Relativistic Effect on the Bistability of Bi {012} Nanofilms

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Relativistic Effect on the Bistability of Bi {012} Nanofilms*

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We perform fully-relativistic first-principles calculations on Bi{012}films which are stable when the film thickness is very small. We find that the 2ML free-standing film has bistability, i,e, the two top atoms are buckled in one geometry and they are nearly flat in the other geometry. The calculated amplitude of the buckling in the buckled structures is 0.17 Å whereas the amplitude is 0.41 Å when the spin-orbit interaction (SOI) is not included in the calculation. Furthermore, the bond lengths between the top and the second top atoms in the buckled structure are alternant when the SOI is included in the calculation. Therefore, the SOI has a significant effect on the geometry. The total energy difference between the two structures is less than 1 meV. Therefore, we expect that one of the two structures appears depending on circumstance such as the interaction between the substrate and the film.
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Keywords: Metal; Insulator; Nanofilm; Density functional theory

I. INTRODUCTION

It is well established that metals grow on semiconductor surfaces preferentially via the Stransky-Krastanov growth mode, i.e., due to stress energy relaxation, the growth of three-dimensional islands follows the initial formation of a flat wetting layer [1–4]. This growth mechanism is a severe drawback for the achievement of flat well-ordered films that are expected to be suitable for nanoelectronics applications. However, exceptional cases were reported [5–9]. For an example, flat films of Pb and Ag on Si(111) surfaces were observed. Stable flat films having specific thicknesses, which are called magic thicknesses, contribute to this novel growth [10]. This stability of magic-thickness films observed at low temperatures was explained by an argument based on the quantum size effect, which originates from the Fabry Perot-like electron confinement in the film-thickness direction. Very recently, magic thicknesses have been observed even at room temperature for Bi films on the Si(111) surface [11], i.e., the even-number atomic layer- film is very stable. This novel stability of flatness is found to be mainly due to the fact that the even-number layer film takes the paired layer structure and is thus relatively less affected by the electron confinement [11, 12]. By utilizing its extremely high crystallinity and flatness, Bi films are used as an intermediate layer for the growth of single crystalline pentacene films on Si substrate [13].

In the initial stage of the Bi growth on Si(111) surface, rugged wetting layers are constructed on the Si(111) surface, then the crystalline Bi ultrathin films are grown. Since the Bi crystal forms an arsenic structure, the film having a substantial thickness forms the arsenic structure. However, when the thickness is small, the film forms a different structure, i.e., the structure is similar to a black phosphorus structure, which is taken by P under room temperature and ambient pressure. This peculiar structure of the Bi thin film is due to the fact that the surface energy of the black phosphorus structure is lower than that of arsenic structure [11, 12].

In a previous paper, we performed first-principles calculations on the two-atomic-layer black-phosphorus-like {012} films [14]. As a result, we found bistability of the films; the two top atoms are buckled in the most stable structure, and the two atoms are nearly flat in a metastable structure.

It has been recognized that the spin-orbit interaction (SOI) has a significant effect on electronic structures of Bi films since the Rashba effect on the (001) film was observed [15–17]. However, the effect of the SOI on the atomic structures of Bi films has not been sufficiently revealed. In this paper, we examine the effect of the SOI by performing fully-relativistic first-principles calculations. We find that the buckling in the most stable structure becomes small due to the spin-orbit coupling and as a result, the energy difference between the most and metastable structures becomes small. Therefore, we conclude that the SOI effect plays an important role in the atomic and electronic structures of Bi films.

II. THEORETICAL METHOD

To include the SOI, we perform fully relativistic calculations based on the norm-conserving pseudo potentials where $5d$ semi core orbitals are taken to be valence orbitals [18]. We use the psudo-atomic localized basis functions consisting of five s, five p and three d atomic orbitals. To include the spin-orbit coupling, we perform fully-relativistic calculations. We use a repeated slab model where the spacing between the neighboring slabs is taken to be 17 Å. The cell lengths a and b are 4.75 Å and 4.53 Å respectively. These values are deduced from the experiment on the 4ML {012}film on the Si(111)7×7 surface [11]. The Brillouin zone is shown in Fig. 1, where $\bar{X}_1$=(0, π/b) and $\bar{X}_2$=(π/a, 0).

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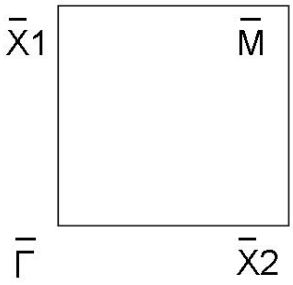

FIG. 1: The Brillouin zone of 2ML-Bi{012} films.

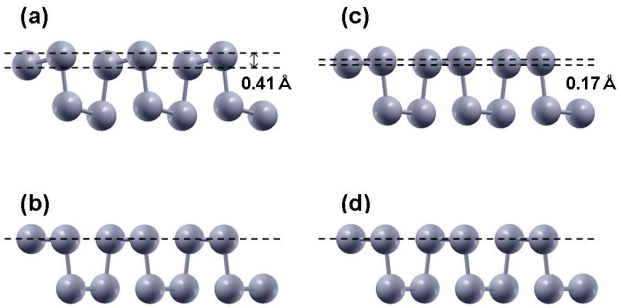

FIG. 2: The buckled structures(a) and nearly-flat structures(b) of the Bi nanofilms calculated without including SOI. The buckling structures(c) and no-buckling structures(d) of the Bi nanofilms fully relativistic calculations.

III. RESULTS AND DISCUSSION

First, we perform calculations without including the SOI. In the most stable structure, the top two atoms are buckled [Fig.2(a)]. The amplitude of the buckling is 0.41 Å, which is close to the value (0.50 Å) in a previous work where a plane-wave basis set was used. In the metastable structure, the two top atoms are nearly flat; the difference between the heights of the two top atoms is 0.02 Å. The energy difference between the most stable and metastable structures is 7 meV.

We next perform calculations by including the SOI. In the buckled structure, the amplitude of the buckling is 0.17 Å, which is smaller than 0.41 Å calculated from no SOI calculation. As a result, the total energy difference between the buckled and no-nearly flat structures is less than 1 meV. We therefore expect that one of the two structures appears depending on circumstance such as the interaction between the Bi film and wetting layer. It was reported that the growth modes of the Bi films in the cases of the Si(111)-7×7 and Si(111)-$\sqrt{3} \times \sqrt{3}$ substrates are different [19]. This experimental result suggests that the interaction between the Bi film and wetting layer plays an important role in the energetics of the film.

The optimized bond lengths and bond angles shown in Fig. 3 are tabulated in Table I. In the buckled structure calculated without the SOI, the average bond angle of the top atom is 90.4° whereas the average bond angle of the second top atom is 100.1°. As reported in a previous

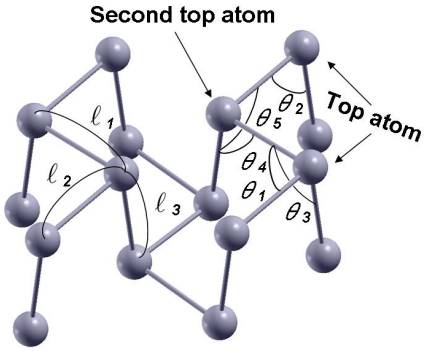

FIG. 3: Atomic structure of 2ML-Bi{012} films.

paper, the wavefunction of the highest occupied state has a p bonding character and the amplitude is large around the second top atom. This is due to the fact that the second top atom has rather large bond angle (100.1°) and thus s component is substantially included in the bonding orbital by the s-p hybridization. This increase of the s-component stabilizes the bonding orbital of the second top atom. As a result, there is an electron transfer from the top atom to the second top atom. This electron transfer which also occurs in the case of the charge density wave stabilizes the buckled structure.

When the SOI is included in the calculation, the amplitude of the buckling becomes small (0.17 Å) and thus the average bond angle of the second top atom is small (96.4°) compared with that in the case of the calculation without SOI (100.1°), whereas the average bond angle of the top atom (90.3°) is close to that calculated without SOI(90.4°). The decrease of the amplitude of the buckling is due to the fact that the SOI reduces the s-p hybridization. Whereas the difference between the bond angles of the top atom and second top atom becomes small in the SOI calculation, the bond lengths between the top and second top atoms are alternate, i.e., the values of ℓ_1 and ℓ_2 in Fig. 3 are different. As seen in Table I, two bond lengths are 3.11 Å and 3.05 Å respectively whereas ℓ_1 and ℓ_2 are identical in the case of calculation without SOI. The bond alternation in the geometry calculated with SOI is expected to stabilize the system as well as the buckling. In the case of the nearly-flat structure, the bond alternation also occurs when the SOI is included in the calculation whereas there is no bond alternation in the case of no SOI calculation. However, the difference between the two bond lengths in the SOI calculation (0.01 Å) is smaller than that of the buckled structure(0.06 Å). We conclude that the SOI has a significant effect on the geometries.

We show the band structures in Fig. 4 for the buckled and nearly-flat structures. The SOI has a significant effect on both band structures of nearly-flat and buckled geometries. We find that the substantial split of bands occur because of the SOI. The density of states calculated by the fully-relativistic method show tiny gaps in both buckled and nearly-flat structures[Fig. 4]. We find that the occupied and unoccupied bonds have nearly degenerated energies at a k point between the $\bar{X}_1$ and $\bar{\Gamma}$ points in the cases of the buckled and nearly-flat structures. This is expected to be the origin of the tiny gaps in the SOI

TABLE I: The bond length ℓ_1, ℓ_2, ℓ_3, and bond angle θ_1, θ_2, θ_3 , θ_4, θ_5 of 2ML-Bi{012}film.

	Without SOI		Fully relativistic	
	buckled structure	nearly-flat structure	buckled structure	nearly-flat structure
ℓ_1	3.05	3.04	3.11	3.01
ℓ_2	3.05	3.04	3.05	3.02
ℓ_3	2.94	2.92	2.99	2.96
θ_1	96.1	96.7	94.9	97.7
θ_2	87.6	94.4	84.9	93.7
θ_3	87.5	94.3	91.2	93.6
θ_4	102.2	94.9	97.1	94.3
θ_5	102.1	94.9	97.1	94.5

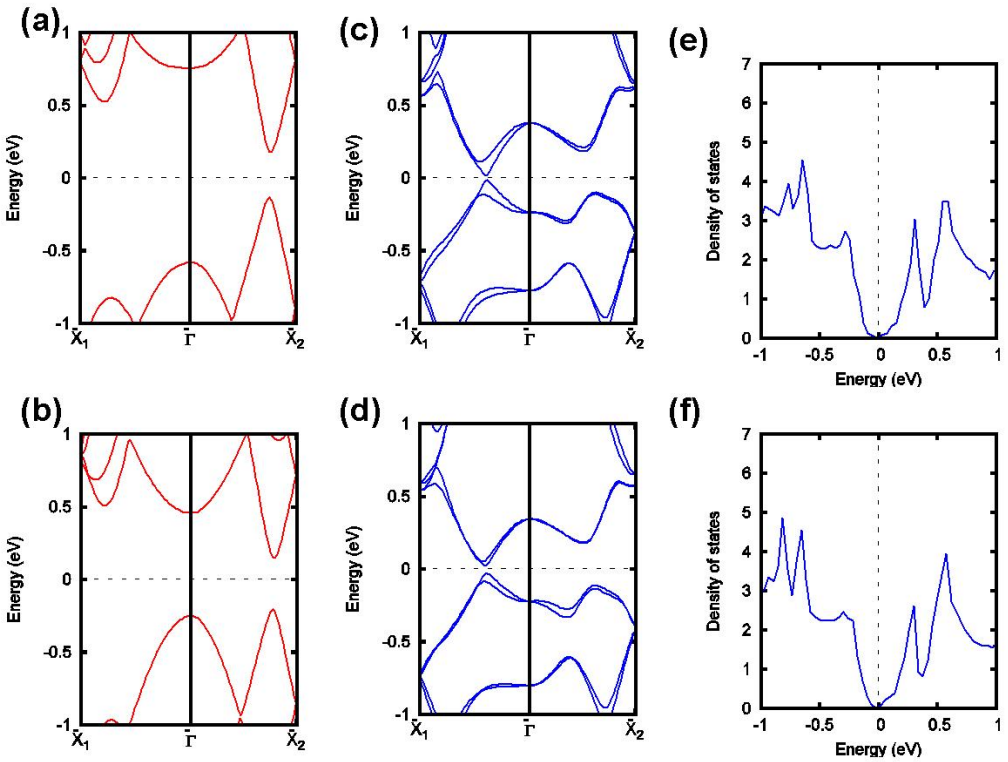

FIG. 4: The band structures of 2ML-Bi {012} film calculated for the buckled(a) and nearly-flat atomic structures(b) without including SOI, and for the buckled(c) and nearly-flat atomic structures(d) based on fully relativistic calculations. The density of states calculated for the buckled(e) and nearly-flat atomic structures(f) based on fully relativistic calculations are also shown. The dashed lines in (e) and (f) denote the Fermi level.

calculations.

As shown in Figs. 4 (c) and (d), the Rashba splitting [20] around the Γ point of buckled structure is larger than that of the nearly-flat structure. In the buckled structure, there is charge transfer from the top atom to the second top atom as was mentioned. Thus the electron potential is expected to have large gradient in the growth direction, which induces a large Rashba parameter.

IV. CONCLUSION

We perform fully-relativistic first-principles calculations on Bi{012}films which are stable when the film thickness is very small. We find that 2ML free-standing films have bistability, i,e, there are buckled and nearly-flat structures. The calculated amplitude of the buckling in the buckled structure is 0.17 Å whereas the amplitude is 0.41 Å when the SOI is not included. For both buckled and nearly-flat structures, the alternation of the bonds between top and second top atoms occurs when the SOI is included in the calculation whereas there is no bond alternation in the case of no SOI calculation. Therefore, the SOI has a significant effect on the geometry. The total energy difference between the two structures is less than 1 meV. Therefore, we expect that one of the two structures appears depending on circumstance, such as the interaction between the substrate and the film.

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