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# Atomic and electronic structure of Bi/GaAs(001)-$\alpha 2(2 \times 4)$

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**Abstract**

We report an *ab initio* pseudopotential calculation for the atomic and electronic structure of Bi/GaAs(001)-$\alpha 2(2 \times 4)$. Three structural models with Bi coverages of $\Theta = 1/4$ are considered, containing one Bi dimer or two Bi–As mixed dimers. According to our calculations for this coverage, the atomic model of the Bi/GaAs(001)-$(2 \times 4)$ reconstruction is similar to the $\alpha 2$ structure of the clean GaAs(001)-$(2 \times 4)$ surface in which the top As dimer is replaced by a Bi dimer. This result is in agreement with the most recent scanning tunneling microscopy work.

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

## 1. Introduction

During the last two decades, atomic and electronic properties of GaAs surfaces have been of great interest in surface science. This is particularly true for the clean and covered GaAs(001) surfaces which are artificially grown by molecular beam epitaxy (MBE) in a variety of reconstruction geometries as a result of different growth conditions, including the method of preparation, substrate temperature, and surface stoichiometry. Among the As-rich surfaces the well studied GaAs(001)-$(2 \times 4)$ reconstruction is found to have several stable phases, namely, $\alpha$, $\beta$, and $\gamma$ [1–3], $\beta 2$ [4], and $\alpha 2$ [5]. Calculations show that among these phases, the $\alpha 2$ structure is found to be energetically the most favorable one, for surfaces with balanced stoichiometry, differing from the $\alpha$ model by an amount of 0.034 eV/$(1 \times 1)$ [5]. For surfaces with more As-rich reconstruction the $\beta 2$ phase will form eventually, and in between, the two phases may coexist [6].

The theoretically predicted $\alpha 2$ structure has two As dimers in the $(2 \times 4)$ surface unit cell, one of which constitutes the first layer, the other one being in the third layer (see figure 1). This structure is also observed experimentally for clean [6, 7], Sb-adsorbed [8], N-adsorbed [9], B-adsorbed [10], In-adsorbed [10], and Bi-adsorbed [11] surfaces. In addition, other adsorbed surfaces like Sb/InAs(001) [7], Bi/InAs(001) and Bi/$GaAs_xN_{1-x}$(001) [12] are confirmed to have the $\alpha 2(2 \times 4)$ phase. As for the stabilized systems, an earlier theoretical work was presented [13] which studied the 3/4, 1/2, and 1/4 ML coverages of Sb-adsorbed GaAs(001)-$(2 \times 4)$ surfaces,

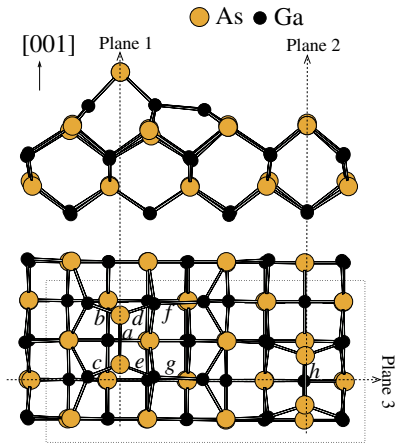


**Figure 1.** Schematic side view and the corresponding top view for the clean GaAs(001)-$\alpha 2(2 \times 4)$ surface. The vertical planes containing the As dimer *a* (plane 1), the As dimer *h* (plane 2), and the Ga–As–Ga–Ga chain (plane 3) are shown using dashed lines. The surface unit cell is also shown using dotted lines.

and found that the 3/4 ML coverage was not stable. The CASTEP calculations included in the work on N, B, and In substitutions on GaAs(001) surfaces [9, 10] also showed that the $\alpha 2$ and $\beta 2$ reconstructions were favored in their corresponding temperature ranges.

Ahola-Tuomi *et al* [11] have recently studied the electronic and structural properties of Bi-terminated reconstruc-

 

tions on GaAs(001) surfaces by means of scanning tunneling microscopy (STM), synchrotron radiation core-level spectroscopy, and low energy electron diffraction (LEED). They have observed that when the Bi-terminated GaAs(001) surface is heated, the reconstruction is changed from $(2 \times 1)$ to $(2 \times 4)$ before Bi desorbs from the surface. Moreover, they have recognized that the surface is of $\alpha 2$ type and, upon Bi adsorption, mainly the top layer As dimer is replaced by a Bi dimer, but the third-layer As dimer remains.

In this work, we have studied the atomic and electronic structure as well as the chemical bonding nature of clean and 1/4 ML Bi-adsorbed GaAs(001)-$\alpha 2(2 \times 4)$ surfaces from first principles and found that the Bi adsorption geometry with the lowest total energy is consistent with the observations of Ahola-Tuomi *et al* [11]. We have presented the energy band structures and electronic charge distributions of important surface states for both the clean and Bi-adsorbed systems.

## 2. Method

We have carried out *ab initio* calculations using the Vienna *ab initio* simulation package (VASP) [14, 15] which is a DFT code operating in a plane-wave basis set. The electron–ion interaction was considered in the form of an ultrasoft pseudopotential [16, 17] with plane waves up to an energy of 32 Ryd. This cut-off was found to be adequate for the structural studies as well as the electronic structure. We do not find any significant improvements in structural parameters when the energy cut-off is increased from 32 to 35 Ryd. The electron–electron interaction was considered within the local density approximation (LDA) of the density functional theory, using the correlation scheme of Ceperley and Alder [18] as parameterized by Perdew and Zunger [19]. Self-consistent solutions were obtained by employing the $(4 \times 2 \times 1)$ Monkhorst–Pack [20] grid of $k$-points for the integration over the Brillouin zone for the $(2 \times 4)$ reconstructed surface unit cell.

In our calculations, GaAs(001) surfaces were modeled by periodically repeated slabs in [001] direction. The unit cell included an atomic slab with nine layers of GaAs substrate (30 Ga atoms, 32 As atoms, 16 H atoms, and 2 Bi atoms) plus a vacuum of thickness ∼11 Å. The two back substrate layers were frozen into their bulk positions, and each As atom at the back surface was saturated with two hydrogen atoms ($Z = 3/4$). All the remaining substrate atoms, the adsorbate atoms, and the saturating H atoms were allowed to relax into their minimum energy positions. Pseudopotentials used for Bi, Ga, and As are $6s^2 6p^3$, $4s^2 4p$, $4s^2 4p^3$, respectively. In this work, for the surface calculations, we used our theoretical equilibrium lattice constant, 5.60 Å, obtained for the bulk GaAs, which is 0.9% smaller than the experimental value, 5.65 Å [21]. It is also smaller than our calculated value of 5.69 Å when the 3d valence Ga potential is taken into consideration. The band gap value for GaAs obtained with the utility of the VASP code came out to be 0.58 eV which is small compared to its experimentally measured value of 1.52 eV [21] due to the underestimation of the LDA method. Furthermore, the band gap, being only 0.12 eV, was even smaller when we treated the Ga 3d electrons as valence electrons. However, our calculated value 0.58 eV with Ga 3d core potentials is comparable with other values calculated using various approximations and codes, VASP [22], CASTEP [22], and FHI98md [23].

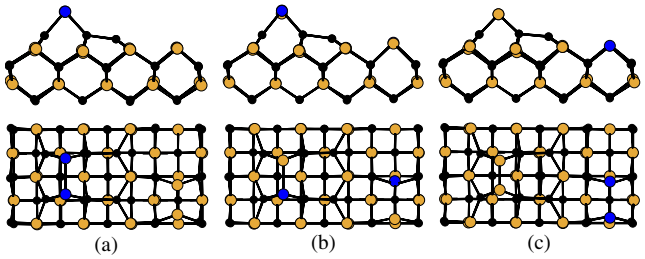


**Figure 2.** Schematic side views and the corresponding top views for 1/4 ML Bi-adsorbed GaAs(001)-$\alpha 2(2 \times 4)$ surfaces: (a) model I, (b) model II, and (c) model III. Larger dark (blue) balls are Bi atoms.

**Table 1.** The calculated bond lengths (in Å) of the bonds (indicated in figure 1) and the energy differences, $\Delta E$ (in eV), for the models shown in figure 2.

| Models | $a$ | $b$ | $c$ | $d$ | $e$ | $f$ | $g$ | $h$ | $\Delta E$ |
|---|---|---|---|---|---|---|---|---|---|
| Clean | 2.48 | 2.42 | 2.42 | 2.48 | 2.48 | 2.50 | 2.50 | 2.49 | — |
| Model I | 3.03 | 2.67 | 2.67 | 2.72 | 2.72 | 2.47 | 2.47 | 2.49 | 0.00 |
| Model II | 2.76 | 2.40 | 2.68 | 2.46 | 2.73 | 2.50 | 2.46 | 2.77 | 0.03 |
| Model III | 2.48 | 2.40 | 2.40 | 2.47 | 2.47 | 2.48 | 2.48 | 3.03 | 0.40 |

## 3. Results and discussion

The GaAs(001) surface exhibits several different surface reconstructions dictated by the preparation conditions. The $(2 \times 4)$ reconstruction on a clean GaAs(001) surface has been well established by different structural models. Among these, the $\alpha 2$ structure is theoretically predicted to be the most stable one in certain temperature ranges corresponding to low As coverage with balanced stoichiometry. This reconstruction is also experimentally observed on clean GaAs(001)-$(2 \times 4)$ and InAs(001)-$(2 \times 4)$ surfaces as well as on Sb-, N-, B-, and Bi-covered surfaces. Before studying the adsorption of Bi on GaAs(001)-$\alpha 2(2 \times 4)$, we have examined the atomic and electronic structure of clean GaAs(001)-$\alpha 2(2 \times 4)$. Later, we studied three possible model surfaces having different adsorption sites for the Bi adsorbate with 1/4 ML concentration (see figure 2). The resulting atomic geometries and band structures will be described and compared with the existing experimental results in the following subsections.

### *3.1. The clean GaAs(001)-α2(2 × 4) surface*

Figure 1 shows the clean $\alpha 2(2 \times 4)$ reconstruction of the GaAs(001) surface, where there are two As dimers within the $(2 \times 4)$ surface unit cell. We labeled the first As dimer located in the top layer of the surface as As dimer $a$ and the second one in the third substrate layer as As dimer $h$. Using our energy minimization procedure, starting with this geometry, we have calculated the totally relaxed structure, and certain key parameters are listed in table 1. We found that the As dimers

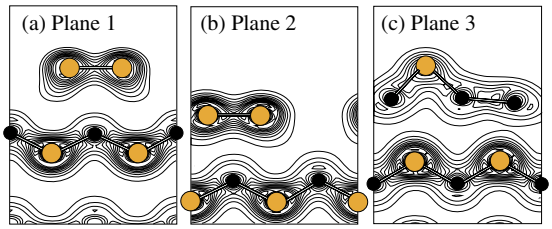


**Figure 3.** Total electronic charge-density plots for the clean GaAs(001)-$\alpha 2(2 \times 4)$ surface for the three planes defined in figure 1.

are symmetric (i.e., there is no buckling), having bond lengths of 2.48 Å for the As dimer *a* and 2.49 Å for the As dimer *h*. These dimer bond lengths are in good agreement with the other theoretical calculations giving values of 2.47 and 2.50 Å [23] and of 2.46 and 2.48 Å [24], respectively.

The total electronic charge-density plots in vertical planes containing the As dimer *a* (plane 1), As dimer *h* (plane 2), and Ga–As–Ga–Ga chain (plane 3) are shown in figures 3(a), (b), and (c), respectively. Figures 3(a) and (b) indicate that both As dimers *a* and *h* are seen to be strongly covalent and perfectly symmetric. In fact, the As dimer bond shows a pronounced double-hump feature, indicating that wavefunction overlap may not be as complete as in the Ga–Ga and Ga–As bonds. Figure 3(c) shows that the Ga–As bonding is partly covalent and partly ionic in nature. The Ga–Ga bond is covalent with some degree of ionicity towards the lower Ga atom.

The electronic band structure in the vicinity of the fundamental band gap region is depicted in figure 4(a). We have identified five occupied surface electronic states labeled as $V_1$–$V_5$, which lie above the bulk valence band continuum but below the valence band top. Their energy levels are found within a range of 0.5 eV. There are also five unoccupied surface states, labeled as $C_1$–$C_5$, which fall into the gap but not below the conduction band minimum as shown in figure 4(a). The orbital features of each surface state at the $\overline{\mathrm{K}}$ point are calculated in terms of their individual partial charge-density plots and the important ones are shown in figure 5.

The lowest unoccupied state $C_1$ corresponds to an antibonding $\sigma^*$ combination of in-plane p orbitals at the As dimer *a* as shown in figure 5(a). The second unoccupied state $C_2$ is related to the empty Ga dangling bonds of the second layer (see figure 5(b)). The next lowest unoccupied state, $C_3$, has a more complex antibonding combination stemming from the As dimer *h*, as seen in figure 5(c).

The highest of the occupied surface states $V_1$ is due to an antibonding $\pi^*$ combination of $p_z$ orbitals localized at As dimer *h* (see figure 5(d)). Only about 0.1 eV lower in energy, we find the state $V_2$ which has mainly $\pi^*$ antibonding contributions from the $p_z$ orbitals localized at As dimer *a* plus some $\sigma$-type contribution from As–Ga bonds between the fourth and fifth atomic layers as shown in figure 5(e). The $V_3$ state is due to $\pi$ bonding of $p_z$ orbitals of the As dimer *a* and has some degree of contributions due to As–Ga bonds of the deeper layers (see figure 5(f)). The $V_4$ state is also due to $\pi$ bonding of $p_z$ orbitals but localized at the As dimer *h*. The lowest state $V_5$, barely in the gap, involves mainly $\sigma$-type

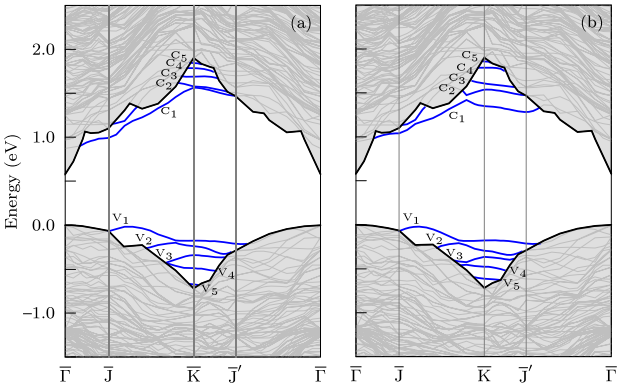


**Figure 4.** Electronic band structure for (a) the clean GaAs(001)-$\alpha 2(2 \times 4)$ surface and (b) the Bi/GaAs(001)-$\alpha 2(2 \times 4)$ system for the model I. The thick solid lines represent the surface bands in the gap. The shaded region is the $(2 \times 4)$-projected bulk band structure for GaAs.

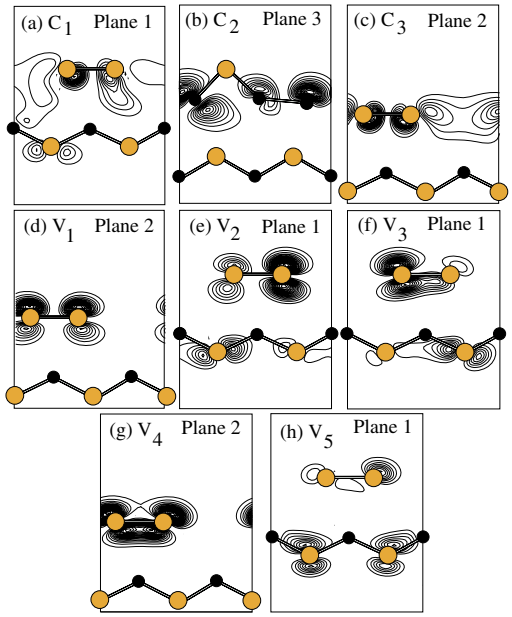


**Figure 5.** Partial charge-density plots at the $\overline{\mathrm{K}}$ point for some of the unoccupied ((a)–(c)) and occupied ((d)–(h)) states indicated in figure 4(a) for the clean GaAs(001)-$\alpha 2(2 \times 4)$ surface.

bonding between As and Ga of the fourth and fifth layers as seen in figure 5(h).

### *3.2. The Bi/GaAs(001)-α2(2 × 4) surface*

In this work, we have considered a total of three possible models for the adsorption of $\Theta = 1/4$ ML Bi on the GaAs(001) surface, with the $\alpha 2(2 \times 4)$ reconstruction. These three models are shown in figure 2. Model I replaces the As dimer *a* with a Bi dimer, while As dimer *h* remains at the third layer. Model II contains mixed dimers on both the first and the third layers. Model III replaces the third-layer As dimer *h* with a Bi dimer, but keeping the As dimer *a* in the first layer. After the energy minimization, the relaxed geometries are obtained and the key parameters for each model are listed in table 1.

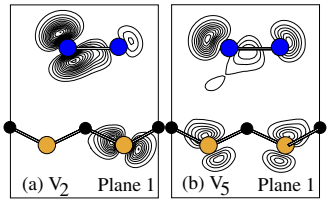


**Figure 6.** Partial charge-density plots at the $\overline{\text{K}}$ point for some of the occupied states $V_2$ and $V_5$ for the Bi/GaAs(001)-$\alpha 2(2 \times 4)$ system shown in figure 4(b).

The Bi dimer *a* in model I and the Bi dimer *h* in model III have the same length, while the As dimer *h* in model I and As dimer *a* in model III have their bond-length values of the clean surface case, as expected. In fact, all the bond lengths close to the Bi dimer get larger as it is longer than the As dimer, and as a result of this it stands higher in the surface due to the difference in their ionic radii. The other dimer (still As) and its environment are not affected, so have bond lengths similar to those found before (the clean case). The only difference then is that in model I the Bi dimer is relaxed outward on the first layer and that lowers the total energy, whereas in model III the Bi dimer is still relaxed outward, however being on the third layer it is still in the trench and has larger total energy. Model II has mixed dimers which are slightly buckled ($b \neq c$, and $d \neq e$) as opposed to other models, since Bi atoms stand higher. We found that model I and model II are energetically somewhat close to each other with only 0.03 eV energy difference. This is in agreement with the experimental observations of Ahola-Tuomi *et al* [11].

In figure 4(b) we show the electronic band structure for the energetically favored Bi/GaAs(001)-$\alpha 2(2 \times 4)$ system, namely, model I. The band structure is quite similar to that of the clean GaAs(001)-$\alpha 2(2 \times 4)$ surface. This is due to having the same reconstruction elements (group V). The occupied surface states lie within an energy range of 0.5 eV of the band edges as seen also for the clean surface case. Their orbital natures are similar to each other as well. The only differences are seen in the states $V_2$ (see figure 6(a)), which is now due to the $\pi$ bonding of $p_z$ orbitals localized at the Bi dimer, instead of $\pi^*$ antibonding of $p_z$ orbitals located at the As dimer *a* in the clean case, and the occupied state $V_5$ which is now dominantly $\pi$-type Bi related (see figure 6(b)), with some contributions from Ga–As $\sigma$ bonds of lower layers. This state is now pushed up about 0.1 eV in energy, compared to the clean case. Being related to the Ga dangling bonds, the unoccupied states are not expected to differ in nature from those for the clean case, and similarly the fundamental gap is still free of surface states. This is very similar to the conclusion obtained from Sb adsorption on GaAs(001)-$(2 \times 4)$ surfaces [13].

We have also calculated the DOS curves for the clean GaAs(001)-$\alpha 2(2 \times 4)$ surface and model I for the Bi-adsorbed case for comparison, which are presented in figure 7. The peaks for the clean surface (dotted lines), at $-3.7$ and $-10.5$ eV, corresponding to less dispersed states, are seen to be dispersed further when the top As dimer is replaced by the Bi dimer. Moreover, there is a small narrowing of about

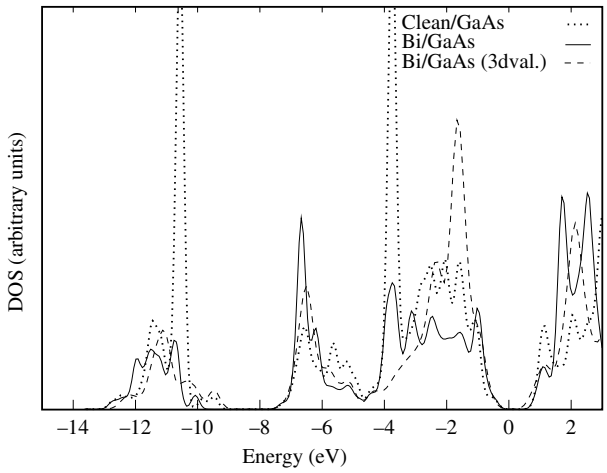


**Figure 7.** The density of states (DOS) curves for model I for the Bi/GaAs(001)-$\alpha 2(2 \times 4)$ system with the use of 3d core (solid line) and 3d valence (dashed lines) potentials. The dotted line shows the curve for the clean GaAs(001)-$\alpha 2(2 \times 4)$ surface for comparison.

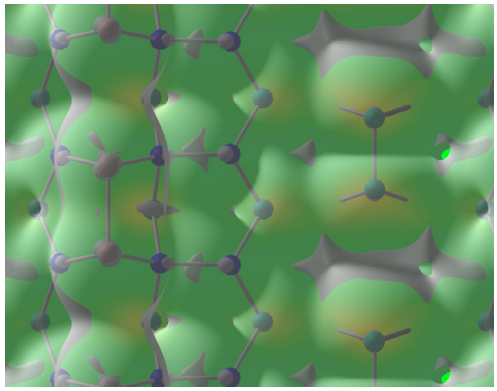

**Figure 8.** Calculated STM image of the Bi adsorption on the GaAs(001)-$\alpha 2(2 \times 4)$ surface.

0.5 eV in the bandwidth around $-9.5$ eV. Considering the possible effects of the lower 3d states of Ga atoms in the higher valence band structure of the GaAs and in the interactions with Bi adatoms in the vicinity, we have repeated the DOS calculation for model I for the Bi-adsorbed system with the use of 3d valence potentials for comparison and observed that the changes in the valence band DOS are only slight, as shown in figure 7. Moreover, the surface states displayed in figure 4(b) did not change at all with the inclusion of d potentials in the calculations. We have calculated the STM image of the Bi adsorption on the GaAs(001)-$\alpha 2(2 \times 4)$ surface, using Bardeen's tunneling formula [25]. The bias voltage of $-1$ V is used to image the surface as seen in figure 8. The upper large protrusion represents the Bi–Bi dimers, while the other protrusion is for the As–As dimer.

## 4. Summary

We have studied the atomic and electronic structure of 1/4 ML Bi coverage on the GaAs(001)-$\alpha 2(2 \times 4)$ surface. We have found that the Bi dimer replacing the As dimer in the first layer

is energetically more favorable than when replacing the third-layer As dimer. However, no significant energy difference is obtained when the two Bi adatoms mix with the dimer As atoms on both the first and the third layers. Comparison of the band gap surface states for the clean and Bi-covered GaAs(001)-$\alpha 2(2 \times 4)$ systems indicates that the occupied state labeled as $V_2$ is now dominantly Bi related and of $\pi$ orbital character.

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