

# Atomic Structure and Energetic Stability of the Bi-covered InAs(110) Surface

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We have performed *ab initio* calculations of the atomic structure and energetic stability of the Bi-covered InAs(110) surface. The calculations were performed within the density-functional theory, using norm-conserving fully separable *ab initio* pseudopotentials. Two experimentally proposed structural models have been considered: (1×1)-ECLS and (1×2). Our total energy calculations indicate that the formation of the (1×2) model is energetically more favourable than the (1×1) model by 41 meV/(1×2). The calculated equilibrium geometries, for the InAs(110)-Bi(1×1) and -Bi(1×2) surfaces, show in general a good agreement with the experimental x-ray measurements carried out by Betti *et al.* [Phys. Rev. B, **59**, 15760 (1999)].

## 1 Introduction

The atomic and electronic structures of two-dimensional semimetal adlayers on semiconductor surfaces have been subject of many experimental studies. It is well known that the Sb- and Bi-covered GaAs(110), and Sb-covered InAs(110) surfaces exhibit a (1×1) surface reconstruction [1–6]. However, a very recent experimental work for the Bi-covered InAs(110) surface, using x-ray diffraction technique, identified an InAs missing row between two adjacent Bi-chains, forming a (1×2) surface reconstruction [7].

In this work we have studied the Bi-covered InAs(110) surface. Two different structural models have been considered: the (1×1) reconstructed epitaxial continued layer structure (ECLS) [8] and the (1×2) reconstructed missing-row model [7].

## 2 Method of Calculation

The calculations were performed in the framework of the density functional theory [9], within the local density approximation using the Ceperley-Alder correlation [10] as parameterized by Perdew and Zunger [11]. The electron-ion interaction was treated by using norm-conserving, *ab initio*, fully separable pseudopotentials [12]. The wave functions were expanded in a plane wave basis set with a kinetic energy cutoff of 16 Ry. The theoretical lattice constant of 5.98 Å were obtained for InAs. To simulate the surfaces we used the repeated slab method [13], with a supercell containing eight atomic layers plus  $\approx 11$  Å of vacuum region. A layer of fractionally charged hydrogen atoms was used to saturate the cation dangling bonds at the bottom layer of the slab. The electronic charge density was calculated using a set of 4 special k-points in the irreducible part of the surface Brillouin zone. The eight topmost layers were fully relaxed within a force convergence criterion of 12 meV/Å.

## 3 Results and Discussion

Figure 1 exhibits the structural models and details of the equilibrium atomic geometry for the Bi-covered InAs(110) surface: (1×1) ECLS [Figs. 1(a) and (b)] and the (1×2) missing-row model [Figs. 1(c) and (d)]. In the ECLS the Bi adatoms occupy the III-V sites in the (110) plane of the InAs adlayer, forming Bi-chains aligned along the  $[1\bar{1}0]$  direction with Bi-Bi bond length of 3.01 Å, which is very close to the sum of the Bi covalent radius (2.92 Å). While the ECLS exhibits a well ordered (1×1) surface reconstruction, the InAs missing row model presents a (1×2) surface reconstruction with two inequivalent and strongly buckled Bi-chains along the  $[1\bar{1}0]$  direction. The Bi-chains are tilted by  $\approx 23^\circ$  with respect to the (110) plane, however, the Bi-Bi bond lengths (3.07 Å and 3.03 Å) are almost the same as those for the ECLS.

In order to verify the energetic stability between these two structural models, we have compared their total energies ( $\Delta E$ ), which can be written as:

$$\Delta E = E_{1\times 2} + E_{InAs}^{bulk} - E_{ECLS}. \quad (1)$$

$E_{1\times 2}$  and  $E_{ECLS}$  represent, respectively, the total energies of the (1×2) model and ECLS.  $E_{InAs}^{bulk}$  represents the total energy of the InAs bulk, calculated using the same calculational procedure as used for the surface calculations. Our results indicate a small total energy difference: 41 meV/(1×2), in favor of the (1×2) model,  $\Delta E = -41$  meV/(1×2). Therefore, the (1×2) model is slightly more favourable in energy than the ECLS.

We next have detailed the equilibrium atomic geometry of the ECLS and (1×2) model. For the ECLS, Figs. 1(a) and 1(b), our calculated results are in quite good agreement with the previous *ab initio* study by Umerski and Srivastava [14]. The topmost Bi-chains are slightly buckled by 0.13 Å, where the Bi adatoms bonded to the substrate In

(As) are at the “up” (“down”) position. Umerski and Srivastava obtained a vertical buckling of 0.15 Å in the same direction. For the III–V (110) clean surfaces the topmost adlayers are tilted considerably due to the cation → anion electronic charge transfer, in order to satisfy the electron counting rule (ECR). For instance, for the InAs(110)–(1×1) clean surface, the topmost InAs bonds are buckled by ≈ 0.75 Å [15] with In (As) adatoms in the “down” (“up”) positions. The electronic charge transfer occur from In towards As adatoms. As a consequence, the In bonds become almost planar,  $sp^2$ -like hybridization and an empty  $p_z$  orbital, while the As bonds become pyramidal: with  $s^2p^3$ -like hybridization with a fully occupied dangling bond. Although the Bi-covered ECLS also satisfies the ECR, the electronic charge transfer in the topmost Bi-chains is quite small. The dangling bonds of the Bi adatoms are fully occupied, since the Bi–Bi and Bi–As bonds exhibit an electronic charge excess. The Bi–In and Bi–As bond lengths, see Fig. 1(a), are also in good agreement with the previous theoretical predictions: 2.85 Å (Bi–In) and 2.67 Å (Bi–As) [14].

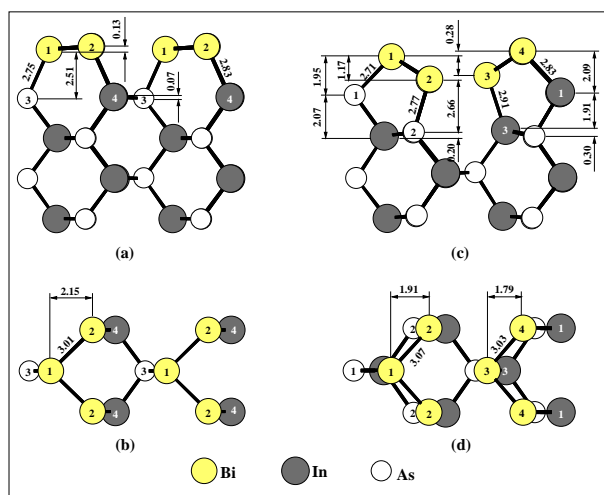


Figure 1. ECLS (a) top and (b) side view, and (1×2) structural model (c) top and (d) side view.

Figures 1(c) and 1(d) exhibit the equilibrium atomic geometry of the Bi/InAs(110)–(1×2) surface. The InAs missing row gives rise to two inequivalent Bi-chains, one bonded to the As atoms and another to the In atoms, both aligned along the  $[1\bar{1}0]$  direction. The vertical buckling of the Bi-chains bonded to the As (In) substrate is 1.17 Å (1.25 Å), which is in good agreement with the experimental results [7]: 1.06 Å (1.21 Å). The same good agreement has also been verified for the Bi–Bi bonds lengths along the chains, ≈ 3.05 Å (exp. [7]: ≈ 2.97 Å). The Bi-chain bonded to the In substrate (Bi<sub>3</sub>–Bi<sub>4</sub>) is slightly higher, 0.20 Å–0.28 Å as compared with the Bi-chain bonded to the As substrate (Bi<sub>1</sub>–Bi<sub>2</sub>). This result is in contrast with the experimental findings by Betti and co-workers. They suggested that the Bi-chain bonded to the As substrate is higher (by 0.46 Å–0.61 Å) than the Bi-chain bonded to the In substrate. Similarly, our calculated Bi–In and Bi–As bond lengths, see Fig. 1(c), do not agree with the experimental measurements [7]. While we obtained 2.70 Å and 2.83 Å for the Bi<sub>1</sub>–As<sub>1</sub> and

Bi<sub>4</sub>–In<sub>1</sub> bond lengths, respectively, the x-ray results [7] indicate: 3.05 Å (Bi<sub>1</sub>–As<sub>1</sub>) and 2.62 Å (Bi<sub>4</sub>–In<sub>1</sub>). It is worth to point out that the sum of the covalent radii: 2.67 Å (Bi–As) and 2.96 Å (Bi–In), support our calculated results. Further experimental as well as theoretical studies are necessary in order to clarify these experimental/theoretical contradictions.

The total charge distributions along the Bi–In and Bi–As bonds for the ECLS and (1×2) model are depicted in Figs. 2 and 3, respectively. For the Bi–As bonds (V–V bonds), the electronic charge concentration on the As sites is determined by a higher electronegativity of As (2.2) compared with Bi (1.7). Figures 3(a) and 3(b) show the (re)bonding of the Bi adatoms with the second sublayer, along the InAs missing row: Bi<sub>2</sub>–As<sub>2</sub> and Bi<sub>3</sub>–In<sub>3</sub>. It is interesting to note that, in general, the total charge densities along the Bi–As or Bi–In bonds are almost identical for both structural models, which is in agreement with the similarities of the Bi–In (2.71 Å – 2.77 Å) or Bi–As (2.83 Å – 2.91 Å) equilibrium bond distances.

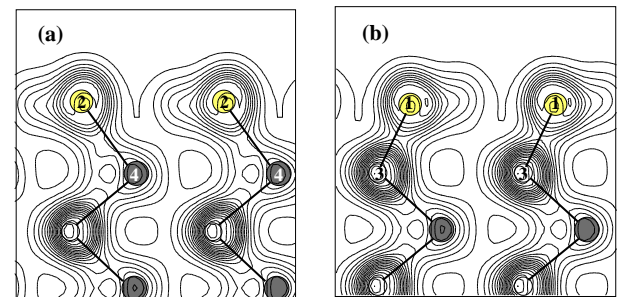


Figure 2. Total charge densities along the (a) Bi–In and (b) Bi–As bonds for the ECLS model.

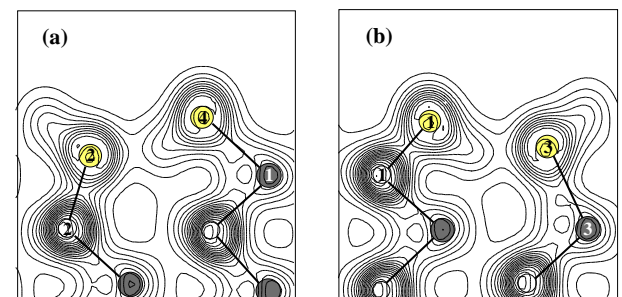


Figure 3. Total charge densities along the (a) Bi–In and (b) Bi–As bonds for the (1×2) model.

## 4 Conclusion

In summary, using first-principles pseudopotential technique, we have investigated the atomic geometry and energetic stability of the Bi-covered InAs(110) surface. We have considered two experimentally proposed structural models: ECLS and (1×2). Our results indicate that the recently proposed (1×2) model [7] is slightly more favourable in energy than the ECLS, thus supporting the experimentally observed ECLS→(1×2) structural transition on the Bi/InAs(110) surface. The calculated atomic equilibrium geometry of the

ECLS compares quite well with the previous works. Similarly for the  $(1 \times 2)$  model, our calculated Bi–Bi bond lengths agree very well with the experimental measurements. However, the same good agreement has not been verified for the Bi–In or Bi–As bond lengths, and for the relative vertical positions of the Bi–chains.

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