# First-principles study of bismuth films on the Ni(111) surface

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A recent experiment suggested that bismuth forms hexagonal films on the Ni(111) surface, of heights three, five, and seven layers. A quantum size effect based on free electrons was proposed in explanation. To test this idea, we calculate the total energies of Bi on the Ni(111) surface using density functional theory. We find that hexagonal film stabilities disagree with the observed odd layer preferences, and the structures are mechanically destabilized by adding capping atoms which pucker the hexagonal layers. Furthermore, we find that rhombohedral films based on the bulk Bi structure are energetically more favorable than the proposed hexagonal films. These structures also favor odd numbers of layers, but owing to covalent chemical bonding rather than confinement of free electrons. Specifically, a strongly bound adsorbed surface monolayer forms, followed by bulk-like rhombohedral bilayers.

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## I. INTRODUCTION

During the growth of thin metallic films, confinement of electrons can favor film heights that are commensurate with half the Fermi wavelength.[1] This well-known quantum size effect (QSE) due to confinement has long been studied in various materials, including bismuth. Bismuth differs from conventional QSE elements because it is a semimetal with an especially long Fermi wavelength (∼40 nm) (Refs. 2 and 3) that causes various physical properties of Bi films to oscillate with long periods.[4] In ultrathin films (∼1 nm), Bi exhibits allotropic transformations from puckered pseudocubic films to bulk-like rhombohedral films on Si(111) and on some quasicrystal surfaces.[5,6] Experiments and first-principles calculations concur that both film types exhibit bilayer growth due to the exotic bonding character of Bi, rather than QSE.[7] In contrast, the initial growth of Bi films on metallic substrates has not been well studied until a recent experiment[8] reported stable three-, five- and seven-layer Bi hexagonal films of Bi on the Ni(111) surface. They attempted to explain the stability by quantum confinement based on a free electron model. A more in-depth theoretical study is needed to understand this possible short period QSE in Bi.

Bulk Bi takes the rhombohedral structure of Pearson type $hR2$ (prototype $\alpha$-As) common to group-V semimetals, which is distorted from the simple cubic structure by a Jones-Peierls mechanism.[9] The bulk Bi structure is best described as a stacking of bilayers in the [001] direction[10] (here we use three-element hexagonal indexing, it would be [111] using rhombohedral indexing). Each bilayer has a height of 1.59 Å and is separated from the adjacent bilayer by 2.35 Å. Within the (001) plane the Bi spacing is 4.53 Å. However, three strong covalent bonds of length 3.06 Å link each Bi atom to others within each bilayer, while three weak metallic bonds of length 3.51 Å connect each Bi atom to others in the adjacent bilayer. The (001) plane is thus a natural cleavage plane, with divisions expected between bilayers. In addition to $hR2$, bulk Bi possesses many allotropes, especially at high pressure, including Pearson structure types $mP4$, $mC4$, $cP1$, and $cI2$, but it does not take the hexagonal structure.

In their experiment,[8] the authors grew Bi on a Ni(111) surface at a temperature of 473 K via vapor deposition. Based on the low-energy electron diffraction (LEED) patterns,

deposition and film growth rates, and low-energy electron reflectivity spectra, the authors proposed that initially a $(7 \times 7)$ wetting layer forms (hereafter referred to as the adsorbed surface monolayer), which transitions to a three-layer hexagonal film with a $(3 \times 3)$ surface cell sitting directly on the Ni substrate, as well as a five-layer hexagonal film with a [3-112] surface cell, as coverage grows. However, at 422 K, Bi formed a seven-layer film with an $(8 \times 8)$ cell[11] surrounded by the three-layer $(3 \times 3)$ film. The proposed three-layer and five-layer Bi films on Ni have in-plane lattice constant 3.7–3.8 Å (see the Appendix 1 for a discussion of lateral strain). The detailed structures are shown in Fig. 2 of Ref. 8. Taking their measured lattice constants, their proposed model, and an assumed free electron valence of five, they calculated that their three-, five- and seven-layer films were, respectively, 2.5, 4.0, and 5.0 Fermi wavelengths in height. As these structures and bond lengths have not been previously observed, and Bi is notoriously *not* free electron-like, a first-principles electronic structure investigation is warranted.

## II. METHODS

We apply electronic density functional theory, using the Vienna *ab initio* simulation package (VASP)[12,13] to solve the Kohn-Sham equations with the Perdew-Burke-Ernzerhof (PBE)[14] parametrization of the generalized gradient approximation (GGA) for the electron exchange correlation potential. We use projector augmented wave potentials[15,16] with a fixed energy cutoff of 269.5 eV (the default for Ni). The $d$ semicore levels of bismuth are treated as valence electrons. Collinear spin polarization is used since Ni is ferromagnetic, though we test noncollinear magnetism to check the importance of spin-orbit coupling (SOC) for some structures. In the noncollinear calculations, we take the relaxed structure from collinear calculations and perform a static calculation. All structures are relaxed holding the cell sizes and bottom layer Ni atoms fixed, with in-plane lattice constants set by the relaxed bulk Ni structure. Energy convergence is carefully checked with respect to the vacuum size, $k$-point mesh, and the number of Ni layers.

We construct models based on four Ni layers normal to the (111) surface with Bi films on one side. Our cells include 22 Å of vacuum, with periodic boundary conditions. Electrostatic
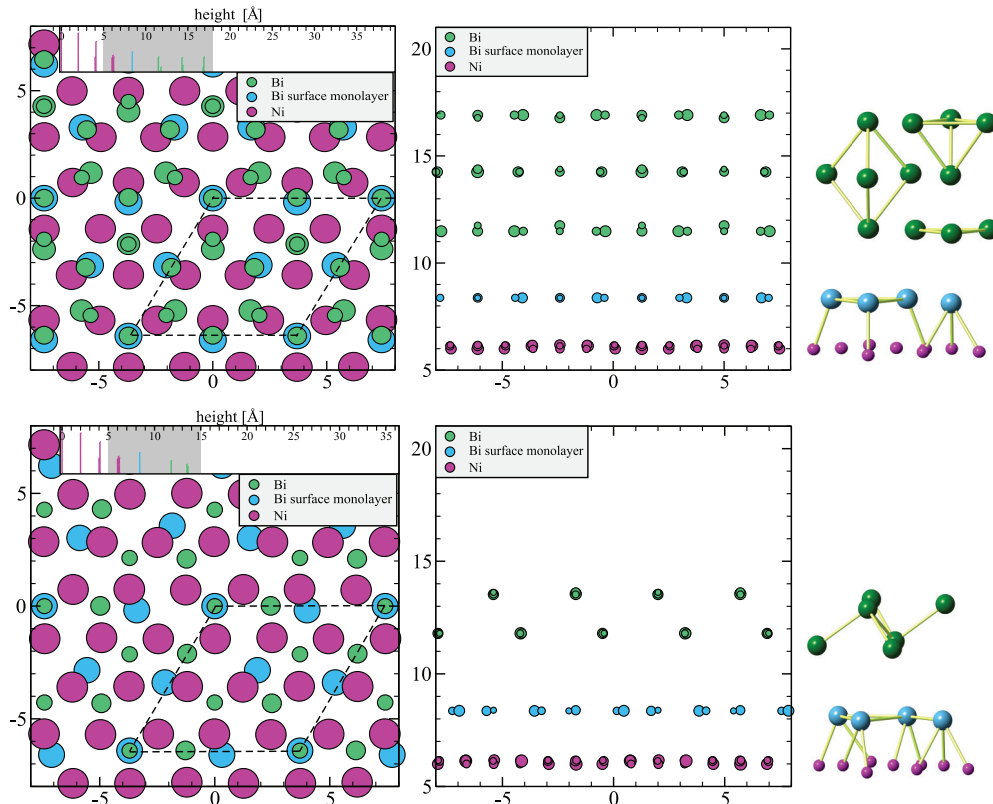
FIG. 1. (Color online) Top view (top left) and side view (top middle) of relaxed four-layer hexagonal Bi film on Ni(111) ($3 \times 3$) cell (dashed). Same for three-layer $hR2$ Bi film (bottom). Insert at top of the left-hand figure is a histogram of atoms at different heights. Shading in insert conveys the region illustrated containing the top layer of Ni, the Bi surface monolayer, and additional Bi layers. Atom size indicates depth (large below small). Length units are in Å. Chemical bonding is shown at right (slightly tilted).

energy created by the asymmetric charge distribution in the presence of Bi is small relative to the differences of surface energies. As an example, the relaxed four-layer hexagonal film on the ($3 \times 3$) cell is shown in Fig. 1. The hexagonal film structures are as described in Ref. 8 with four Bi atoms per layer in the ($3 \times 3$) cell and hexagonal $AB$ stacking. The relaxed three-layer $hR2$ film (our model) on the ($3 \times 3$) cell is also shown in Fig. 1. The $hR2$ films contain an adsorbed surface monolayer with four Bi atoms on the ($3 \times 3$) cell similar to the hexagonal film. However, bulk-like Bi (001) films which contain three Bi atoms per layer on the ($3 \times 3$) cell sit on top of the surface monolayer. Henceforth, when we say "$hR2$ film" we include the surface monolayer and the bulk-like Bi (001) film on top.

## III. RESULTS AND DISCUSSION

We first compare the relative surface energies of the proposed Bi hexagonal films of different thickness on Ni(111). Several quantities are needed to define relative surface energy: the total energy $E_{tot}$ of the $N_{Bi}$ atoms of Bi on the surface of the four-layer Ni slab; the slope $E_{Bi}$, which is the linear part of $E_{tot}$ as it depends on $N_{Bi}$; the energy $E_{Ni}^{slab}$ of the Ni slab including its two free surfaces, each of area A. The slope $E_{Bi}$ can be considered as the energy of bulk Bi in the hexagonal structure with the in-plane lattice constant determined by the surface cell.[17] With these definitions, relative surface energy

is

$$\gamma_{rel} = \left[ E_{tot} - E_{Ni}^{slab} - E_{Bi} N_{Bi} \right] \big/ A. \quad (1)$$

Figure 2 shows the relative surface energies of the ($3 \times 3$) and [3-112] hexagonal films. A structure is relatively stable if the second derivative of its relative surface energy with respect to film thickness is positive.[18] Relative stability occurs for ($3 \times 3$) cells of one, three, four, six, and eight layers and for the [3-112] cells of one, four, six, eight, and ten layers. The asymptotic period 2 oscillations of relative surface energies are reminiscent of the QSE. However, these predicted stabilities disagree with the experimentally discovered film heights. Specifically, the predicted relatively stable four-layer ($3 \times 3$) film is not seen experimentally and we do not confirm the stability of the five-layer hexagonal [3-112] film.

Also shown in Fig. 2 are data points for films with single Bi adatoms. These data points lie below the relative surface energies of integer layer coverage, revealing that terminating on complete hexagonal layers is unfavorable. Strong puckering of the hexagonal layers occurs during relaxation of structures with adatoms. Relative surface energies calculated with SOC are shown for the ($3 \times 3$) films. SOC influences the relative surface energies quantitatively but does not alter the sequence of stable structures.

The relatively stable four-layer ($3 \times 3$) structure is illustrated in Fig. 1. The first-layer Bi atoms strongly bond with the Ni surface atoms. On top of the first layer, Bi atoms
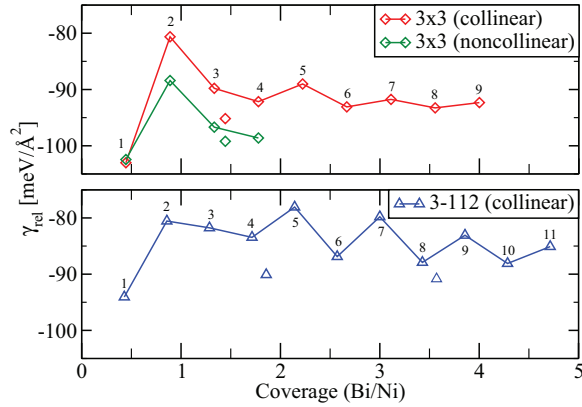
FIG. 2. (Color online) Relative surface energies of hexagonal Bi films with $(3 \times 3)$ (top) and [3-112] (bottom) Ni(111) surface cells. Note the energy conversion factor is 1 eV/Å$^2$ = 16.0 J/m$^2$. Red and blue points are from collinear calculations, green points are noncollinear. Data points connected by line segments correspond to coverage of integer numbers of monolayers (1–9 for $(3 \times 3)$, 1–11 for [3-112]). Extra data points in the $(3 \times 3)$ cell are three-layer films with one extra capping atom at a valley site. Extra points in the [3-112] cell are four layer plus one atom, and eight layer plus one atom at valley sites.

form slightly puckered layers to achieve short Bi bonds with adjacent layers. These short covalent bonds lower the relative surface energy.

To test the proposed free-electron model of QSE, we have done a genuine first-principles study of QSE in freestanding hexagonal Bi films (see the Appendix 2) and find that the actual predicted oscillation period is close to three layers. Understanding this QSE requires incorporating band structure effects and cannot be understood on the basis of a free-electron model. Thus our first-principles calculations cast doubt on both the hexagonal structure model and the proposed explanation in terms of QSE of hexagonal films.

We now seek alternate film structures. Inspecting Fig. 1 we note that the interaction of the upper layer Bi with the surface monolayer is weak, so strong deviations of structure and bonding from bulk Bi due to the Ni substrate are not anticipated. Thus bulk-like $hR2$ Bi (001) films are good candidates to grow on top of the surface monolayer. For example, a three-layer $hR2$ film (see Fig. 1) consists of the surface monolayer plus an $hR2$ (001) bilayer. The in-plane lattice constant of bulk $hR2$ Bi is 4.53 Å (see the Appendix 1). Meanwhile, $\sqrt{3}$ times the Ni interatomic spacing is 4.31 Å, which differs by only 5%. Furthermore, in our calculated energy of strained freestanding Bi(001) films, the energy minimum occurs at in-plane lattice constants 4.3, 4.4, and 4.5 Å for one, two, and three bilayer films, respectively. Thus the stable thin bilayer films match with Ni very well.

To illustrate the relative stability of various structures, we compare the surface enthalpy of formation, which is defined as

$$\Delta H/A = \left[ E_{\text{tot}} - E_{\text{Ni}}^{\text{slab}} - E_{\text{Bi}}^{\text{bulk}} N_{\text{Bi}} \right] / A, \qquad (2)$$

which differs from the relative surface energy $\gamma_{\text{rel}}$ in Eq. (1) only in our choice of reference energy for pure Bi, $E_{\text{Bi}}^{\text{bulk}}$ is the relaxed Bi bulk energy in the $hR2$ structure.
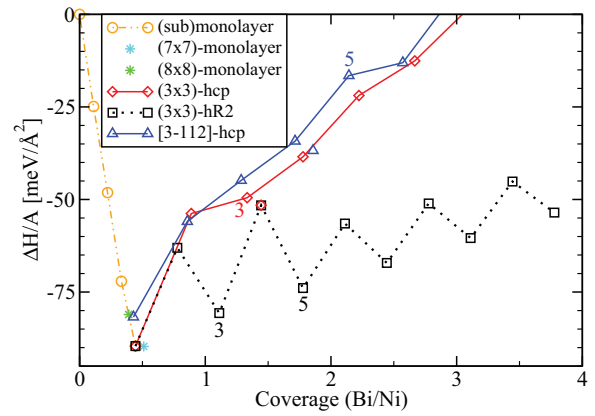


FIG. 3. (Color online) Enthalpy of formation. Dot-dashed orange points are the (sub)monolayer structures with $(3 \times 3)$ cell. Cyan and green stars are the $(7 \times 7)$ and $(8 \times 8)$ surface monolayer, respectively. Red points are hexagonal films and black are $hR2$ Bi films on the $(3 \times 3)$ cell. Blue points are hexagonal Bi films on the [3-112] cell. Color and plotting symbol are shared with Fig. 2 for $(3 \times 3)$ and [3-112] cells.

Figure 3 shows the enthalpy of formation for various surface structures with different thickness. Notice that both the $(8 \times 8)$ and $(7 \times 7)$ surface monolayer structure touch the convex hall, which implies they are both energetically stable. The stable $(3 \times 3)$ surface monolayer is equivalent to both one-layer hexagonal film and $hR2$ film with a $(3 \times 3)$ cell. Moreover, for higher coverage, $hR2$ films have much lower energy than the hexagonal films. For instance, at the same total coverage of $16/9 = 1.8$ Bi/Ni, the total energy the five-layer $hR2$ film is 1.5 eV lower than the four-layer hexagonal film on the bare $(3 \times 3)$ surface. This energy difference is much larger than the thermal energy, $k_B T = 40$ meV at 473 K. The $hR2$ films are thus much more likely to form than the hexagonal films. The $hR2$ films favor an odd number of layers (surface monolayer + integer bilayers) which is consistent with the experimental observations of three-, five-, and seven-layer films. However, the stability is due to the exotic chemical bonding of Bi rather than QSE.

To further illustrate the stable sequence from equilibrium thermodynamics, we calculate the surface free energy. This quantity is the Legendre transform of the enthalpy of formation [Eq. (2)], replacing the surface coverage with relative chemical potential $\Delta \mu_{\text{Bi}}$. From equilibrium thermodynamics, the most stable structure at a certain Bi chemical potential $\Delta \mu_{\text{Bi}}$ minimizes the surface free energy[19]

$$\gamma = [\Delta H - \Delta \mu_{\text{Bi}} N_{\text{Bi}}] / A, \qquad (3)$$

where $\Delta H$ is the enthalpy of formation [Eq. (2)], $\Delta \mu_{\text{Bi}} = \mu_{\text{Bi}} - E_{\text{Bi}}^{\text{bulk}}$ is the Bi chemical potential relative to unstrained bulk Bi. The results in Fig. 4 show the stable sequence of surface structures is from bare surface to one atom on the $(3 \times 3)$ cell at $\Delta \mu_{\text{Bi}} = -1.16$ eV, to three atoms on the $(3 \times 3)$ cell at $-1.11$ eV, to $(8 \times 8)$ surface monolayer at $-0.83$ eV to four atoms [$(3 \times 3)$ surface monolayer] at $-0.82$ eV, to the $(7 \times 7)$ surface monolayer at $-0.01$ eV, and then finally to the 11-layer $hR2$ films at around 0.06 eV. Extrapolating to an infinite height strained film yields a limiting vertical line at $\Delta \mu_{\text{Bi}} = 0.05$ eV (not shown).
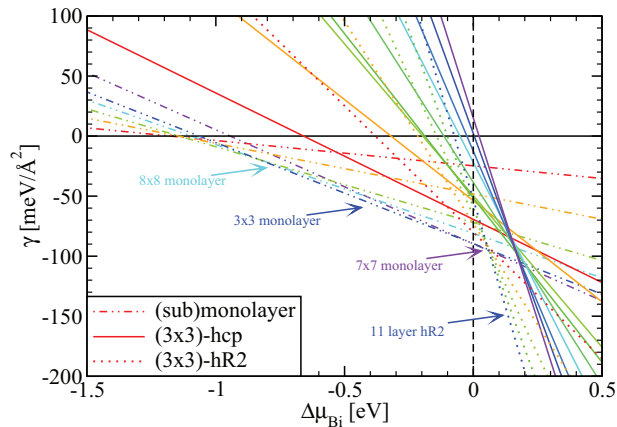
FIG. 4. (Color online) Surface free energy. Dashed-dotted lines stand for monolayer or less. Solid and dotted lines stand for hexagonal and $hR2$ films on $(3 \times 3)$ cells, respectively. Different slopes indicate different coverage according to Eq. (3). Stable sequence is indicated by arrows for monolayer or more. Vertical line at $\Delta\mu = 0$ indicates chemical potential of unstrained bulk Bi.

Other structures are thermodynamically unstable. However, since the growth is kinetically prevented from forming infinite height films, metastable structures with low energies (e.g., finite thickness $hR2$ films) will appear in actual growth. The hexagonal-based structures lie systematically above the $hR2$ ones. By studying the bulk Bi energy with different lateral strains, we confirm that the underlying reason that $hR2$ films are more favorable than hexagonal films is that Bi favors a bilayer structure with strong covalent bonding (see the Appendix 1).

Besides the hexagonal and $hR2$ (001) films, we also studied the energy of freestanding $hR2$ (012) films. The one and two bilayer $hR2$ (012) films are more stable on Si(111) than $hR2$(001) films.[5] However, with the Ni lattice constant rather than Si, the commensurate bilayer (001) film has lower energy by 30 meV/atom, and thus the (012) films are not favorable. This is also consistent with the experimental observation that no pseudocubic structure appears.

## IV. CONCLUSION

We study the growth of Bi on the Ni(111) surface using first-principles calculations. The proposed hexagonal films pucker under relaxation and are energetically and mechanically unstable to adding capping atoms. In the experiment, the authors identified the surface cell to be $(3 \times 3)$ and [3-112], and proposed a hexagonal structure based on LEED patterns. However, film heights and Bi-Bi in-plane separation were inferred indirectly based on deposition rates and electron reflectivity curves. Their free electron model introduced to interpret their results is of doubtful validity. We find instead, using a full *ab initio* treatment, that bulk-like (001)-oriented $hR2$ films above the surface monolayer are more energetically favorable than hexagonal films. One large difference between these two models is the in-plane distance of Bi, 3.7 Å for hexagonal and 4.3 Å for $hR2$ which can be further examined by the experiment. We have not investigated why different film thickness favor different surface cells.

If our model is correct, growth on Ni(111) might provide a useful synthesis of uniform $hR2$ bilayers, which have been shown to act as two-dimensional topological insulators.[20,21] Besides the surface growth, phenomena of Bi at Ni interfaces also has attracted attention recently. Liquid Bi penetrates and segregates at Ni grain boundaries forming bilayer structures[22] in a stable grain boundary phase called a complexion.[23,24] These bilayer interfacial structures can possibly explain the longstanding puzzle of the liquid metal embrittlement. However, the underlying mechanisms of bilayer segregation and their relation with embrittlement have not been revealed at the quantum level. Our study of Bi on Ni surfaces serves as a precursor to this interfacial study. In particular, we note that a pair of surface monolayer films, one on each surface at a grain boundary, provides an attractive model for the observed Bi bilayers. We hope our theoretical work can trigger more interesting work, both theoretical and experimental in these subjects.

## APPENDIX

### 1. Lateral strain

The proposed Bi hexagonal films have in-plane lattice constant $a = 3.7$ Å $(3 \times 3)$ and 3.8 Å ([3-112]), while the $hR2$ films commensurate to Ni(111) have $a = 4.3$ Å. To explain why the $hR2$ films are more favorable than the proposed hexagonal films we investigate the bonding character of Bi by calculating bulk Bi energies with different $a$. We adopt bulk cells with a $(1 \times 1)$ unit cell in the $xy$ plane and six atomic layers in the $z$ direction. The $a$'s are fixed while lattice constants $c$'s are fully relaxed. For $a$ less than 3.9 Å, both the relaxed hexagonal and $hR2$ structures are evenly spaced. For larger $a$ values, Bi in both structures pair up to bilayer structures. Figure 5 shows Bi hexagonal and $hR2$ bulk energies with fixed $a$. Clearly, the paired $hR2$ bilayer structures with $a \approx 4.6$ Å are more favorable than the proposed hexagonal structures with $a \approx 3.5$ Å. By paring up, the Bi chemical bonds change from metallic to covalent in nature. This strongly affects the periods and amplitudes of surface energy oscillation of freestanding Bi films.

### 2. Quantum size effect

In thin metallic films, electrons are confined in the vertical direction. At low temperature, the energies of the confined electrons varying with film thickness governs the relative stability of the films. This leads to "electronic growth",[1] a type of QSE. Based on the usual quantization rule, the energy oscillation period in a free electron model is half of the Fermi wavelength.[25] In a solid, taking account of the band structure, the actual energy oscillation is the superposition of different oscillations at high symmetry points in the surface Brillouin
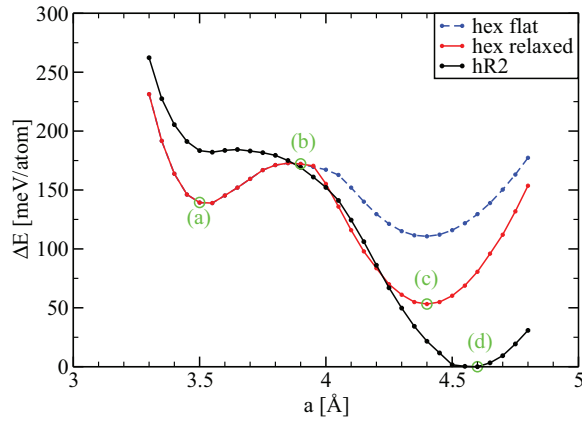
FIG. 5. (Color online) Bi bulk energy of hexagonal and $hR2$ structures. Black is the relaxed $hR2$ structure. Red is the relaxed hexagonal structure. Blue is the evenly spaced hexagonal structure. Points (a), (b), (c), and (d) correspond to the structures whose energies are plotted in Fig. 6.



FIG. 6. (Color online) Surface energies of freestanding Bi films with different in-plane lattice constants $a$ (units of Å). Black and red curves are using collinear calculation, green using noncollinear.

zone.[26] For hexagonal metal, the (001) electron confinement energy can be written as

$$E(N) = A_{\bar{\Gamma}} \sin(2k_{\bar{\Gamma}} Nd + \phi_{\bar{\Gamma}}) + A_{\bar{M}} \sin(2k_{\bar{M}} Nd + \phi_{\bar{M}})$$
$$+ A_{\bar{K}} \sin(2k_{\bar{K}} Nd + \phi_{\bar{K}}), \qquad (A1)$$

where $\bar{\Gamma}$, $\bar{M}$, and $\bar{K}$ are three high symmetry points in the surface Brillouin zone, $k$'s are the Fermi wave vectors, $A$'s characterize the importance of those three points, $\phi$'s are the phase shift of three oscillations, $N$ is the number of layers, and $d$ is layer spacing. The resulting energy is the superposition of those three oscillations. We compare the band structure prediction and the total energy oscillation of Bi films.

Figure 6 shows the surface energy oscillation with different $a$ values. Here the surface energy is defined as

$$\gamma_{\text{surf}} = \frac{1}{2A}[E_{\text{tot}} - E_{\text{Bi}} N_{\text{Bi}}], \qquad (A2)$$

where $E_{\text{tot}}$ is the energy of the film, $N_{\text{Bi}}$ is the number of Bi atoms in the film, $A$ is the surface area, and $E_{\text{Bi}}$ is the linear part of the total energies of the film structures as in Eq. (1). Shown in Fig. 6(a), for hexagonal films with $a = 3.5$ Å, the oscillation is complex in both period and amplitude
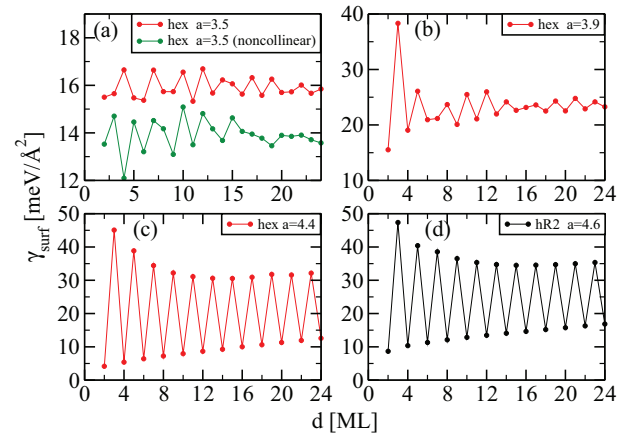
reflecting the superposition of multiple periodicities. Fourier analysis of $\gamma_{\text{surf}}$ yields a period of around three layers. From our band structure calculation, the bulk Fermi wave vectors at $\bar{\Gamma}$, $\bar{M}$, and $\bar{K}$ are, respectively, $0.59\pi/d$, $0.33\pi/d$, and $0.13\pi/d$. Averaging over these three frequencies, the resulting oscillation period is 2.9 layers, which agrees well with the total energy calculation $\gamma_{\text{surf}}$. This QSE due to electron confinement does govern the energy oscillation of the freestanding hexagonal film with $a = 3.5$ Å. However, the energy oscillation amplitude is much smaller than the energy oscillation of Bi hexagonal films on Ni(111), implying that quantum size effect is not the dominant factor in determining the stability of Bi hexagonal film on Ni(111). Also, unlike Bi on Ni(111), SOC does alter the relative stability of freestanding hexagonal films with $a = 3.5$ Å.

Figure 6(b) shows the surface energies of hexagonal films with $a$ equal to 3.9 Å where the bulk Bi atoms start to pair up. The energy oscillation period is close to two layers, which is different from the band structure prediction of 3.2 layers. Figures 6(c) and 6(d) show the energies of hexagonal films with $a$ equal to 4.4 Å and $hR2$ films with $a$ equal to 4.6 Å, respectively. In both cases, the energies show bilayer oscillation with much larger amplitude than the oscillation due to this QSE. We conclude that the oscillations of $\gamma_{\text{surf}}$ are not due to this QSE for $a > 3.9$ Å, instead it is due to covalent bonding into bilayers which is a different type of QSE.

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