STM Images and Energetics of the Bi-covered ($\sqrt{3} \times \sqrt{3}$) Reconstructed Si(111) Surface

T. M.Schmidt[†], R. H. Miwa[†], and G. P. Srivastava[‡]

[†]*Faculdade de Física, Universidade Federal de Uberlândia, C.P. 593, 38400-902, Uberlândia, MG - Brazil*

[‡]*School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, United Kingdom*

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Bi-covered ($\sqrt{3} \times \sqrt{3}$) reconstructed Si(111) surface has been studied by first principles calculations. Three different Bi coverages have been considered: 1 monolayer (ML), 1/3 ML and 2/3 ML, leading to the milkstool, T_4 and the honeycomb structural models, respectively. Our total energy calculations show that the milkstool model is the energetically most stable structure for high Bi coverages followed by the T_4 model for low Bi coverages, without going through a stable structure for the honeycomb model. We performed theoretical STM simulations for the three structures. For 1 ML coverage we observe the formation of Bi-trimers for occupied states, and a honeycomb image for empty states. It is suggested that the experimentally obtained STM image of a honeycomb structure does not correspond to a Bi-coverage of 2/3 ML, but it could represent a STM image of empty states localized in the T_4 sites aside the Bi-trimers of the milkstool model.

1 Introduction

The silicon surface covered with metallic elements 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, has been improved by prior deposition of group V elements (As, Sb and Bi). These elements act as surfactants, segregating as top layer during the growth, and promoting the layer-by-layer (Frank-van der Merwe) growth process [1].

A number of experimental [3-10] and theoretical [11, 12] works have been performed to determine the atomic and electronic structures of the Si surface covered with 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], and confirmed by Shioda *et al.* [4] and Nogami [5]. However, they obtained three different scanning tunneling microscopy (STM) images: trimers (milkstool model), honeycomb, and monomers (T_4 model), depending of the tip-sample applied bias voltage. On the other hand Woicik *et al.* [6] observed only the honeycomb structure. STM experiments [7] showed three different structures depending of the Bi coverage: T_4, honeycomb, and milkstool models, for 1/3 ML, 2/3 ML and 1 ML, respectively. 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.

2 Method of Calculation

Our calculations were performed in the framework of the density functional theory, within the local density approximation. The electron-ion interaction was treated by using norm-conserving, *ab initio*, fully separable pseudopotentials [13]. A non-linear core correction was included to describe the Bi pseudopotential. The wave functions were expanded in a plane wave basis (energy cutoff of 12 Ry), and the sampling of the Brillouin zone was performed using a set of 5 Monkhorst-Pack special k points with $3\times3\times1$ grid. To simulate the Bi-covered Si(111) surface we used the repeated slab method, considering a $\sqrt{3} \times \sqrt{3}$ reconstructed supercell. We used a layer of hydrogen atoms to saturate the Si dangling bonds at the other side of the slab, and to avoid the artificial electrostatic field we used the dipole correction method.

3 Results and Discussion

In Fig. 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 ($\theta_{\rm Bi}$): T_4 ($\theta_{\rm Bi}$ = 1/3 ML), honeycomb ($\theta_{\rm Bi}$ = 2/3 ML), and milkstool ($\theta_{\rm Bi}$ = 1 ML).

For the T_4 model, in the equilibrium geometry as shown in Fig. 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).

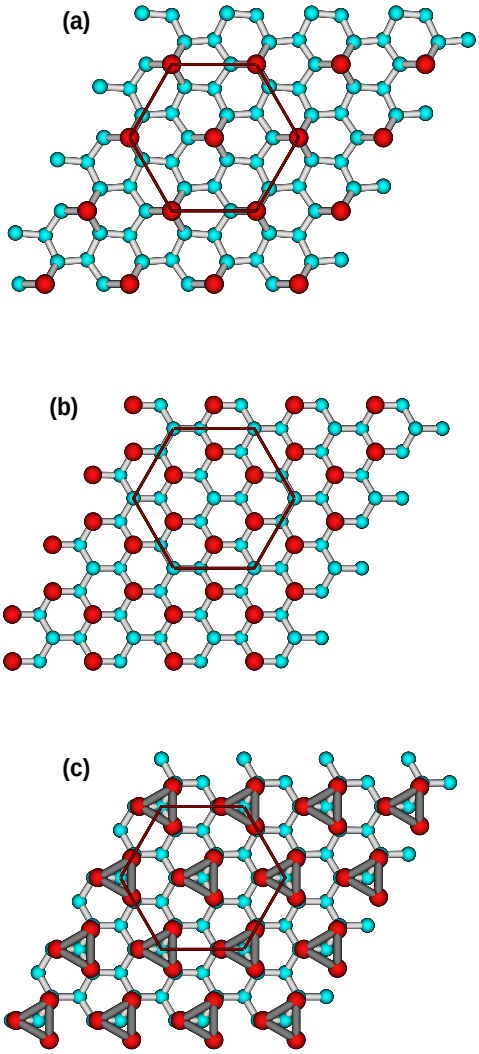

Figure 1. Top view of the atomic structure of the Bi/Si(111-($\sqrt{3} \times \sqrt{3}$) surface for three different Bi coverages: (a) 1/3 ML (T_4 model) , (b) 2/3 ML (honeycomb model) and (c) 1 ML (milkstool model).

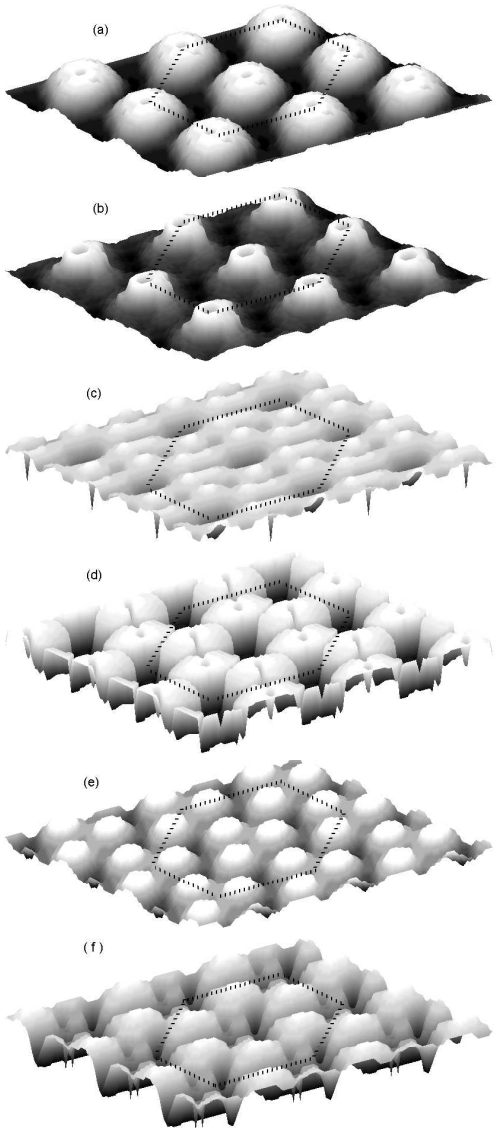

Figure 2. Theoretical STM images for Bi coverage (a) and (b) 1/3 ML; (c) and (d) 2/3 ML; (e) and (f) 1 ML. The first figure for each coverage is for occupied states at -0.8 V, and the second figure for unoccupied states at +0.8 V.

Fig. 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 leaving one Si rest atom per $\sqrt{3} \times \sqrt{3}$ unit cell. The equilibrium atomic geometry of the milkstool model is shown in Fig. 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 of the Bi in the solid crystalline phase (3.10 Å in the rhombohedral structure).

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. For high concentration of Bi, the milkstool model represents the energetically most stable structure. Reducing the Bi concentration, the T_4 model 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. 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 Refs. [6, 7, 10].

The calculated band structures of the two stable structures, T_4 and milkstool, indicate that the surfaces are semiconducting. The energetically unfavorable 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 [14]. The STM images for 1/3 ML and 2/3 ML "translate" the T_4 and the honeycomb structures, respectively as shown in Figs 2(a), 2(b), 2(c) and 2(d). However, for 1 ML Bi coverage a bias dependence image is obtained. As we can see in Fig. 2(e), 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, the STM image for the unoccupied states (Fig. 2(f)) suggests a tunneling current into empty states localized in the T_4 sites, forming a honeycomb image. This bias dependence of the STM images have been verified experimentally before [4, 5]. Therefore, based upon our simulated STM images, we suggest that the experimentally observed honeycomb image [6, 7, 10] does not correspond to a Bi coverage of 2/3 ML, but it could represent the STM image of empty states localized in the T_4 sites aside the Bi-trimers of the milkstool model.

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 results show that for high concentration of Bi (1 ML), the milkstool model formed by Bi-trimers represents the energetically most 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 energetically most stable 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. These results suggest that the honeycomb structure (for a Bi coverage of 2/3 ML) is not expected to occur, and that the experimentally obtained honeycomb STM images may have been misinterpreted.

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