Energetic stability, equilibrium geometry, and electronic properties of Bi-induced Si(001)-$(2\times n)$ surfaces

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We have performed *ab initio* theoretical investigations of the equilibrium geometry, energetic stability, and electronic properties of the Bi covered Si(001)-$(2\times n)$ surface. We have examined the currently proposed $(2\times n)$ phases, with n between 2 and 15, formed by Bi dimer blocks separated by a missing dimer line (MDL). It is pointed out that the formation of defect-free MDLs plays an important role in determining the energetic stability of the $(2\times n)$ phases. Our total energy results suggest an upper as well as a lower limit for the number of Bi dimers in the Bi dimer block of the $(2\times n)$ structure. Our calculated equilibrium geometries compare very well with recent experimental measurements. Furthermore, our theoretically simulated scanning tunneling microscopy (STM) images of the occupied states reveal formation of bright Bi dimer blocks separated by MDLs, in confirmation with experimentally obtained STM pictures.

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I. INTRODUCTION

Adsorption of group V elements is known to result in nonreactive and noninterdiffusive interfaces with IV-IV(001) and III-V(110) surfaces, thus providing excellent prototypical systems for unambiguous experimental and theoretical investigations. Moreover, the Si(001)/V (V=As,Sb,Bi) monolayer systems are considered to play an important role as strain-relaxing surfactants in Si/Ge heteroepitaxy.[1] Considering adsorption on the Si(001)-(2×1) surface, As forms an ordered monolayer, and Sb forms small (2×1) domains. However, deposition of Bi on Si(001) is unique, in that it can form either a two-dimensional net[2–4] or a one-dimensional line.[5–10] The electronic and structural properties of both the ordered stable $(2\times n)$ phases of the Bi/Si(001) surface [hereafter called Bi$(2\times n)$], and the quasi-one-dimensional Bi-nanolines, have been the subject of numerous studies, mainly motivated by their possible applications in engineering of devices.

When deposited below the Bi-desorption temperature ($\sim$500 °C) on the Si(001) substrate, Bi atoms form a two-dimensional structure. The Bi atoms deposit in the form of dimers with the ad-dimer rows being perpendicular to the Si dimer rows on the Si(001) substrate. However, as the Bi atomic size is much larger than the Si atomic size, a full monolayer deposition, leading to a 2×1 reconstruction, is unattainable due to build up of strain in the interface region between the Bi layer and the top Si layer. From electron diffraction experiments, and consistent with the above consideration, Hanada and Kawai[2] proposed the Bi$(2\times n)$ structure. This surface reconstruction is obtained by removing every nth Bi dimer, and ordering the dimer defects thus created. The resulting surface reconstruction thus exhibits periodic arrays of Bi dimer blocks separated by a missing dimer line (MDL). Underneath the Bi dimer blocks the substrate dimers are broken and the Si atoms reside close to the ideal bulk position. Scanning tunneling microscopy (STM) investigations carried out by Park *et al.*[3,4] verified the formation of the Bi$(2\times n)$ phase with n ranging from 5 up to 12, as a function of the Bi coverage (θ): $\theta=1-1/n$. For a reduced Bi concentration of $\theta\leqslant 0.8$ monolayer (ML) the (2×5) domain disappears, giving rise to rectangular "clusters of vacancies" of Bi dimers: $(2\times 5)\rightarrow$ "clusters of vacancies." Previous works[11,12] have inferred that the stability of such ordered $(2\times n)$ domains results from a short-range attractive interaction (between Bi dimer vacancies along the MDL) and a long-range elastic and anisotropic repulsive interaction (between the MDLs', separated Bi dimer blocks). However, there are no reports of *ab initio* calculations supporting these ideas.

Similar to the other group V elements adsorbed on Si(001), the dangling bonds of the Bi$(2\times n)$ surface are fully occupied, clearing the fundamental Si band gap of the surface states originated from the Si(001) clean surface. Indeed, photoemission experiments verified "a clear semiconducting behavior"[13] on the Bi$(2\times n)$ surface, in accordance with *ab initio* calculations performed by Gay *et al.*[14] Subsequent photoemission experiments indicate a semiconducting behavior for a Bi coverage of half ML, and a weak semimetallic character for a Bi coverage of $\sim$1 ML. The authors attributed such a semimetallic character to "an extended orbital overlap in the Bi-Bi bands."[15] Further photoemission experiments[16] suggested the formation of occupied electronic levels close to the Si midgap, which was attributed to the formation of metallic Bi clusters on the topmost layer of the Bi$(2\times n)$ surface. Very recently Mark *et al.*,[17] based upon inverse photoemission measurements, verified that the unoccupied π^* states from the buckled Si dimers on the Si(001) clean surface are eliminated with the formation of the Bi$(2\times n)$ surface, leaving the bulk band gap clear of unoccupied surface states. In the same work, we have supported the experimental findings through *ab initio* and empirical pseudopotential calculations, considering a Bi(2×1) surface. Jedrecy *et al.*[18] have provided the equilibrium atomic geometry of the Bi$(2\times n)$ surface from a detailed analysis of x-ray diffraction measurements. Very recently, He and Che,[19] based upon strain relief arguments, have established the energetic stability of the Bi(2×5) surface. However, no con-

clusive evidence has been reported for the relative stabilities of different Bi($2\times n$) reconstructions. There is also no theoretical explanation of the observed STM images for the optimum Bi($2\times n$) reconstruction.

In this work we have performed *ab initio* theoretical investigations of the Bi($2\times n$) surface for the plausible range of 2 to 15 for n. The calculated relaxed atomic geometries for $n=5-7$ are favorably compared with recent x-ray diffraction analysis. The repulsive interaction between parallel MDL, and the attractive interaction between dimer vacancies along the MDL are analyzed. The electronic structure of the Bi($2\times n$) surface has been examined, and the semiconducting nature established. Finally, STM images have been simulated, which clearly indicate the formation of MDL between Bi dimer blocks as well as the localization of the occupied electronic states near the bulk silicon fundamental band gap region.

II. METHOD OF CALCULATION

Our calculations were performed in the framework of the density functional theory,[20] within the local density approximation using the Ceperley-Alder correlation[21] as parametrized by Perdew and Zunger.[22] The electron-ion interaction was treated by using norm-conserving, *ab initio*, fully separable pseudopotentials.[23,24] The wave functions were expanded in a plane wave basis set with a kinetic energy cutoff up to 12 Ry. The theoretical lattice constant of 5.40 Å was obtained for Si. To simulate the surfaces we used the repeated slab method,[25] with a supercell containing nine atomic layers plus eight layers of vacuum region. A layer of hydrogen atoms was used to saturate the dangling bonds at the bottom layer of the slab, and a dipole correction scheme as suggested by Neugebauer and Scheffler[26] and corrected by Bengtsson[27] was applied to eliminate the presence of the microscopic electric field extending over the supercell. The electronic charge density was calculated using a set of three special **k** points in the irreducible part of the surface Brillouin zone. The eight topmost layers were fully relaxed to within a force convergence criterion of 25 meV/Å.

III. RESULTS AND COMMENTS

Figure 1 presents the structural models for a few Bi($2\times n$) surfaces considered in this work. The ($2\times n$) surface is characterized by a Bi dimer block with ($n-1$) dimers, and a MDL separating neighboring dimer blocks. For example, we have a dimer block with five Bi dimers separated by a MDL for the Bi(2×6) model shown in Fig. 1(b). The topmost Bi dimers are aligned orthogonally to the underlying Si dimers.

Initially we determined the equilibrium geometry of the Bi($2\times n$) structural models for $n=5$, 6 and 7, depicted in Figs. 1(a)–1(c), respectively. The atomic distances were determined within an accuracy of ±0.04 Å. The Bi dimers equilibriate in a symmetric configuration, i.e., with no vertical buckling, and the calculated dimer bond length of 3.12 Å is in good agreement with the recent experimental result of 3.12 Å obtained from x-ray diffraction method,[18] and with previous *ab initio* results of 3.06 Å (Ref. 14) for the

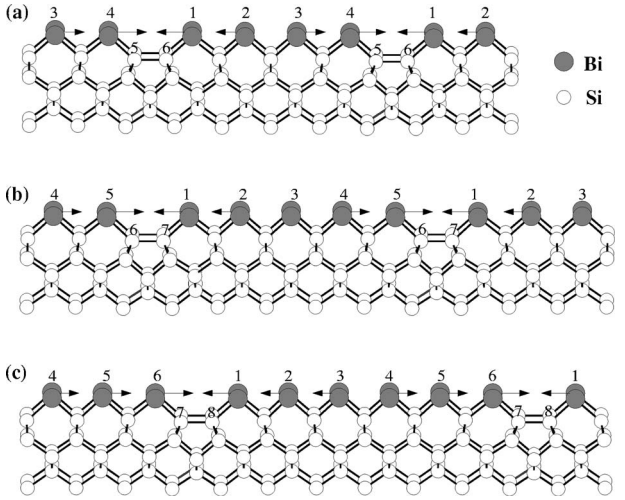

FIG. 1. Side view of the Bi($2\times n$) structural models: (a) 2×5, (b) 2×6, and (c) 2×7. The arrows indicate the atomic relaxation directions. The magnitudes of these lateral displacements are presented in Table I.

Si(001)-Bi(2×1) surface. In order to reduce the number of dangling bonds, the second layer Si atoms, along the MDL, are rebonded forming Si dimers orthogonally to the topmost Bi dimers. The bond length of these subsurface Si dimers is 2.48 Å, being severely stretched by ~0.25 Å (i.e., by more than 10%) compared with the bond length of Si dimers on the Si(001) clean surface. These results are in accordance with the recent theoretical investigations performed by He and Che.[19] X-ray diffraction measurements[18] indicate that the topmost Bi dimers lie at 1.86 Å from the second layer Si dimers. This results in nice agreement with our calculated vertical height of 1.85 Å for the Bi dimers adsorbed at the edge of the dimer block. However, due to the rebonding process of the Si dimers along the MDL, the edge Bi dimers are pulled down by 0.08 Å, compared with the Bi dimers in the central part of the dimer block. For instance, in Fig. 1(a) Bi dimers 1 and 4 lie lower by 0.08 Å compared with dimers 2 and 3. Similar results have been verified for the (2×6) and (2×7) models. Along the MDL the Bi–Si bond length is 2.76 Å, while the Bi–Si bond length in the central region of the Bi dimer block is 2.70 Å. These results are also in accordance with the experimental measurement of 2.68 Å for the Bi–Si bond distance.[18]

The MDL plays a fundamental role for the strain relief process along the (compressed) Bi dimer rows, giving rise to the Bi dimer blocks. Such a strain relief process is clearly verified from the lateral displacements of the Bi dimers, indicated by arrows in Fig. 1. The magnitudes of these displacements, with respect to the bulk position, are presented in Table I. Within our calculated Bi($2\times n$) models, we find that the net lateral displacement is proportional to the size of the Bi dimer block, i.e., proportional to n. We also find that the dimers at the edge of a block experience the maximum amount of lateral displacement. This feature of the strain relief has also been noted in the x-ray diffraction work[18] and the previous theoretical work.[19]

Experimental works[2–4] indicate the formation of Bi($2\times n$) surfaces with n varying from 5 up to 12 (Refs. 3 and 4)

TABLE I. Lateral displacements (in Å) of the Bi dimer atoms indicated in Fig. 1 with respect to their bulk positions.

		Atoms/dimers		
Model		1	2	3
2×5	Present work	0.52	0.13	⋯
	X-ray diffraction[a]	0.59	0.15	⋯
2×6	Present work	0.57	0.20	0.00
	X-ray diffraction[b]	0.50	0.28	0.00
2×7	Present work	0.57	0.32	0.12
	X-ray diffraction[b]	0.45	0.30	0.15

[a]Reference 19.
[b]Reference 18.

or 13 (Ref. 2). That is, formation of "clusters of vacancies" on the Bi(2×5) surface is more favorable than the formation of well-ordered Bi(2×n) phases with n=2–4. And for high coverage of Bi the formation of Bi dimer blocks with n >12 is energetically less favorable compared with the Bi(2×12) surface coexistent with three-dimensional Bi islands. Aiming to provide theoretical support for this picture, we calculated the formation energy (Ω_n) per 2×1 surface unit cell,

$$\Omega_n(\mu_{\mathrm{Bi}}) = \frac{1}{n}[E(2\times n) + 2\mu_{\mathrm{Bi}} - E(2\times 1)].$$

Here $E(2\times n)$ represents the total energy of the Bi(2×n) structure and $E(2\times 1)$ represents the total energy of the Si(001)-Bi(2×1) surface, with a Bi coverage of 1 ML. As the Bi(2×n) and Bi(2×1) surfaces are not stoichiometrically equivalent with respect to the Bi concentration, we have to include the Bi chemical potential μ_{Bi}. The total energy of the Si(001)-Bi(2×1) surface, $E(2\times 1)$, was calculated by using the same 2×n surface unit cell as used in the calculation of $E(2\times n)$ for the Bi(2×n) surface. The upper limit for μ_{Bi} corresponds to the chemical potential of its bulk phase, $\mu_{\mathrm{Bi}} \leqslant \mu_{\mathrm{Bi}}^{\mathrm{bulk}}$.[28] In order to make the calculations computationally feasible, we have used an energy cutoff of 8 Ry for the plane wave basis set. We find that the calculated values of Ω_n are converged within an energy range of 0.008 eV/2×1 compared with those results obtained by using the higher energy cutoff of 12 Ry. Also since we are comparing the total energies of Bi(2×n) surfaces with different periodicities (thus with different Brillouin zone sizes), we have estimated the total energy error with respect to different **k** point sampling of the Brillouin zones. We find that our calculated values of Ω_n are converged with respect to the **k** point sampling within an energy interval of 0.003 eV/2×1. Thus, considering total energy convergence with respect to the basis set and the Brillouin zone sampling, we estimate the precision of 0.01 eV/2×1 for the formation energy results.

Figure 2 presents our results for Ω_n as a function of the bismuth chemical potential relative to the chemical potential of its bulk phase, $\mu_{\mathrm{Bi}}-\mu_{\mathrm{Bi}}^{\mathrm{bulk}}$. We find that under Bi-rich condition ($\mu_{\mathrm{Bi}}-\mu_{\mathrm{Bi}}^{\mathrm{bulk}} \to 0$) the formation energies of Bi(2×n) surfaces with n between 5 and 12 are very close, within an interval of 0.047 eV. Upon reduction of Bi concentration ($\mu_{\mathrm{Bi}}-\mu_{\mathrm{Bi}}^{\mathrm{bulk}}<0$) Bi(2×$n$) phases with smaller values of n become energetically more stable, thus increasing the density of MDLs on the surface. For the bismuth poor condition $\mu_{\mathrm{Bi}}-\mu_{\mathrm{Bi}}^{\mathrm{bulk}} \approx -1.1$ eV, Bi(2×3) becomes the energetically most stable phase. It is interesting to note that for $-0.40\ \mathrm{eV} \leqslant \mu_{\mathrm{Bi}}-\mu_{\mathrm{Bi}}^{\mathrm{bulk}} \leqslant -0.25$ eV, the Bi(2×5), Bi(2×6), and Bi(2×7) phases are energetically equivalent, suggesting a coexistence of these three phases. It is important to point out that our formation energy results are obtained for the ground state configuration, while the Bi adatoms are deposited at 480 °C and annealed at 350 °C. With these considerations in mind, we establish that the Bi(2×n) phases within an energy interval of around 0.06 eV will exhibit almost the same probability of occurrence. Indeed in Ref. 18 the authors verified a structural phase mixing between Bi(2×6) and the Bi(2×7) structures.

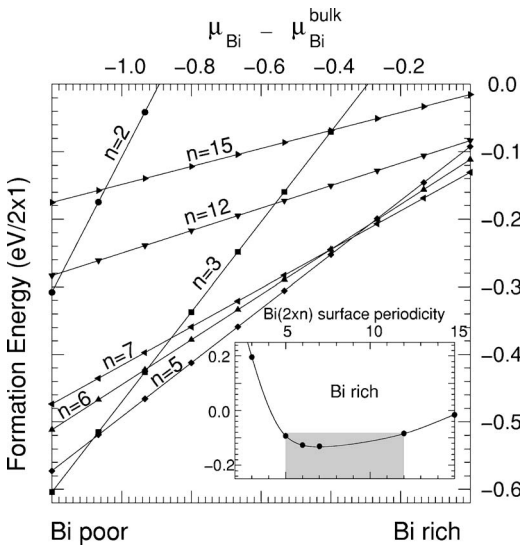

FIG. 2. Variation of the formation energy Ω_n of the Bi(2×n) surface with the bismuth chemical potential ($\mu_{\mathrm{Bi}}-\mu_{\mathrm{Bi}}^{\mathrm{bulk}}$). In the inset we present the formation energy difference, as a function of the surface periodicity (n) under Bi-rich condition ($\mu_{\mathrm{Bi}}-\mu_{\mathrm{Bi}}^{\mathrm{bulk}}=0$).

In the inset of Fig. 2 we present our results for $\Omega_n(\mu_{\mathrm{Bi}})$ under Bi-rich condition ($\mu_{\mathrm{Bi}} \to \mu_{\mathrm{Bi}}^{\mathrm{bulk}}$) as a function of the surface periodicity (n). The results suggest that compared to Bi(2×1), the formation energy of the Bi(2×2) surface (containing a Bi dimer separated by a MDL) Ω_2 =0.808 eV/2×1 is too high. As expected, for very large values of n (i.e., $n \to N$) the formation energy Ω_n goes to zero, thus making Bi(2×N) almost as stable as Bi(2×1). We find that the experimentally estimated range for n ($5 \leqslant n \leqslant 12$), shown by the shaded region in Fig. 2, compares very well with our calculated range for the energetically stable Bi(2×n) surface, i.e., $\Omega_n<0$. The energy minimum occurs for n between 6 and 7, with the formation energy of approximately −0.13 eV/2×1 under Bi-rich condition.

Energetically stable structures on the clean Si(001) surface have been established with the presence of both monodimer vacancies[29] and di-dimer vacancies.[30,31] On the clean

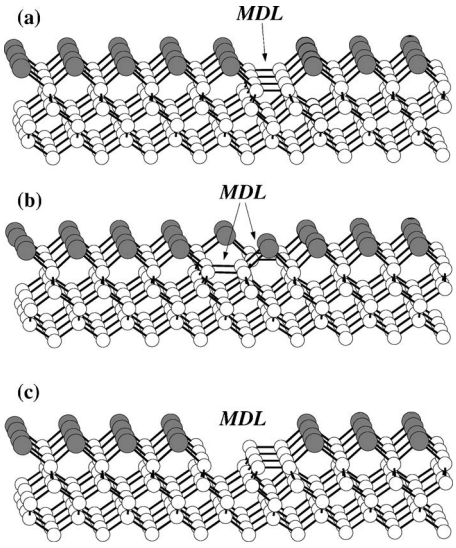

FIG. 3. Structural models of (a) aligned (type II), (b) nonaligned (type I) MDLs for the Bi($2\times n$) surface, and (c) MDL formed by di-vacancies of Bi dimers.

Si(001) surface there is a "short range attractive interaction between mono-vacancies located on adjacent dimer rows,"[12] forming a "type-II"-like defects pair as proposed by Aruga and Murata,[11] thus avoiding the formation of kinks along the MDLs. A similar kind of attractive interaction has been proposed for the Bi($2\times n$) structures.[3,4] We find that the type-II-like MDL configuration [shown in Fig. 3(a)] is energetically more stable by 0.045 eV/(1×1) compared with the "type-I"-like MDL geometry [shown in Fig. 3(b)].[32] The formation of type-II-like MDL is strongly related to the experimentally verified short-range attractive interaction between adjacent Bi dimers on Si(001).[33] We have recently confirmed such attractive interaction between Bi dimers from *ab initio* total energy investigations.[34] As a further possibility we considered another MDL structure formed by di-vacancies of Bi dimers, as shown in Fig. 3(c). Comparing the total energies of MDLs formed by mono-vacancies and di-vacancies of Bi dimers, we find that the MDLs of mono-vacancies are energetically more stable by 0.32 eV/(1×1). Indeed, the energetic preference of mono-vacancies can be attributed to the presence of a larger number of Si dangling bonds along the MDLs upon the formation of di-vacancies [cf. Figs. 3(a) and 3(c)]. Our total energy findings thus strongly support the formation of the Bi($2\times n$) phase with aligned Bi dimer blocks separated by MDLs of mono-vacancies of Bi dimers.

Our electronic structure calculations indicate that the Bi($2\times n$) surfaces exhibit a semiconducting character, with no electronic states due to Bi dimers in the midgap region. This result is in nice agreement with previous *ab initio* calculations for the Bi(2×1) surface,[14,17,35] and photoemission experiments.[13] However, the absence of Bi states in the midgap region is in contrast with the photoemission study performed in Refs. 15 and 16. In agreement with the explanation provided in Ref. 16, we believe that the experimentally detected Bi states in the Si midgap in Refs. 15 and 16 are due to the formation of Bi metallic clusters on the topmost layer of the Bi($2\times n$) surface.

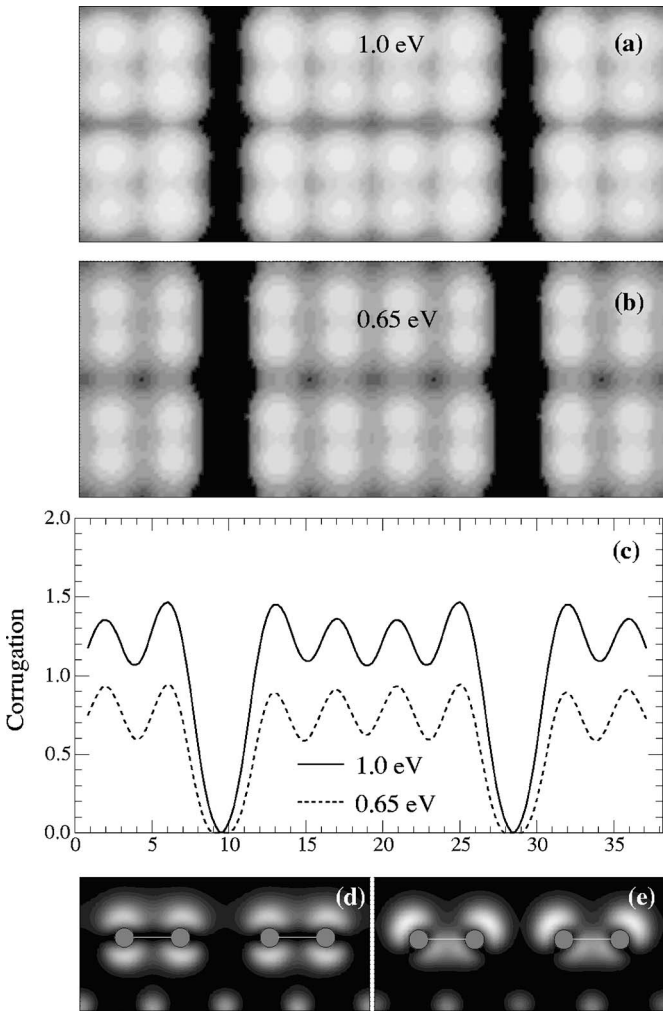

FIG. 4. Theoretically simulated STM images of the 2×5 model for the occupied states within an energy interval of (a) 1.0 eV and (b) 0.65 eV below the calculated Fermi energy. (c) Averaged surface corrugation along the Bi dimer rows. The corrugations and the lateral position, along the dimer rows, are both in Å. (d), (e) The occupied states with orbital characters π^* and π, respectively.

In order to examine the electronic structure, and to relate that to available experimental observations, we employed the Tersoff-Hamann approach[36] and simulated STM images for the Bi($2\times n$) structures. In this approach, the tunneling current $I(\vec{r})$ is proportional to the local density of states $\rho(\vec{r},\epsilon)$:

$$I(\vec{r}) \propto \int_{E_F}^{E_F+V_b} \rho(\vec{r},\epsilon)d\epsilon,$$

where V_b represents an energy interval with respect to the Fermi level (E_F). We have considered two energy intervals within the occupied states: 0.65 and 1.0 eV.

Figure 4 presents the STM images for the Bi(2×5) model. For the energy interval of 1.0 eV [Fig. 4(a)] we observe the formation of bright protrusions along the Bi dimers, with the dimer blocks being separated by dark MDLs. We find that the Bi dimers at the edge of the dimer blocks are slightly brighter than the Bi dimers along the cen-

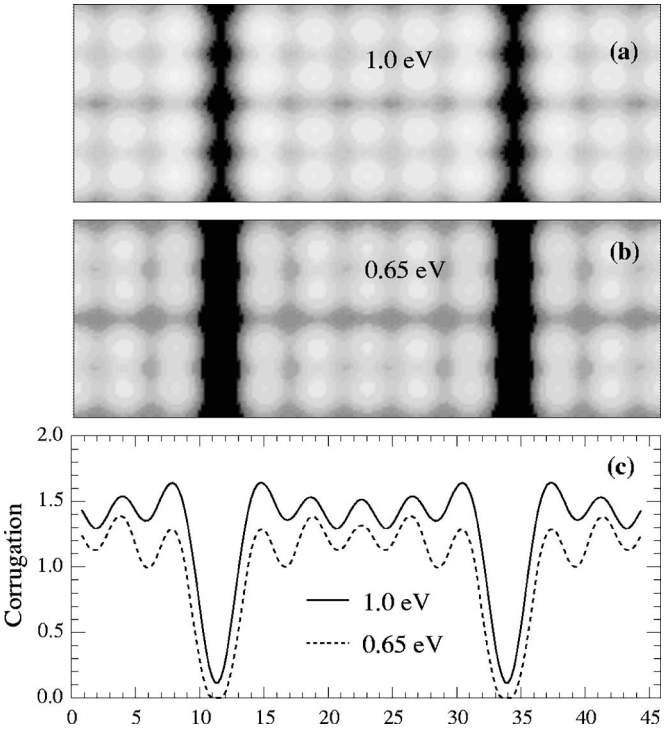

FIG. 5. Theoretically simulated STM images, for the 2×6 model, of the occupied states within an energy interval of (a) 1.0 eV and (b) 0.65 eV below the calculated Fermi energy. (c) Averaged surface corrugation along the Bi dimer rows. The corrugations and the lateral position, along the dimer rows, are both in Å.

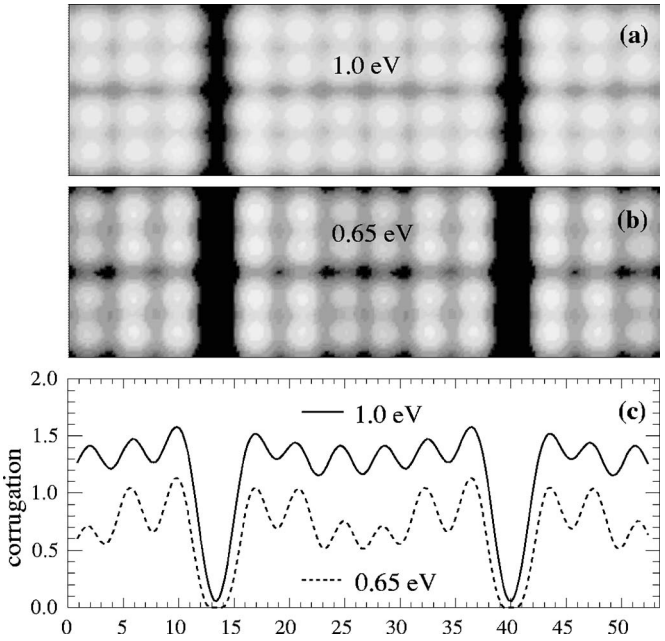

FIG. 6. STM images, for the 2×7 model, of the occupied states within an energy interval of (a) 1.0 eV and (b) 0.65 eV below the calculated Fermi energy. (c) Averaged surface corrugation along the Bi dimer rows. The corrugations and the lateral position, along the dimer rows, are both in Å.

tral part of the dimer blocks. For a slightly reduced energy interval of 0.65 eV [Fig. 4(b)] we observe almost the same brightness along the Bi dimer block. Figure 4(c) presents the averaged surface corrugation along the dimer rows obtained by computing the average vertical height. This represents the vertical positions of the "tip" for the STM images indicated in Figs. 4(a) and 4(b). We find that the lateral distance between the two peaks (attributed to the Bi dimers adjacent to the MDLs) is 7.08 Å, which is 0.5 Å larger than the lateral distance of 6.60 Å between the Bi dimers, as indicated in Fig. 1(a) and Table I. The hybridization of the $6s$ and $6p_z$ orbitals along the Bi dimers, forming a π^* band state [Fig. 4(d)], gives rise to the highest occupied state for the Bi($2\times n$) surface. Lying at ~0.1 eV below, we find the second highest occupied state formed by π bands along the Bi dimers [Fig. 4(e)]. From the energy positions of the π^* and π band states we find that the bright spots in the STM picture obtained for an energy range of 0.65 eV [Fig. 4(b)] are due to the tunneling current from the π^* states localized on the Bi dimers. On the other hand, for an energy interval up to 1.0 eV [Fig. 4(a)] the STM tunneling current comes from both the π^* and π band states of the Bi dimers.

Figures 5 and 6 present the simulated STM images for the Bi(2×6) and Bi(2×7) models, respectively. In both cases, for $V_b=1.0$ eV, the edge Bi dimers are brighter than the central ones, as shown in Figs. 5(a) and 6(a). Reducing the energy range within the occupied states to $V_b=0.65$ eV, we observed two differences: (i) The central Bi dimers of the dimer block for the Bi(2×6) structure are slightly brighter than the edge Bi dimers [Figs. 5(b) and 5(c)]. From this we infer that the π^* bands are slightly more concentrated at the central part of the dimer block. (ii) For the Bi(2×7) phase, similar to Bi(2×5), the π^* and π bands are more concentrated along the edge of the Bi dimer blocks, as shown in Figs. 6(a)–6(c). It is also interesting to note that for both Bi(2×5) and Bi(2×7) the lateral distance between the two consecutive peaks, i.e., MDL width [Figs. 1(a) and 1(c)], is about 0.5 Å larger compared with the equilibrium geometry of the MDL. However, for the Bi(2×6) model the lateral distance between those corrugations peaks (6.5 Å) is equal to the width of the MDL [Fig. 1(b)].

The formation of bright Bi dimer blocks separated by (dark) MDLs in our simulated STM images compare very well with the experimentally obtained STM pictures for Bi($2\times n$) surfaces.[3,4,17] However, the finer details obtained in our simulation regarding the bias dependence of the brightness across the dimer blocks cannot be verified from available experimental STM images. More refined experimental STM images would be helpful in this respect.

IV. SUMMARY AND CONCLUSION

In summary, we have performed *ab initio* total energy investigations of the currently proposed Bi($2\times n$) surface, considering a range of n from 2 up to 15. Our calculated equilibrium geometries are in nice agreement with recent x-ray measurements. In addition, we find that the net lateral displacement of the Bi dimers is proportional to the size of the Bi dimer blocks. The results of formation energy calculations reveal useful insight about the relative stabilities of

these structures. (i) Under Bi-rich condition, the Bi($2\times n$) phases with n between 5 and 12 are very close in energy, with Bi(2×7) being energetically most stable. (ii) Within a reasonable reduction range of the Bi concentration, we find that the Bi(2×5)$-$(2×7) phases exhibit almost the same formation energy, suggesting a structural mixing among these phases. (iii) Under Bi-poor condition, the Bi($2\times n$) surface with smaller values of n, viz. Bi(2×3), becomes energetically more stable, *albeit* characterized with an increased density of MDLs on the surface. Comparing the formation energy Ω_n as a function of n in the Bi-rich limit, we find that plausible stable phases are the structures Bi($2\times n$) with n ranging from 5 up to 12. This range of n values is in accordance with the existing experimental verifications. Further total energy investigation indicates that the formation of kinks or di-vacancies along the MDL are not expected to occur, thus indicating an attractive interaction between vacancies located on adjacent dimer rows along the MDLs. These results strongly support the formation of Bi($2\times n$) phases with aligned Bi dimer blocks separated by MDLs of mono-vacancies of Bi dimers. In contrast with some experimental findings, which indicate that the Bi($2\times n$) surfaces are semimetallic, our electronic structure calculations suggest clear semiconducting character for Bi($2\times n$). Finally, our simulated STM images for occupied states confirm the experimentally observed STM features of bright Bi dimer blocks separated by MDLs.

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