ELSEVIER

Materials Science and Engineering B 140 (2007) 160–165

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Growth of noble metal nanostructures on the Bi nanoline surface: A first-principles study

H. Koga*, T. Ohno

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

Abstract

Recent experiments suggest that self-assembled Bi nanolines on the passivated Si(0 0 1) surface can be used as templates to grow one-dimensional arrays of noble-metal (Au, Ag) nanoclusters. In order to ascertain this template effect, the gold atom on the H-terminated Si(0 0 1) surface and that on the Bi line are examined by density-functional methods. The calculation indicates that the gold atom enters a Si dimer on the H-terminated surface and the Bi–Si backbonds of a Bi dimer on the Bi line. The gold atom is 0.6 eV more stable on the Bi line than on the H-terminated surface. This result suggests the preferential adsorption of gold on the Bi line and confirms its template effect.

Keywords: First-principles calculation; Surface structure; Gold; Silicon; Bismuth

1. Introduction

Gold nanoclusters are receiving growing attention in nanoscience and technology. The nanoclusters (below ∼5 nm in diameter) on an oxide support exhibit extraordinary catalytic activities [1]. In nanoelectronics research, the nanoclusters are used as key components of single-electron tunneling devices [2,3] and in ohmic nanocontacts [4,5]. Ordered arrays of the nanoclusters (∼50 nm) are investigated for their potential as plasmonic wave guides [6]. The nanoclusters can be used also in biochemical sensors [7].

Most of these applications require the nanoclusters with uniform size and shape, and in some applications, they must be arranged regularly. Preferential adsorption on nano-sized patterns is thus the key to fabricating such nanostructures. One way to prepare nano-sized patterns is scanning-probe lithography. For example, the array of H vacancies drawn on the H-terminated Si(0 0 1) surface by a scanning probe is used as a template for that of silver nanoclusters [8]. Alternatively, self-organized patterns can be used as templates, eliminating the need for pattern drawing. Self-assembled Bi nanolines [9–11] on the Si(0 0 1) surface, in particular, are actively investigated as templates [12–14] for 1D nanostructures including nanocluster arrays, because the Bi lines have a well-defined atomic structure (two straight lines of Bi dimers spaced 6.3 Å apart [15,16]) that can extend over ∼500 nm without defects. Furthermore, the Si(0 0 1) surface can be passivated with hydrogen [11] or ammonia [13] after the Bi lines are formed, to prevent materials (such as gold) from reacting with silicon. According to experiments, indium deposited on the Bi line-covered surface (passivated with ammonia) formed nanoislands elongated along the Bi line [13], while noble metals (Ag, Au, and Pt) deposited formed very small (∼1 nm) nanoclusters on the Bi lines [14].

First-principles calculations are very important in explaining such growth behaviors and also in finding new applications for the nanostructures. The calculation by Orellana and Miwa [17] has predicted that the one-dimensional array of iron atoms on the Bi line shows a magnetic half-metal behavior. In our previous study [18], a silver atom has been found 0.7 eV more stable on the Bi line than on the H-terminated Si(0 0 1) surface. However, the behavior of gold on the Bi line has not been theoretically studied.

In this first-principles study, therefore, we examine the geometry and energy of the H-terminated Si(0 0 1) surface with the Bi line and a gold atom. We find that gold adsorbs preferentially on the Bi line, thus confirming its template effect. This paper is organized as follows. In Section 2, the calculation methods are explained. In Section 3, the calculation results are presented and discussed. First, we examine the gold atom on the Si(0 0 1) monohydride surface and find that it enters a Si dimer (Section 3.1). Then, we examine the gold atom on the Bi line and find that it enters the Bi–Si backbonds of a Bi dimer (Section 3.2).

* Corresponding author. Tel.: +81 29 859 2496; fax: +81 29 859 2601.
E-mail address: koga.hiroaki@nims.go.jp (H. Koga).

0921-5107/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2007.03.014

We find that the gold atom is more stable on the Bi line than on the monohydride surface, thus confirming the preferential adsorption of gold on the Bi line. In Section 4, conclusions are given.

2. Method

The optimized geometries and their energies reported in this paper are obtained in a standard density-functional theory (DFT) [19] plane-wave pseudopotential calculation within the generalized gradient approximation (GGA) [20]. (First-principles methods in surface science are explained e.g. in Chapter 3 of Ref. [21].) The Kohn–Sham equations [22] are solved [23] self-consistently for one-electron orbitals by plane-wave expansion. The electron density and total energy are calculated from the occupied orbitals. The plane-wave cutoff energy used is 16 Ry for the orbitals and 196 Ry for the charge density. The forces are also calculated and used in geometrical optimization. Ultrasoft pseudopotentials [24] are used where localized valence orbitals (Au 5d and H 1s) are involved, while norm-conserving ones [25] are used elsewhere [26]. These first-principles pseudopotentials reduce the cutoff energy required by accurate calculation [27].

The model of the Si(0 0 1) monohydride surface (Fig. 2, inset) used in Section 3.1 and that of the Bi line (Fig. 1) used in Section 3.2 are the same as those used in Ref. [18]. The monohydride model consists of five Si(0 0 1) layers, terminated in H at the bottom. The top Si atoms are dimerized and hydrogenated. The size of the unit cell is 4×4, where 1×1 is the primitive cell of the ideal Si(0 0 1) surface. The k-point grid used is 2×2. The model of the Bi line is derived from a six-layer Si(0 0 1) slab, also terminated in H at the bottom. The size of the unit cell and the k-point grid are 6×4 and 1×1, respectively. As the side view of Fig. 1 shows, the two Bi dimer lines are bonded to the hexagonal Si ring, which is surrounded by the alternation of five- and seven-membered rings [16]. The area of the surface off the Bi line is in the Si(0 0 1) monohydride structure.

The energetic stability of an adsorption configuration is expressed in terms of the adsorption potential energy (E_a), defined as

$$E_a = E - E_0 - \varepsilon_{Au}, \quad (1)$$

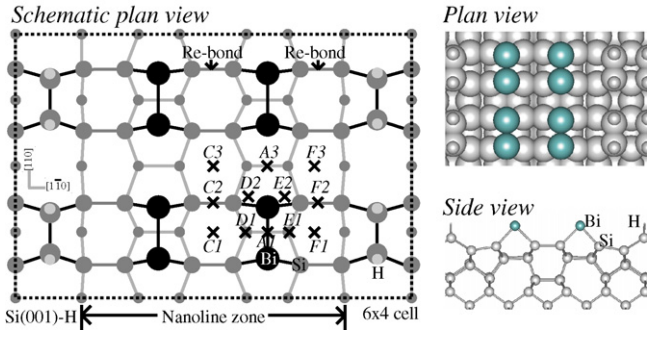

Fig. 1. Model of the Si(0 0 1) monohydride surface with a Bi line. Crosses denote points examined for Au adsorption sites.

Table 1
Energy difference ΔE (eV) between $D1$ and $E1$ (see Fig. 3e below) calculated at various conditions

Cell	N_l	k-point	E_{cut}	ΔE	
6×4	6	1×1	16	−0.050	Present
6×4	6	1×1	**20**	−0.051	Higher cutoff
6×4	6	$\mathbf{1 \times 2}$	16	−0.048	More k points
$6 \times \mathbf{8}$	6	1×1	16	−0.051	Longer cell
$\mathbf{8} \times 4$	6	1×1	16	−0.056	Wider cell
6×4	**8**	1×1	16	−0.031	8-layer slab
6×4	**10**	1×1	16	−0.032	10-layer slab

N_l denotes the number of Si layers in the slab. E_{cut} (Ry) denotes the cutoff energy.

where E is the total energy of the surface with the gold atom, E_0 the total energy of the substrate, and ε_{Au} is the energy of a free, spin polarized gold atom. (Note that this definition does not affect energy differences, which are the quantities of interest.) This quantity, or that with the reversed sign, is commonly used in the literature (Ref. [21], p. 110). In the present definition, the lower the E_a, the more stable the configuration.

The accuracy of the results has been ascertained by calculating the energy difference between the two lowest-energy configurations, namely $D1$ and $E1$ (see Fig. 3e below), at various conditions. The results are presented in Table 1. As the table shows, the increase in the cutoff energy, the number of k points, and the size of the unit cell changes the energy difference by not more than 6 meV. These parameters are thus considered sufficiently large. The increase of the slab thickness to 8 layers changes the energy difference by 19 meV, but further increase has little effect. Thus, an energy difference larger than ∼20 meV can be considered significant. This confirms the energy ordering between the two lowest-energy configurations. In addition, elemental properties are calculated and compared with experimental data. The calculated lattice constant, cohesive energy, and bulk modulus of gold (4.16 Å, 3.00 eV, and 158.7 GPa) are in reasonable agreement with experimental data (4.08 Å, 3.81 eV, and 173.2 GPa) [28] and also reproduce other GGA results (4.18 Å and 3.08 eV [29]).

3. Results and discussion

3.1. Gold atom on the Si(0 0 1) monohydride surface

In order to discuss the preferential adsorption of gold on the Bi line, we must examine the gold atom on the Bi line and that on the passivated area, and compare their energies. In this section, we examine the gold atom on the Si(0 0 1) monohydride surface and find that the energy is lowest when it is inserted into a Si dimer. The gold atom on the Bi line is examined in the next section.

Fig. 2 shows the optimized geometries and their energies. Two kinds of configurations are considered. The first kind ('attachment') has the gold atom attached to a Si dimer row (B, $B2$, P) or to the groove between dimer rows (C, H). The second kind ('insertion') has the gold atom inserted into a Si–H bond (R) or into a Si dimer (Bo).