Bi covered Si(111) surface revisited

2003 J. Phys.: Condens. Matter 15 2441

(http://iopscience.iop.org/0953-8984/15/17/302)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) 2441–2447 PII: S0953-8984(03)56595-X

Bi covered Si(111) surface revisited

R H Miwa[1], T M Schmidt[1] and G P Srivastava[2]

[1] Faculdade de Física, Universidade Federal de Uberlândia, CP 593, 38400-902, Uberlândia, MG, Brazil
[2] School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, UK

Received 25 November 2002
Published 22 April 2003
Online at stacks.iop.org/JPhysCM/15/2441

Abstract

We have performed an *ab initio* study of the stability, atomic geometry and electronic structure of the Bi-covered $(\sqrt{3} \times \sqrt{3})$ reconstructed Si(111) surface. We find that the energetically stable structure changes from the *milkstool* model (for 1 monolayer (ML) coverage) to the T_4 model (for 1/3 ML coverage), without going through a stable structure for the honeycomb model (2/3 ML coverage). Our theoretical scanning tunnelling microscopy (STM) simulation for the 1 ML coverage reveals the formation of Bi trimers for occupied states, and a honeycomb image for empty states. This result, together with the energetically unstable structure for 2/3 ML coverage, suggests that the experimentally observed STM image in the form of the honeycomb structure does not mean that the minimum energy configuration corresponds to Bi coverage of 2/3 ML, but rather represents current tunnelling into the empty states localized between Bi trimers for the *milkstool* model with 1 ML coverage.

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

1. Introduction

The silicon surface covered with metallic elements has been studied for many years. In particular this surface is of great interest for the development of new electronic and optoelectronic devices. Recently, artificially grown materials, as well as the formation of nanostructures on the Si substrate, have attracted special attention. The heteroepitaxial growth process of Ge on the Si surface by molecular beam epitaxy (MBE), has been improved by prior deposition of group V elements (As, Sb and Bi). These elements act as surfactants, segregating as a top layer during the growth, and promoting the layer-by-layer (Frank–van der Merwe) growth process [1]. On the other hand, the formation of self-organized structures has been verified on the Bi-covered Si(001) surface [2], leading to the formation of a Bi-wire system on the Si substrate.

In fact, a number of experimental [3–10] as well as theoretical [11, 12] works have been performed to determine the atomic and electronic structures of the Si surface covered with

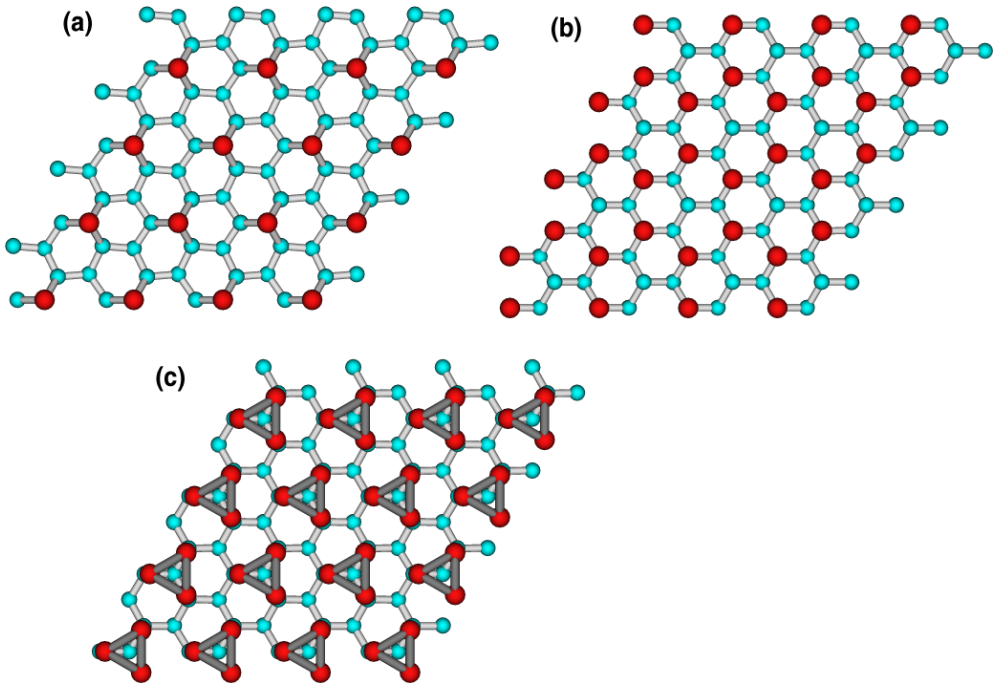

Figure 1. Top view of the atomic structure of the Bi/Si(111-($\sqrt{3} \times \sqrt{3}$)) surface for three different Bi coverages: (a) 1/3 ML (T_4 model), (b) 2/3 ML (honeycomb model) and (c) 1 ML (milkstool model).

Bi adatoms. The formation of the Si(111)-Bi($\sqrt{3} \times \sqrt{3}$) reconstructed surface, formed by Bi trimers for a Bi coverage of 1 monolayer (ML), was proposed by Takahashi *et al* [3]. This structure was confirmed by Shioda *et al* [4] and Nogami [5]. However, they obtained three different scanning tunnelling microscopy (STM) images: trimers (milkstool model), honeycomb and monomers (T_4 model), depending on the tip–sample applied bias voltage. These models are shown in figure 1. In contrast, the bias voltage dependence could not be verified in the experimental studies by Woicik *et al* [6]. They observed only the honeycomb structure: interpreted as two Bi adatoms adsorbed in the T_1 sites for high coverage of 2/3 ML of Bi adatoms. On the other hand, STM experiments by Bakhtizin *et al* [7] identified three different structures depending on the Bi coverage: T_4, honeycomb and milkstool models, for 1/3, 2/3 and 1 ML, respectively. Surface x-ray diffraction (SXD) experiments by Nakatani *et al* [8] verified the T_4 and milkstool models, but not the honeycomb model. Roesler *et al* [9], through photoelectron holography experiments, also pointed out that the honeycomb model is incorrect for high coverage of Bi, supporting the milkstool model. The energetic stability of the T_4 and milkstool models was also determined by Cheng and Kunc [11], based on *ab initio* total energy calculations. However, very recently, Schmidt *et al* [10] studying the surfactant action of Bi on the growth process of Ge on the Si(111) substrate, indicated the formation of the honeycomb model on the Bi-covered Si(111) surface.

Our concern is to clarify some controversial points with respect to the atomic and electronic structures of the Bi-covered ($\sqrt{3} \times \sqrt{3}$) reconstructed Si(111) surface. In this work we have performed first-principles total energy calculations of the Si(111)-Bi($\sqrt{3} \times \sqrt{3}$) surface, considering the three different models: T_4, honeycomb and milkstool. The equilibrium atomic

geometry for each structure has been calculated. Our total energy calculation indicates that the T_4 and milkstool models represent the most energetically stable structures for low and high concentrations of Bi adatoms, respectively. We find that our simulated STM images are dependent on the bias voltage, which can lead to a misinterpretation of the surface atomic structure.

2. Method of calculation

Our calculations for atomic geometry and electronic structure were performed in the framework of the density functional theory, within the local density approximation (LDA) using the Ceperley–Alder correlation, as parameterized by Perdew and Zunger [13]. The electron–ion interaction was treated by using norm-conserving, *ab initio*, fully separable pseudopotentials [14, 15]. A non-linear core correction [16] was included to describe the Bi pseudopotential, but was found not to influence the results. The wavefunctions were expanded in a plane wave basis (energy cutoff of 12 Ryd), and the sampling of the surface Brillouin zone was performed using a set of 5 special $k_{\parallel}$ points. To simulate the Bi-covered Si(111) surface we used the repeated slab method, considering a $\sqrt{3} \times \sqrt{3}$ reconstructed supercell. A layer of hydrogen atoms to saturate the Si dangling bonds at the other side of the slab, and a vacuum region equivalent to twice the lattice constant, was included. To avoid the artificial electrostatic field, which arises due to the inequivalence of the two sides of the atomic slab, we used the dipole correction method as proposed by Neugebauer and Scheffler [17]. To obtain the equilibrium geometry, atoms in the four topmost layers were fully relaxed to within a force convergence criterion of 25 meV Å^{-1}.

3. Results and discussion

In figure 1 we show the structural models in the calculated equilibrium atomic geometry of the Bi-covered Si(111) surfaces studied in this work. We have considered three structural models for different coverages of Bi (θ_{Bi}):T_4 ($\theta_{\text{Bi}} = 1/3$ ML), honeycomb ($\theta_{\text{Bi}} = 2/3$ ML) and milkstool ($\theta_{\text{Bi}} = 1$ ML).

For the T_4 model, in the equilibrium geometry as shown in figure 1(a), the Bi adatoms are adsorbed in the T_4 sites. The bond length between the top layer Bi adatom and the second layer Si atoms is 2.83 Å, which is appreciably bigger than the sum of the covalent radii of Bi and Si atoms (2.63 Å). The vertical distance between the second layer Si atoms and the top layer Bi adatoms is calculated to be 2.00 Å, which is in quite good agreement with the value obtained by Cheng and Kunc [11]. However, XRD experiments by Nakatani *et al* [8] suggested a vertical distance of 1.60 Å. Due to the surface reconstruction, the Si–Si bonds between the third and fourth layers, aside the Bi adatoms, are stretched by 0.10 Åwith respect to the calculated Si-bulk bond length (2.32 Å), and the Si–Si bonds beneath the Bi adatoms are compressed by 0.09 Å. Figure 1(b) shows the honeycomb model for the Bi coverage of 2/3 ML. In this model two Bi adatoms are adsorbed in the T_1 sites, forming a line of Bi along the $[1\bar{1}0]$ direction and leaving one Si rest atom per $\sqrt{3} \times \sqrt{3}$ unit cell. The Si rest atoms are displaced upward by 0.06 Å, with respect to the Si atoms bonded with the Bi adatoms. In general, the bonds in the Si substrate are weakly perturbed compared with the Si bulk. Thus, we can infer that the surface strain induced by Bi adatoms is reduced in the honeycomb model, compared with the T_4 model. The equilibrium atomic geometry of the milkstool model is shown in figure 1(c). In this model, the Bi trimers are adsorbed in the T_4 sites. The bond length between Bi adatoms within the trimer is 3.10 Å, which is quite close to the bond length

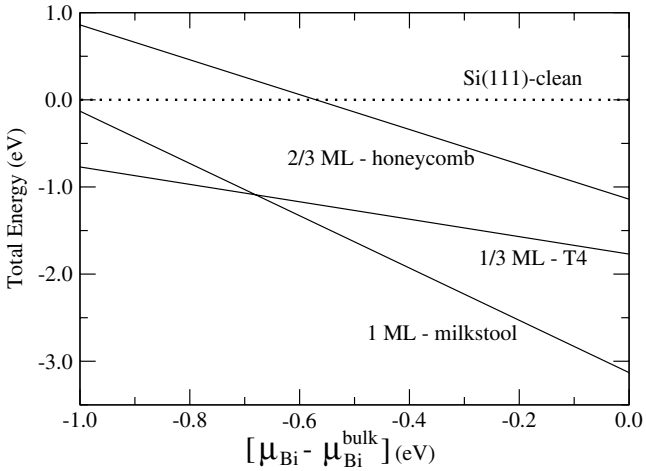

Figure 2. Total energy results for the Bi/Si(111-($\sqrt{3}\times\sqrt{3}$)) surface indicating the change from the milkstool structure (1 ML coverage) to the T_4 structure (1/3 ML coverage), without going through the honeycomb structure.

of the Bi in the solid crystalline phase (3.10 Å in the rhombohedral structure). The Si–Si bonds between the third layer and fourth layer below (aside) the Bi trimers are slightly compressed (stretched) by 0.02 Åwith respect to the Si bulk bond length. Similar to the honeycomb model, in the milkstool model the substrate bond distortions are also reduced compared with the T_4 model.

We have examined the energetic stability of the Si(111)-Bi($\sqrt{3}\times\sqrt{3}$) surface by calculating the formation energy as a function of the Bi adatom concentration. The formation energy, with respect to the clean and unreconstructed Si(111) surface, can be written as:

$$\Delta E(n) = E[\mathrm{Si}(111) - \mathrm{Bi}(n)] - E[\mathrm{Si}(111)] - n \times \mu_{\mathrm{Bi}},$$

where $E[\mathrm{Si}(111) - \mathrm{Bi}(n)]$ represents the total energy of the Si(111)-Bi($\sqrt{3}\times\sqrt{3}$) surface, covered with n adatoms of Bi per $\sqrt{3}\times\sqrt{3}$ unit cell. $E[\mathrm{Si}(111)]$ represents the total energy of the Si(111) clean and unreconstructed surface. The Bi chemical potential (μ_{Bi}) is subject to its maximum value, being the chemical potential of the Bi solid phase in the rhombohedral structure (μ_{Bi}^{bulk}): $\mu_{\mathrm{Bi}} \leqslant \mu_{\mathrm{Bi}}^{bulk}$. The calculation of the μ_{Bi}^{bulk} was performed using the same calculation procedure as used for the surface calculations. Our results of $\Delta E(n)$ are summarized in figure 2. For high concentration of Bi ($\mu_{\mathrm{Bi}} \rightarrow \mu_{\mathrm{Bi}}^{bulk}$) the milkstool model ($n = 3$) represents the most energetically stable structure. Reducing the Bi concentration, the T_4 model ($n = 1$) becomes energetically more stable than the milkstool and honeycomb models. Thus, our total energy results indicate that the honeycomb model is not expected to occur on the Si(111)-Bi($\sqrt{3}\times\sqrt{3}$) surface. Total energy calculations performed by Cheng and Kunc also indicated that the milkstool and T_4 models are energetically stable, and the honeycomb model was not verified. Our results support the experimental findings, based upon different techniques: STM images by Shioda *et al*, XRD measurements by Nakatani *et al*, and the photoelectron holography images by Roesler *et al*, except for the honeycomb structure (2/3 ML of Bi) interpreted in [6, 7, 10].

The calculated band structures of the two stable structures, T_4 and milkstool, indicate that the surfaces are semiconducting (see figure 3). Surface states are present in the gap region, and particularly for the milkstool structure, the bulk band gap is narrowed. As shown in

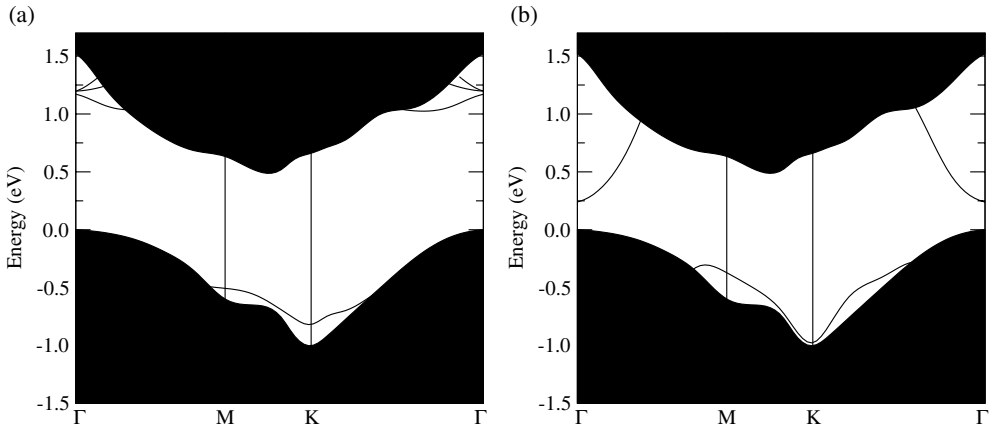

Figure 3. Band structure for the Bi/Si(111-($\sqrt{3} \times \sqrt{3}$)) surface for: (a) 1/3 ML coverage of Bi, and (b) 1 ML coverage of Bi.

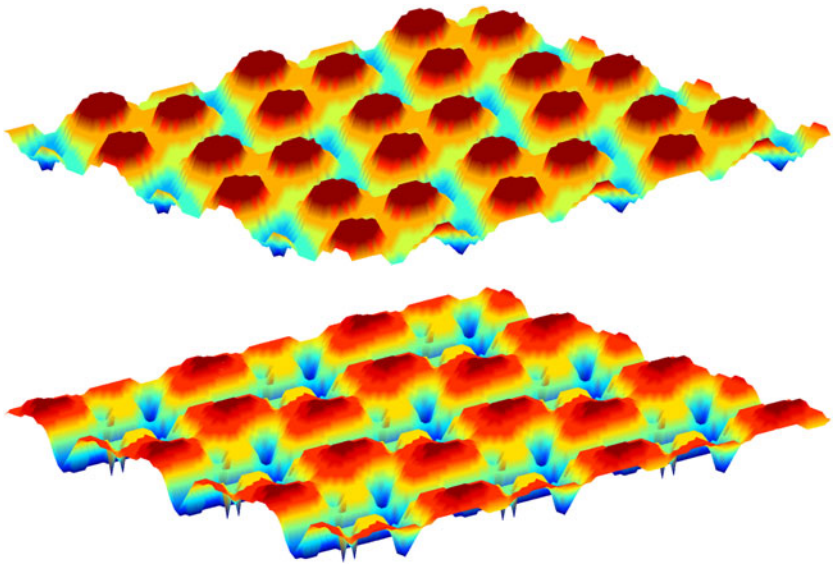

Figure 4. Theoretical STM images for Bi coverage of 1 ML: for (top) occupied states at −0.8 V, showing the Bi trimer structure, and for (bottom) unoccupied states at +0.8 V, showing a honeycomb image, which does not correspond to the honeycomb structure.

figure 3(b), the first unoccupied state is clearly a surface state located inside the bulk band gap. The energetically unfavourable honeycomb surface structure, if present, would be metallic. In order to understand the electronic structure of the different surface reconstructions we have performed a constant current STM within the Tersoff–Hamann approach [18]. The STM images for 1/3 and 2/3 ML 'translate' the T_4 and the honeycomb structures, respectively. However, for 1 ML Bi coverage a bias dependence image is obtained. The STM images of the milkstool structure for occupied (unoccupied) states were obtained within an energy interval of 0.8 eV below (above) the valence band maximum (conduction band minimum). Figure 4(a) shows the calculated STM image of the occupied states. The formation of the Bi trimers

is clearly verified: protrusions (maximum height) are localized on the Bi trimer atoms and the minimum height occurs between Bi trimers. Our simulated STM image is in quite good agreement with the experimentally obtained STM image for Bi coverage of 1 ML [4, 5, 7]. Thus, we can infer that our STM image supports the formation of the milkstool model for high coverage of Bi adatoms. On the other hand, a quite different STM image was obtained for the unoccupied states, as shown in figure 4(b). This image suggests a tunnelling current into empty states localized in the T_4 sites, aside the Bi trimers, forming a honeycomb image. Thus our results indicate a bias dependence of the STM images. The bias dependence of the STM images was verified experimentally by Shioda *et al* and Nogami. Therefore, based upon our simulated STM images, we suggest for the first time that the experimentally observed honeycomb structure [6, 7, 10] does not correspond to Bi coverage of 2/3 ML, but rather represents the STM image of the empty states localized in the T_4 sites aside the Bi trimers of the milkstool model. It should be remarked that our theoretical STM images of empty states are obtained using the LDA eigensolutions. It is well known that empty states in LDA calculations are always lower in energy compared with their experimental counterparts. This lowering happens for all states, but the symmetry of the states is correctly reproduced.

4. Conclusions

In summary, we have performed a first-principles total energy study of the Si(111)-Bi($\sqrt{3}\times\sqrt{3}$) surface, considering three structural models for different concentrations of Bi adatoms. Our formation energy calculations indicate that for high concentrations of Bi (1 ML), the milkstool model formed by Bi trimers represents the most energetically stable structure. Upon reducing the coverage of Bi adatoms to 1/3 ML, the T_4 model, formed by Bi monomers adsorbed in the T_4 sites, becomes the most energetically stable structure. The structural transition, from T_4 to milkstool, as a function of the Bi coverage, occurs without the verification of the honeycomb structure. The theoretically simulated STM images for Bi coverage of 1 ML show tip–sample bias voltage dependence: the milkstool structure for occupied states and a honeycomb image for unoccupied states. Based upon this bias dependence, and from our total energy calculations, we conclude that the honeycomb structure (for a Bi coverage of 2/3 ML) is not expected to occur on the Si(111)-Bi($\sqrt{3}\times\sqrt{3}$) surface, and that the experimentally obtained STM images may have been misinterpreted to represent the honeycomb atomic geometry of the surface.

Acknowledgments

R H Miwa and T M Schmidt acknowledge financial support from the Brazilian agencies CNPq and FAPEMIG.

References

[1] Copel M, Reuter M C, Horn von Hoegen M and Tromp R M 1990 *Phys. Rev.* B **42** 11682
[2] Shimomura M, Miki K, Abukawa T and Kono S 2000 *Surf. Sci.* **447** L169
[3] Takahashi T, Nakatani S, Ishikawa T and Kikuta S 1987 *Surf. Sci.* **191** L825
[4] Shioda R, Kawazu A, Baski A A, Quate C F and Nogami J 1993 *Phys. Rev.* B **48** 4895
[5] Nogami J 1994 *Surf. Rev. Lett.* **1** 395
[6] Woicik J C, Franklin G E, Liu Chien, Martinez R E, Hwong I-S, Bedzyk M J, Patel J R and Golovchenko J A 1994 *Phys. Rev.* B **50** 12246
[7] Bakhtizin R Z, Park Ch, Hashizume T and Sakurai T 1994 *J. Vac. Sci. Technol.* B **12** 2052
[8] Nakatani S, Takahashi T, Kuwahara Y and Aono M 1995 *Phys. Rev.* B **52** R8711
[9] Roesler J M, Miller T and Chiang T-C 1998 *Surf. Sci.* **417** L1143

[10] Schmidt T, Falta J, Materlik G, Zeysing J, Falkemberg G and Johnsom R L 1999 *Appl. Phys. Lett.* **74** 1391
[11] Cheng C and Kunc K 1997 *Phys. Rev.* B **56** 10283
[12] Gay S C A, Jenkins S J and Srivastava G P 1998 *J. Phys.: Condens. Matter* **10** 7751
[13] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048
[14] Kleinmann L and Bylander D M 1982 *Phys. Rev. Lett.* **48** 1425
[15] Gonze X, Stumpf R and Scheffler M 1991 *Phys. Rev.* B **44** 8503
[16] Louie S G, Froyen S and Cohen M 1982 *Phys. Rev.* B **26** 1739
[17] Neugebauer J and Scheffler M 1992 *Phys. Rev.* B **46** 16067
[18] Tersoff J and Hamann D R 1985 *Phys. Rev.* B **31** 805