Density-functional calculations for self-assembled Bi-nanolines on the InAs(100) surface

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(Received 30 June 2009; accepted 4 August 2009; published online 10 September 2009)

We have performed an ab initio investigation of the stability, atomic geometry, and electronic properties of the self-assembled bismuth (Bi)-nanolines on the Bi-stabilized indium arsenide (InAs)(100) surface. Our calculations were performed within the local density approximation of the density functional theory, using pseudopotentials to describe the electron-ion interactions. We have examined several metastable Bi nanolines arrangements on the top of the Bi-stabilized InAs(100) surface. Our total energy calculations suggest that the most stable configuration of the Bi nanolines is formed by Bi dimers parallel to the Bi dimers on the Bi/InAs(100) surface. We have found that the structure is metallic with several occupied and unoccupied surface states within the bulk InAs gap region. These states are mainly due to the top and first sublayer Bi atoms. Our theoretically simulated scanning tunneling microscope (STM) image shows a very bright line along the [011] direction, which is consistent with the experimental STM images. © 2009 American Institute of Physics. [doi:10.1063/1.3213373]

I. INTRODUCTION

There has been much effort devoted to fabricating self-assembled low-dimensional structures, such as nanolines. The formation of such nanoscale structures has remarkable use as templates for growing other one-dimensional structures with desired electronic, optical, and magnetic properties. In particular, two nanoscale systems are being investigated by a large number of groups. These are the quasi-one-dimensional structures formed by deposition of indium (In) nanowires on Si(111) surface and Bi nanolines on Si(100) surface.

Using angle resolved photoemission spectroscopy (ARPES), Abukawa et al. proposed the formation of In nanowires on the Si(111) surface. This structure was grown by depositing In atoms on the Si(111)(7×7) surface at about 430 °C. The atomic geometry of these nanowires was initially investigated by Bunk et al. using x-ray techniques. Furthermore, Yeom et al. determined the electronic structure of these nanowires using the ARPES experiment. Miwa and Srivastava presented an ab initio theoretical study of the structural and electronic properties of these In nanowires.

Moreover, the formation of self-organized, defect-free, and kink-free Bi nanolines on the Si(100) provides another example of such a system. The Bi nanolines were formed by annealing the Bi-covered Si(100) surface at around the Bi desorption temperature (at about 580 °C). Presently, there have been three different atomic proposals for the formation of the Bi nanolines on the Si(100) surfaces. From careful investigations of scanning tunneling microscope (STM) images, Miki et al. reported that two parallel Bi dimers form a Bi line with a missing dimer row between them, known as the Miki model. Naitoh et al. (Naitoh model), on the other hand, suggested that the Bi lines are formed by two parallel and adjacent Bi dimers substituting for four Si dimers, with a missing dimer row next to each Bi dimer. In the Haiku model, Owen et al. demonstrated that the Bi dimers are separated by a missing Si dimer line and the Si substrate below the Bi lines is heavily reconstructed, forming fivefold and sevenfold Si rings. Several theoretical works have been reported on the structural and electronic properties of the Bi nanolines on the Si(100) surface. Total energy calculations indicate that the Haiku model represents the energetically most favorable configuration for Bi nanolines on the Si(100) surface. Despite many experimental and theoretical studies for Bi nanolines on Si or Ge surfaces, the formation of nanoline-like structures on the technologically important III-V surfaces has attracted little attention.

Recently, Laukkonen et al. and Ahola-Tuomi et al. have observed a single-domain uniform array of Bi nanolines on the top of the Bi-stabilized InAs(100)(2×1) reconstruction. The separation of the Bi nanolines was found to be 4.3 nm, which is twice the lattice constant of the InAs(100) interface surface unit cell, suggesting a (2×10) reconstruction. The Bi nanolines structure has been experimentally fabricated by depositing 1.5 ML of Bi on InAs(100)(4×2) at room temperature and annealing it at 250 °C for 1 h until a (2×6) pattern was observed. After that the sample was heated again at the same temperature (250 °C) for a longer time (12 h) until the pattern changed into the (2×1). They provided STM and low-energy electron diffraction studies for the resultant nanoline structure. In the light of the STM results, the proposed atomic models consist of two rows of adjacent Bi dimers located parallel to the Bi dimers of the (2×1) substrate. However, their results for the most stable configuration of the Bi nanolines on the Bi-stabilized InAs(100) surface and its basics properties remain inconclusive. It is of great importance to note the difference between the Bi nanolines on the InAs(100) surface and the self-assembled Bi nanolines on the Si(100) surface. The former

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Bi nanolines are grown by depositing Bi atoms on a fully two-dimensional Bi-covered InAs surface. However, heating the system at 250 °C leads to the formation of the one-dimensional uniform array of nanolines. The latter Bi nanolines are grown by depositing Bi atoms on the bare Si(100) surface and annealing at around the Bi desorption temperature of 580 °C. Having established the energetically most stable structure for the Bi nanolines on the InAs(100) surface, it could be a perfect template for generating more interesting and useful nanostructures and nanoscale systems. The adsorption of group III elements such as In, Al, etc. and noble metals (such as Au, Ag, etc.) provide examples of such nanoscale systems. It is also possible to form ferromagnetic lines aside or inside the Bi nanolines by adsorption of transition metals (such as Fe and Mn).

In the present work, the atomic and electronic structures of such self-assembled Bi nanolines on the Bi-stabilized InAs(100)(2×6) reconstruction have been theoretically investigated using the pseudopotential method and the local density approximation (LDA) of the density functional theory (DFT). We have considered several atomic arrangements for the Bi nanolines structure. Our first-principles calculations reveal that the most plausible structure of the Bi nanolines is formed with Bi dimers, parallel to the Bi dimers of the Bi/InAs(100)(2×6) surface. Furthermore, details on the electronic and atomic structures as well as the orbital natures of the highest occupied molecular orbital and lowest unoccupied molecular orbital states will be presented using partial charge density plots and STM simulations.

II. COMPUTATIONAL METHOD

To simulate the Bi-covered InAs(100) surface we used the repeated slab method, considering a 2×6 reconstructed supercell, with eight atomic layers of In and As covered with five (two) Bi dimers in the subsurface (surface), and a vacuum region equivalent to twice the bulk lattice constant. It is found that the (2×6) reconstructed InAs(100) surface mesh represents the minimum acceptable size from energetics point of view. Increasing the cell size to (2×8) and (2×10) decreases the total energy, respectively, by 0.012 and 0.023 eV/(2×1) unit cell. In order to reduce the interaction between the Bi lines, they are separated by five Bi dimers. To avoid the artificial electrostatic field, which arises from the application of the periodic boundary conditions, we used the dipole correction method as proposed by Neugebauer and Scheffler. The dangling bonds at the bottom layer were saturated with fractionally (Z=0.75) charged pseudohydrogen atoms.

Our calculations were performed in the framework of the DFT (Ref. 17) within the LDA. For the many-body electron-electron interaction we employ the exchange and correlation potential by Ceperley and Alder as parametrized by Perdew and Zunger. Electron-ion interactions were treated by using norm-conserving, fully separable pseudopotentials. The single-particle Kohn–Sham wave functions were expanded in a plane wave basis set with a kinetic energy cutoff of 12 Ryd. During the calculations we use the calculated InAs equilibrium lattice constant of 6.03 Å. Self-consistent solutions of the Kohn–Sham equations were obtained by employing four special k points in the irreducible part of the surface Brillouin zone. The Hellmann–Feynmann forces on ions were calculated and minimized to obtain the relaxed atomic geometry. The equilibrium atomic positions were determined by relaxing all atoms in the unit cell except the bottom P-layer, which was frozen into its bulk position.

III. RESULTS AND DISCUSSION

Figure 1 presents the suggested atomic configurations of the Bi nanolines on the Bi-stabilized InAs(100)(2×6) surface. In these arrangements, the Bi dimers, on the top of the surface, represent the building block of the Bi nanolines. The nanolines are composed of two parallel and adjacent lines of Bi dimers. Our total energy calculations indicate that the model (M1) shown in Fig. 1(a), with Bi dimers parallel to Bi dimers of the Bi/InAs(100)(2×6) surface, represents the energetically more favorable configuration for Bi nanolines on the Bi/InAs(100)(2×6) surface than models M2 [Fig. 1(b)] and M3 [Fig. 1(c)] by approximately 0.68 and 0.57 eV/(2×1), respectively.

For the most stable configuration, detailed in Fig. 2, the Bi lines are formed by two parallel Bi dimers aligned along the [011] direction, with a width (along the [011] direction) equivalent to 4.22 Å. The calculated Bi dimer bond length of the Bi line is 3.02 Å. These results are in good agreement with the experimental measurements done by Ahola-Tuomi et al., 4.30 and 3.0 Å, respectively. The sublayer Bi dimer, beneath the Bi line, is broken (distance ~4.41 Å) and the other Bi dimers equilibrate in a symmetric configuration (i.e., with no vertical buckling). The calculated Bi dimer bond length of 3.24 Å is slightly larger than the value obtained for Bi-covered Si(100) surface of 3.16 Å. However, this value is very comparable with those obtained for the α2(2×4):0.5 ML (3.26 Å) and β2(2×4):0.5 ML (3.30 Å) structures of the InP(001)(2×4) reconstruction. Clearly indicates that Bi–Bi dimer length depends on the atomic size of the species forming the substrate layer. The average Bi–Bi back bond is measured to be 3.26 Å, which is very close to the Bi dimer bond length. It is noticed that the vertical height between the Bi line and the first sublayer Bi atoms is 2.33 Å. The calculated Bi–In bond length of 2.95 Å is in agreement with the sum of their covalent radii. However, this value is slightly larger than the value that was obtained in previous theoretical work. The first sublayer Bi atoms are at 2.02 Å above the In layer. The In–As bond length of 2.60 Å, on the other hand, is quite similar to the ideal bulk bond length.

Figure 3 shows the calculated electronic band structure of the Bi nanolines on the Bi-stabilized InAs(100)(2×6) surface. The shaded regions represent the projected bulk band structure of the InAs(100)(2×6) surface. Our band structure calculation indicates that the system is metallic. It is clear that the bands are less dispersive along the ΓJ′ direction (i.e., perpendicular to the Bi nanolines), indicating less interaction between the lines. On the contrary, we find that the bands along the ΓJ′ direction (i.e., parallel to the Bi
FIG. 1. (Color online) Schematic top views of the three proposed atomic geometries for the Bi nanolines on the Bi/InAs(100) surface. The most stable configuration is shown in panel (a).

FIG. 2. (Color online) Details of the (a) side and (b) top views of the most stable atomic structure of the self-organized Bi nanolines on the Bi/InAs(100) surface.
nanolines) produce much more dispersion, which indicates large interactions between the Bi atoms forming the Bi nanolines. These interactions, however, lead to the metalliclicity of the system (band V1 in Fig. 3). This suggests that the Bi nanolines are not metallic in nature but the present metallicity is attributed to have risen from the area between the nanolines. There are several filled (occupied) and empty (unoccupied) surface states, which have been identified within the bulk gap region in energy range of 0.35 eV above and below the Fermi level. These surface states are actually due to the first and top Bi atomic layers. Our partial charge density plots, shown in Fig. 4, reveal that the highest filled surface state, V1, originates from the clean Bi-stabilized InAs(100) surface. The second highest surface state, V2, is primarily localized on the Bi atom in the top layer as well as the In atom in the third layer. The conduction states C1 and C2, on the other hand, originate from the top-layer Bi atom with large $p_z$ orbital nature.

Using our total energy results, we simulated occupied-state STM image, in the constant-current mode, of the Bi dimers on the surface. We followed the Tersoff–Hamann approach\textsuperscript{25} considering an energy interval of 2.0 V below the valence band maximum (VBM). The plotting plane of the simulated STM image passes through the Bi–Bi dimers forming the Bi nanolines. Our simulated STM image, depicted in Fig. 5, clearly shows significantly large values of local charge density accumulation on both components of the Bi–Bi dimers along the dimer row (Bi nanolines). However, this indicates the formation of the nanoline along the [011] direction (i.e., the parallel direction to Bi–Bi dimers). Our simulated STM image for the occupied states shows a good agreement with the experimental filled-state STM image of the Bi/InAs(100) reconstruction obtained by Ahola-Tuomi et al.\textsuperscript{14} In their experimental image, it is clearly observed that the bright lines (white lines) run along the [011] direction.

**IV. SUMMARY AND CONCLUSION**

In summary, this work has clarified the most plausible geometry for self-assembled Bi nanolines on the Bi-stabilized InAs(100)(2 × 6) surface. Within the framework of the DFT scheme, the atomic geometry, electronic states, and atomic orbitals of the most energetically preferable structure...
have been investigated. In the most stable geometry, the Bi nanolines are constructed of two parallel and adjacent Bi dimers in the top layer parallel to the Bi dimers in the subsurface layer. The band structure calculations indicate that the system is metallic. We have identified occupied and unoccupied surface states within the bulk gap region. These surface states originate from both the top and subsurface Bi layers. Our theoretically simulated STM image suggests a very bright line running in the [011] direction, supporting the recently proposed model of the Bi nanolines on the Bi-stabilized InAs(100) surface.

ACKNOWLEDGMENTS

A.Z.A. gratefully acknowledges financial support from King Abdulaziz University (KAU), Saudi Arabia. The calculations reported here were performed using the University of Exeter’s SGI Altix ICE 8200 supercomputer.