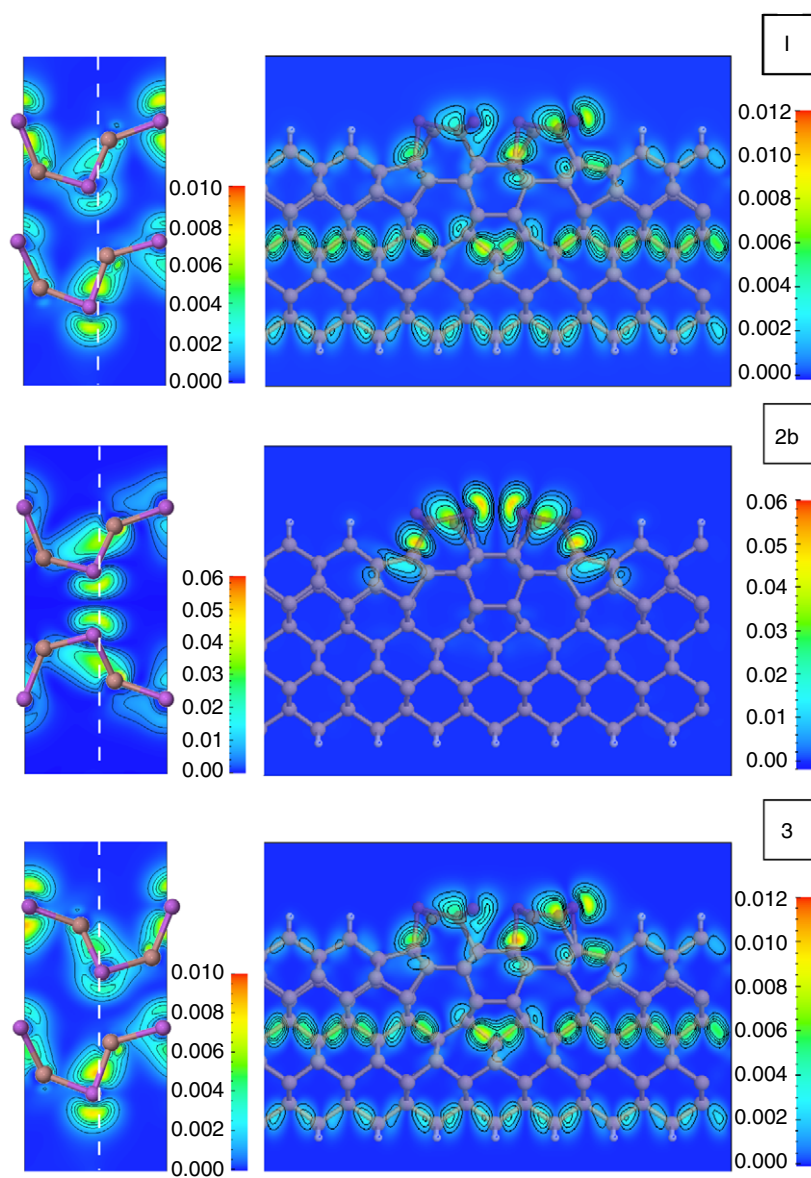


**Figure 4.** Electron localization function (ELF) isosurface plots and electron density contour map for the HOMO for three isomers. The electron density is localized on the Bi atoms. In 1 and 3, the Bi atoms are in almost identical positions, but with differing In positions. Either structure matches filled-state STM images. For structure 2b, the Bi atoms are quite close to one another, distorting their electron clouds. This distortion may account for the higher energy of structures 2 & 2b in DFT simulations.

connected to them (made clear both by the spatial localization of the band, and by the higher electron densities seen in the plot). This indicates localized strain of these bonds, caused by the electrostatic repulsion between the Bi atoms, which raises their energy significantly, by about 0.2 eV in DFT. Second, there is a much weaker positive interaction between the outer In–Bi bonds and the underlying Si dimers. Structures (2, 3) have both In–Bi bonds opposite a Si dimer, while structure (1) has one, and structures (2b, 3b) have none. Finally, comparison of the plots for structures 1 and 3 with that of the clean Bi nanoline on a H-terminated surface [29] suggests that the In zigzag chain is in fact more relaxed than the clean nanoline, where the HOMO is concentrated in the triangular core region below the Bi dimers. The relaxation of the nanoline core may also contribute to the low energy of the zigzag structure.

While the eigenvalues (and hence band structure) derived from density functional theory are not rigorously correct, DFT can give general guidance on electronic structure. A more detailed consideration of the electronic structure of these chains will be given in a future work. However, here we note various important features: first, the bandgap of the zigzag is





**Figure 5.** Electron density contour plots for the HOMO for three isomers in the plane of the surface (left) and in a vertical plane perpendicular to the nanowires (right), as marked by the white dotted line. The electron density is localized on the Bi atoms. In 1 and 3, the Bi atoms are in almost identical positions, but with differing In positions; in both cases, the outer Bi atoms have higher electron densities, in good agreement with STM images. For structure 2b, the electron density has shifted from the outer Bi atoms to the inner two. These atoms are quite close to one another, distorting their electron clouds. This distortion explains the higher energy of structures 2 & 2b in DFT simulations. Note that the scale for structure 2b is rather larger than that for structures 1 and 3.

smaller than that of the bare Bi nanoline, and is comparable to the bandgap of the underlying Si substrate, making this nanoline semiconducting; second, the different isomers have different gaps, depending on their energy (with less stable isomers having a slightly smaller bandgap);

finally, as might be expected, the filled bands nearest the Fermi level are located predominantly on the Bi atoms and the Bi–Si bonds, while the lowest-lying empty bands are localized on the In atoms in the zigzag chain.

We have discovered a one-dimensional III–V semiconductor structure, consisting of a chain of In and Bi atoms. Each species is able to take up its low-energy hybridization, with all bonds either filled or empty, accounting for the stability and the semiconducting character of this structure. Several different candidate structures for a double zigzag have been compared to STM data, and it has been found that the isomer with the lowest energy in DFT is also the one observed in STM. The less-accurate tight-binding simulation was also able to identify the lowest-energy isomer, although the weak repulsive interaction between Bi atoms was not captured. Nevertheless, comparison with the DFT results here validate the use of the tight-binding method to test quickly much more complex structures seen in the two-level In–Bi islands [6]. Lastly, by replacement of either of the two species with another element (in practice, it will be easier to replace the In, by depositing a mixture of metal atoms), it may be possible to dope this structure, and therefore produce a 1D conducting atomic chain.

This work was partly funded by MEXT, Japan (Special Coordination Funds for Promoting Science and Technology) and by the Royal Society (DRB). We are grateful to Dr K Miki for useful conversations.

## References

- [1] Bowler D R 2004 *J. Phys.: Condens. Matter* **16** R721
- [2] Evans M M R and Nogami J 1999 *Phys. Rev. B* **59** 7644
- [3] Hashizume T, Heike S, Lutwyche M I, Watanabe S, Nakajima K, Nishi T and Wada Y 1996 *Japan. J. Appl. Phys.* **2** **35** L1085
- [4] Baski A A, Saoud K M and Jones K M 2001 *Appl. Surf. Sci.* **182** 216
- [5] Gurlu O, Adam O A O, Zandvliet H J W and Poelsema B 2003 *Appl. Phys. Lett.* **83** 4610
- [6] Owen J H G and Miki K 2005 *Nanotechnology* **17** 430
- [7] Miki K, Owen J H G, Bowler D R, Briggs G A D and Sakamoto K 1999 *Surf. Sci.* **421** 397
- [8] Owen J H G, Miki K, Koh H, Yeom H W and Bowler D R 2002 *Phys. Rev. Lett.* **88** 226104
- [9] Owen J, Bowler D and Miki K 2002 *Surf. Sci. Lett.* **499** L124
- [10] Owen J H G and Miki K 2006 *Surf. Sci.* submitted
- [11] Owen J H G, Bowler D R, Kusano S and Miki K 2005 *Phys. Rev. B* **72** 113304
- [12] Goringe C M, Bowler D R and Hernández E H 1997 *Rep. Prog. Phys.* **60** 1447
- [13] Goedecker S 1999 *Rev. Mod. Phys.* **71** 1085
- [14] Bowler D R and Owen J H G 2002 *J. Phys.: Condens. Matter* **14** 6761
- [15] Li X P, Nunes R W and Vanderbilt D 1993 *Phys. Rev. B* **47** 10891
- [16] Bowler D R, Fearn M, Goringe C M, Horsfield A P and Pettifor D G 1998 *J. Phys.: Condens. Matter* **10** 3719
- [17] Bowler D R 2000 *Phys. Rev. B* **62** 7237
- [18] Wang Y and Perdew J P 1991 *Phys. Rev. B* **44** 13298
- [19] Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15
- [20] Zotov A V, Saranin A A, Ignatovich K V, Lifshits V G, Katayama M and Oura K 1997 *Surf. Sci.* **391** L1188
- [21] Ferhat M and Zaoui A 2006 *Phys. Rev. B* **73** 115107
- [22] Miwa R H, MacLeod J M, McLean A B and Srivastava G P 2005 *Nanotechnology* **16** 2427
- [23] Owen J H G, Bowler D R, Kusano S and Miki K 2005 *Surf. Sci.* **596** 163
- [24] Bowler D R, Owen J H G and Miki K 2006 *Nanotechnology* **17** 1801
- [25] Becke A D and Edgecombe K E 1990 *J. Chem. Phys.* **92** 5397
- [26] Silvi B and Savin A 1994 *Nature* **371** 683
- [27] Owen J H G, Bowler D R, Goringe C M, Miki K and Briggs G A D 1995 *Surf. Sci. Lett.* **341** L1042
- [28] Schofield S R, Curson N J, O'Brien J L, Simmons M Y, Clark R G, Marks N A, Wilson H F, Brown G W and Hawley M E 2004 *Phys. Rev. B* **69** 085312
- [29] Owen J H G, Bowler D R and Miki K 2003 *Surf. Sci. Lett.* **527** L177