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# Misoriented Bi dimers blocking Ag nanowire growth along the Bi nanoline: a first-principles study

H Koga and T Ohno

Computational Materials Science Center (CMSC), National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

E-mail: [koga.hiroaki@nims.go.jp](mailto:koga.hiroaki@nims.go.jp) and [ohno.takahisa@nims.go.jp](mailto:ohno.takahisa@nims.go.jp)

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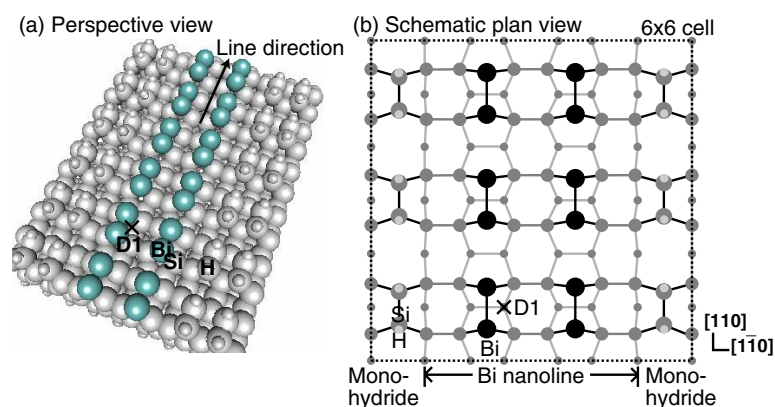
## Abstract

Growth of Ag nanostructures on the Bi nanoline template (a double line of Bi dimers self-assembled on the Si(001) surface) is examined at the level of the generalized gradient approximation. The aim is to find whether Ag adsorption induces the misorientation of Bi dimers (i.e. those oriented transversely), because the misoriented dimers would block Ag nanowire growth along the line. The calculation finds that the Ag tetramer on misoriented Bi dimers is more stable than that on oriented dimers. To grow Ag wires hence requires suppression of the transformation to the misoriented configuration. The calculated energy barriers indicate that it is possible to suppress the transformation without inhibiting the Ag migration to the Bi nanoline. Furthermore, the greater stability of Ag wire nuclei compared to less wetting ones such as the icosahedral Ag<sub>55</sub> cluster also supports the feasibility of Ag wire growth. On the other hand, allowing the misorientation can be useful in growing uniform Ag nanoclusters; an optimum size (~50 atoms) is found for the pyramidal islands that are bounded by misoriented Bi dimers.

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

## 1. Introduction

The ability to control the shape of nanostructures is essential to nanoscience and technology. Nanowires should be thick and continuous to carry an electric current, while arrays of uniform nanoclusters could conduct plasmons [1]. In scanning-probe lithography, the shape is determined by lithographic patterns; e.g. if Ag is deposited on the patterned H-terminated Si(001) surface, elongated islands grow along dangling bond wires, whereas clusters form on isolated dangling bond sites [2]. However, if self-assembled structures such as Bi nanolines [3, 4] (figure 1) are used as templates instead of the dangling bond wires, it is unclear



**Figure 1.** Model of the Si(001) surface covered with Bi nanolines and terminating H. A Bi nanoline consists of two Bi dimer lines. Note that the Bi dimers are oriented parallel to the line direction. The most stable site (backbond site D1) for the Ag adatom [6] is indicated.

how the template structure defines the shape of, and is affected by, the nanostructure growing on it: in experiments [5] on growing Ag nanowires on Bi nanolines, Ag formed clusters instead of wires. To complicate matters, the clusters could hide the changes to the line structure induced by Ag adsorption.

As a first step in clarifying these issues, we have examined from first principles the behavior of a single Ag atom on the Si(001) surface covered with Bi nanolines and terminating H [6]. The calculation has indicated that an Ag atom incident on the H-terminated surface rapidly migrates to a Bi nanoline (barrier 0.14 eV), enters its backbond (gaining 0.7 eV), and then migrates along the nanoline, moving through backbonds (barrier 0.33 eV). The calculation thus confirms that Ag adsorbs preferentially on the Bi nanoline. It also indicates that a Bi dimer could become misoriented (i.e. oriented perpendicular to the line), with Ag inserted into its Bi–Si backbond. Such a misoriented Bi dimer would block Ag wire growth along the line, promoting island growth.

In this first-principles study, accordingly, we examine whether Ag adsorption induces the misorientation of Bi dimers. We also examine how the orientation of Bi dimers affects the shape of the resulting nanostructures. This paper is organized as follows. The calculation methods are described in section 2. The results are presented and discussed in section 3. First, we find the misorientation to be energetically favorable and kinetically feasible when Ag nuclei are very small (section 3.1). Then, we examine Ag wire nuclei, assuming that the misorientation is kinetically suppressed (section 3.2), and find that three-layer nuclei would grow along the line to form a wire rather than change into taller islands. Thereafter, we examine the effect of allowing the misorientation and find the optimum size for Ag islands bounded by misoriented Bi dimers (section 3.3). Lastly, conclusions are given (section 4). The relative stability of Ag nanowires with various lattice orientations [7] and the feasibility of single-atom-wide Ag lines [8] are examined elsewhere.

## 2. Method

Methods and models used in the present calculation are similar to those used in our previous study [6, 7]. The optimized geometries and their energies are obtained in a density functional theory (DFT) [9, 10] plane-wave pseudopotential [11, 12] calculation within the

**Table 1.** Total energy difference (eV) between the linear and misoriented configurations of the Ag tetramer (see figure 4, I and V) calculated under various conditions.

Present	0.21
Cut-off increased to 20 Ryd	0.22
Cell elongated to $6 \times 6$	0.22
Cell widened to $8 \times 4$	0.22
Si layers increased to 8	0.18
Si layers increased to 10	0.18

generalized gradient approximation (GGA) [13]<sup>1</sup>. The plane-wave cut-off energy is 16 Ryd for wavefunctions and 196 Ryd for the charge density.

The slab model of the Bi nanoline surface (figure 1) is as thick as six Si(001) layers and terminated in H at the bottom. The atomic structure determined in [14] is adopted; note that Bi dimers are oriented parallel to the line. The surface off the Bi nanoline is in the monohydride structure. The  $6 \times 4$  cell ( $1 \times 2$   $k$  points) is used in section 3.1 and the  $6 \times 6$  cell ( $1 \times 2$   $k$  points) elsewhere; the  $1 \times 1$  cell denotes the primitive cell of the ideal Si(001) surface. The Ag wire nuclei examined below are positioned so as to occupy as many D1 sites as possible, since D1 has been found to be the most stable site for the Ag adatom [6] (figure 1). As in [6, 7], the energetic stability of an Ag nucleus is expressed in terms of the adsorption potential energy ( $E_a$ ) calculated according to

$$E_a = (E - E_0)/n - \varepsilon_{\text{Ag}}, \quad (1)$$

where  $E$  is the total energy,  $E_0$  is the energy of the substrate,  $n$  is the number of Ag atoms, and  $\varepsilon_{\text{Ag}}$  is the energy of a free, spin polarized Ag atom. In this definition, low  $E_a$  indicates greater energetic stability. As found in [7], the difference of  $\sim 0.01$  eV in  $E_a$  can be discussed. As for the length of the cell, the separation of 0.4 nm between periodic images of Ag nuclei is sufficient: the difference in  $E_a$  between the nuclei shown in figures 5(a) and (d) changes by no more than 2 meV if we shorten the cell to  $6 \times 4$ , although the separation falls below 0.4 nm. The  $6 \times 6$  cell is hence sufficiently large for the longest nuclei (figures 5(c) and (f)), where the separation is 0.55 nm.

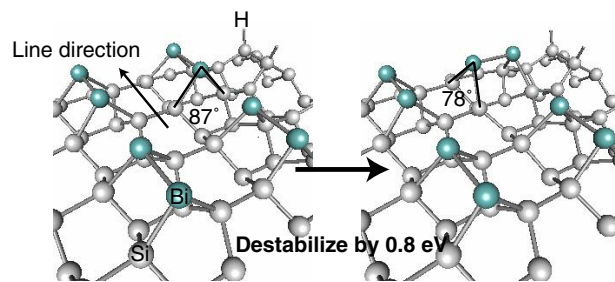
Furthermore, we have calculated the total energy difference between the linear and misoriented configurations of the Ag tetramer (see figure 4, I and V) under various conditions in order to confirm the greater stability of the latter. The results are displayed in table 1. As can be seen, increasing the slab thickness to eight layers changes the difference by 0.03 eV, but a further increase has little effect. The effect of other changes is small. Thus, the energy ordering is unlikely to be reversed.

### 3. Results and discussion

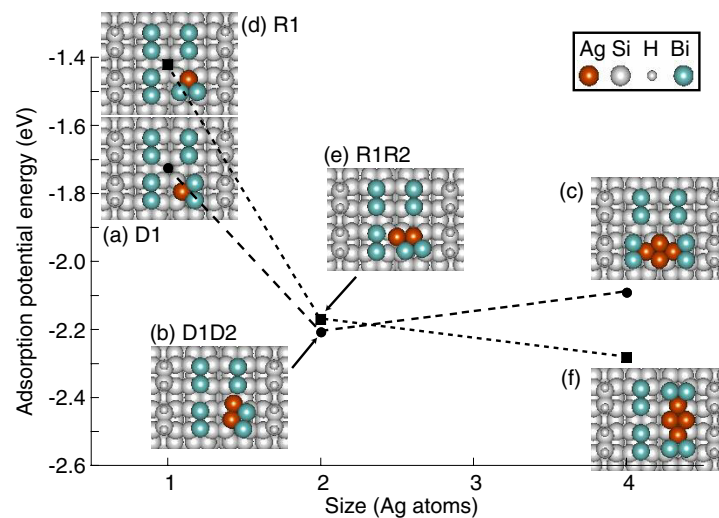
#### 3.1. Misoriented Bi dimers stabilized by small Ag nuclei

In this section, we examine whether Ag nuclei stabilize misoriented Bi dimers at the early stage of growth, because the misoriented Bi dimers, being perpendicular to the line, would prevent Ag nuclei from growing along the line, promoting island growth instead of wire growth. We find that the misorientation becomes energetically favorable and kinetically feasible for an Ag tetramer.

<sup>1</sup> Simulation Tool for Atom TEchnology (STATE) Ver. 5.01, Research Institute for Computational Sciences (RICS), National Institute of Advanced Industrial Science and Technology (AIST), 2002.



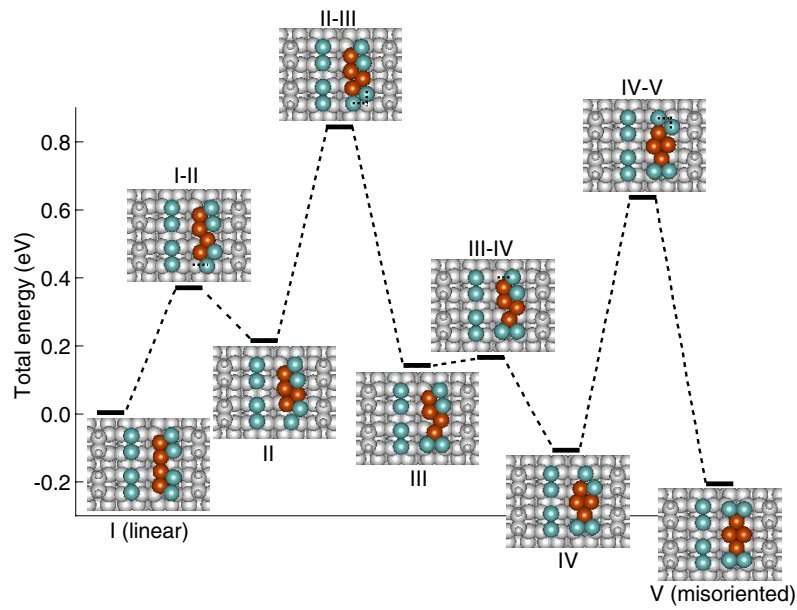
**Figure 2.** On the pristine surface, the misoriented Bi dimer is 0.8 eV higher in total energy than the oriented one (perspective view of optimized geometries). Si–Bi–Si angles are indicated.



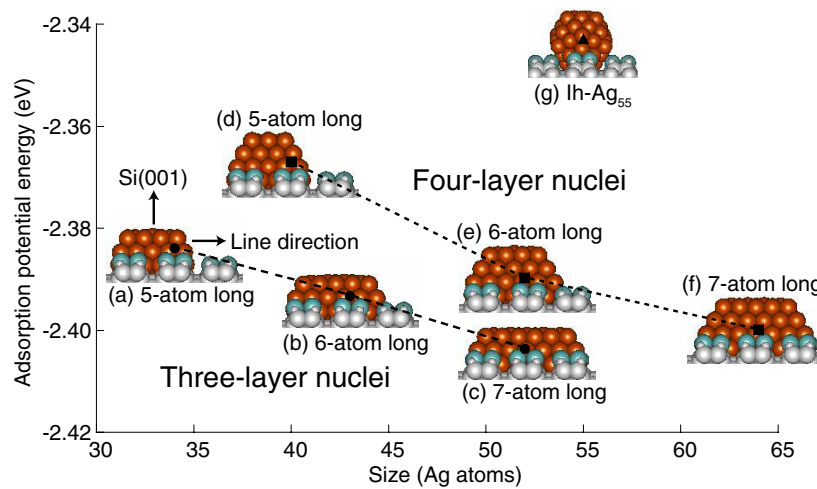
**Figure 3.** Relative stability of oriented (a)–(c) and misoriented (d)–(f) configurations (plan view of optimized geometries). The plot shows the variation of  $E_a$  (eV) with size (Ag atoms). D1 (a) and D1D2 (b) are the most stable configurations found in [6].

On the pristine surface, the misoriented Bi dimer is found 0.8 eV higher in total energy than the oriented one (figure 2). The metastability of the misoriented dimer can be seen also in the straining of the Si–Bi–Si angle indicated in the figure; the angle in the oriented dimer is close to the  $p^3$  bonding angle favored by Bi, whereas that in the misoriented one is not. Thus, misoriented Bi dimers are unlikely to appear before Ag adsorption.

However, Ag adatoms break Bi–Si backbonds [6], making the Si–Bi–Si angle irrelevant. As figure 3 shows, the difference in  $E_a$  between the oriented and misoriented configurations decreases to 0.3 eV for an Ag monomer (figures 3(a) and (d)) and to 0.04 eV for an Ag dimer (figures 3(b) and (e)). Finally, the misoriented rhombic tetramer becomes more stable than the oriented one (figures 3(f) and (c)); the oriented tetramer crosses over the ridge of the underlying Si surface and becomes buckled (middle Ag atoms raised 0.05 nm), whereas the misoriented tetramer fits to a trough and remains planar. Thus, misoriented configurations can become stable at the early stage of growth, when Ag nuclei are very small. (Unfortunately, the experiment [5] was unclear about this possibility, since it did not examine the early stage.) To grow Ag wires hence requires suppression of the transformation to the misoriented configuration.

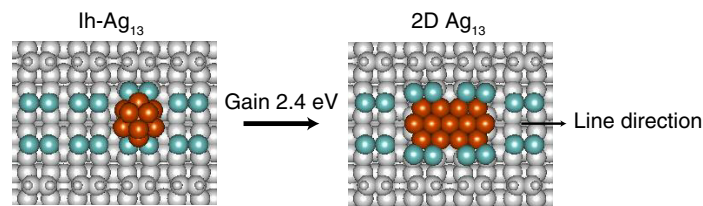


**Figure 4.** Energy diagram for the transformation into the misoriented Ag tetramer. Optimized geometries (plan view) are shown for the initial state (linear chain, I), final state (misoriented tetramer, V), intermediate states (II, III, IV), and the transition states (I–II, II–III, III–IV, IV–V) connecting them. The total energy (eV) is with respect to that of the initial state (I). The backbond being re-formed (I–II, III–IV) and the two backbonds being switched (II–III, IV–V) are marked with dotted lines.



**Figure 5.** Ag wire nuclei (a)–(f) and the icosahedral  $Ag_{55}$  cluster (g) on oriented Bi dimers (side view of optimized geometries). The plot shows the variation of  $E_a$  (eV) with size (Ag atoms).

Figure 4 shows the calculated energy diagram for the transformation into the misoriented tetramer. (As in [6], the transition-state geometries are calculated by the force inversion method [15]. The relaxation of these geometries yields the local minima that they connect.)



**Figure 6.** The icosahedral  $\text{Ag}_{13}$  cluster is 2.4 eV higher in total energy than the two-dimensional wire nucleus of the same size (plan view of optimized geometries).

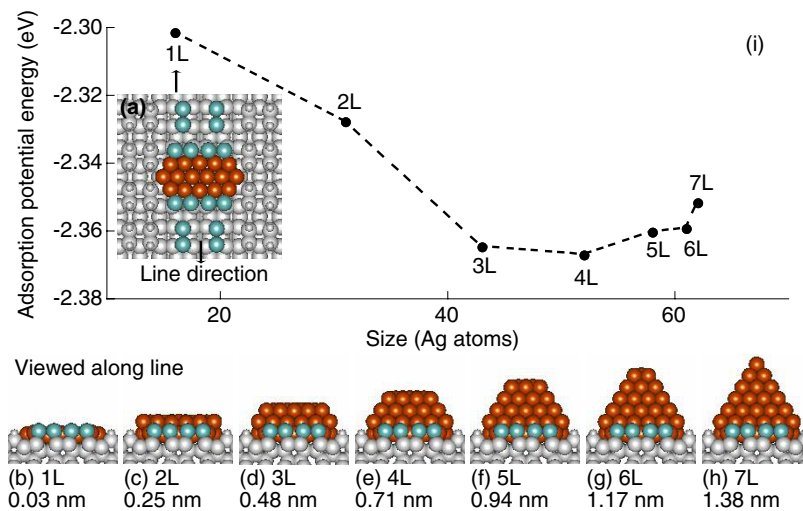
The linear chain (I) is chosen as the initial state, since Ag adatoms migrate one-dimensionally once they reach a Bi line [6]. This linear chain is found 0.21 eV higher in total energy than the misoriented rhombic tetramer (V). This is as expected from the greater number of Ag–Ag bonds in the latter, and the reliability of this energy difference has been ascertained in section 2. The tetramer transforms by the re-formation of a Bi–Si backbond (I–II and III–IV) and the switching of backbonds (II–III and IV–V). The barriers of the switching are relatively high (0.63 and 0.75 eV respectively) and larger than that (0.14 eV [6]) of Ag migration to a Bi nanoline. Barriers of this height can be expected for backbond switching in general, since a Si atom becomes overcoordinated (i.e. to have more than four bonds) while switching two Bi–Si backbonds. It is therefore possible to suppress the transformation without inhibiting the migration to a Bi nanoline.

However, the transformation is feasible at room temperature which was used in the experiment [5]. A few Ag nuclei may remain oriented, but their growth along the line will eventually stop when they meet misoriented nuclei. The experiment [5] indeed found a few elongated islands but no wires. In contrast, indium inserts itself into Bi dimer bonds to form InBi zigzag chains [16, 17]. It is hence unlikely that Bi dimers become misoriented and block the longitudinal growth of In islands.

### 3.2. Ag wire nuclei on oriented Bi dimers

In this section, we examine nuclei of Ag wires, supposing that the transformation to the misoriented configuration is kinetically suppressed. We focus on the nuclei of those wires that have been found to have the greater stability by DFT calculation [7], namely those with the  $\text{Ag}(111) \parallel \text{Si}(001)$  and  $\text{Ag}[110] \parallel \text{Si}[110]$  orientation. The improvement in energetic stability with increasing thickness of wire [7] indicates that Ag forms three-dimensional nuclei (incomplete wetting). However, the four-layer wire has been found only as stable as the three-layer wire [7], although the former is larger than the latter. This could imply that three-layer nuclei are more stable than four-layer nuclei of a similar size and that hence three-layer nuclei grow in the line direction to form wires rather than become taller. To ascertain this, we have calculated the stability of three- and four-layer wire nuclei shown in figure 5. These nuclei are Ag(111)-faceted, truncated trigonal pyramids, representing partially wetting nuclei.

The plot of the calculated energy ( $E_a$ ) against the cluster size (figure 5) shows that the three-layer nuclei are more stable than the four-layer ones of a similar size, as expected. Furthermore, the icosahedral  $\text{Ag}_{55}$  cluster (figure 5(g)), a nonwetting nucleus, is found less stable than the wire nuclei. The icosahedral  $\text{Ag}_{13}$  cluster is also found less stable than the two-dimensional wire nucleus of the same size (figure 6). Thus, the calculation suggests that Ag partially wets the Bi nanoline and that the three-layer Ag wire nuclei would grow along the line rather than become taller. This trend is favorable to the growth of Ag wires.



**Figure 7.** Ag islands bounded by misoriented Bi dimers. (a) Plan view of the largest monolayer island. (b)–(h) Optimized geometries of islands of one to seven layers (viewed along line direction). The calculated heights are also shown. (i) Variation of  $E_a$  (eV) with size.

### 3.3. Ag islands bounded by misoriented Bi dimers

If we allow the misorientation, Ag nuclei would grow into islands rather than wires, because they are surrounded by misoriented Bi dimers and the passivated Si surface (figure 7(a)). In this section, we examine such islands and find their optimum size.

The calculated islands (figure 7) are Ag(111)-faceted, truncated trigonal pyramids with the Ag(111)  $\parallel$  Si(001) orientation, representing partially wetting nuclei. They are similar to the wire nuclei examined in section 3.2 except that the misoriented islands have the Ag[110]  $\parallel$  Si[1 $\bar{1}$ 0] orientation. The base of these islands is Ag<sub>16</sub> (figure 7(a)). This is the largest close-packed (i.e. Ag(111)) two-dimensional structure that fits to the space bounded by misoriented Bi dimers and the passivated Si surface. The tallest Ag(111)-faceted pyramid with this base is the seven-layer island (figure 7(h)). Accordingly, we have calculated the pyramids of one to seven layers.

The calculated heights of the islands are displayed in figure 7. (The height is measured from the pristine Bi line.) Some of the peaks (0.5, 0.7, 0.9, 1.2, 1.4 nm) in the cluster height histograms obtained by scanning tunnelling microscopy [5] are close to the calculated heights of the islands of three to seven layers. Unique identification, however, requires more experimental data.

Figure 7(i) shows the variation of the calculated energy with the island size. As can be seen, the islands of three and four layers, which are about 50 atoms in size, have the greatest stability. Thus, allowing the misorientation can be useful in growing uniform Ag islands.

## 4. Conclusions

Growth of Ag on the Bi nanoline has been examined at the GGA level. We have focused on misoriented Bi dimers, because they would block Ag nanowire growth along the line, promoting island growth. First, we have found that the Ag tetramer stabilizes misoriented Bi dimers. It is however possible to suppress the transformation to misoriented configurations



without inhibiting Ag migration to a Bi nanoline in order that Ag wires can grow; the calculated energy barrier ( $\sim 0.75$  eV) of the transformation is larger than that (0.14 eV [6]) of the migration. Furthermore, on the oriented Bi dimers, the three-layer wire nuclei would grow along the line to form wires rather than become taller; the three-layer wire nuclei have been found more stable than four-layer ones and nonwetting nuclei such as the icosahedral  $\text{Ag}_{55}$  cluster. Finally, allowing the misorientation can be useful in growing uniform Ag clusters; an optimum size ( $\sim 50$  atoms) has been found for the pyramidal islands bounded by misoriented Bi dimers.

### Acknowledgments

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