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Theoretical investigations of Sb-induced (3×8) and (1×3) reconstructions on the GaAs(111)*B* surface

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We have performed a detailed theoretical study of the atomic geometry, stability, and electronic structure of the GaAs(111)B−Sb(3×8) and GaAs(111)B−Sb(1×3) surfaces using *ab initio* pseudopotential calculations. The (3×8) surface is semiconducting, with the highest occupied and lowest unoccupied surface states mainly localized on the unbonded As atoms and the Sb trimers, respectively. The (1×3) surface is stabilized by a strain relieving mechanism, but does not satisfy the electron counting rule and gives rise to partially occupied states which are mainly localized on the unbonded As atoms. Our calculations reveal that the (1×3) surface becomes energetically favorable for lower coverages of Sb, in agreement with the STM images obtained by Moriarty *et al.* of the (3×8)→(1×3) phase transition as the annealing temperature is increased.

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I. INTRODUCTION

The (111) semiconductor surfaces covered by (semi)metallic elements have been the subject of many experimental works.[1–7] In particular, the As- and Bi-covered As terminated GaAs(111) surface, hereafter referred to the GaAs(111)B surface, present very well-defined (2×2) and $c(2\times4)$ reconstructions formed by As-trimers[5,6] and Bi-trimers,[7] respectively. However, the Sb-covered GaAs(111)B surface presents a different character. An annealing process (at ≈375 °C) of the GaAs(111)B surface covered by three monolayers (ML) of Sb atoms gives rise to a family of complex reconstructions, which are constrained to the electron counting rule (ECR). The ECR sets some basic requirements for the electronic charge distribution on polar semiconductor surfaces: the number of available electrons on the surface layer should be equal to the number of electrons necessary to fill all the dangling bonds of the electronegative elements (As and Sb in the present case), leaving empty all the dangling bonds of the electropositive elements (Ga in the present case). This rule was initially proposed by Pashley,[8] in the study of the GaAs(001) and ZnSe(001) surfaces. Scanning tunneling microscopy (STM) images obtained by Moriarty *et al.*[1–3] indicate that the Sb-covered surface presents predominantly a (3×8) reconstruction, with a coverage of 3/4 ML of Sb atoms. The GaAs(111)B−Sb(3×8) surface is formed by Sb-trimers separated by pairs of Sb-chains along the $[\bar{1}10]$ direction. Recent x-ray photoemission experiments by Cafolla *et al.*[4] support this surface reconstruction. On the other hand, increasing the annealing temperature of the Sb-covered GaAs(111) surface to ≈475 °C, a structural transition has been observed: the locally ordered trimer- and chain-based GaAs(111)B−Sb(3×8) surface reconstruction converts to a new GaAs(111)B−Sb(1×3) reconstruction that shows long-range order formed only by Sb-chains along the $[\bar{1}10]$ direction, with a Sb coverage of 2/3 ML, but does not satisfy the ECR.

Although the formation of the GaAs(111)B−Sb(1×3) surface is not electronically favorable (as does not satisfy the ECR), the stability of this model was attributed to the reduced local bonding distortion on the Sb-chains, relatively to the Sb-trimers on the GaAs(111)B−Sb(3×8) surface.[2] This suggests that the reduction of the stress on the surface provides a driving force for the (3×8)→(1×3) structural transition as a function of the Sb coverage. There are some theoretical studies[5,9,10] that confirm the experimentally observed formation of As-trimers on the GaAs(111)*B*-(2×2) surface. However, to our knowledge, there are no theoretical studies for the Sb-covered GaAs(111)B surface, which can provide support for the experimental studies carried out by Moriarty *et al.* Since the combination of the trimer-plus-chain combination on the Sb-covered surface represents a completely different model than that observed the As- and Bi-covered structures, we strongly believe that the Sb-covered GaAs(111)B surface is an interesting system which deserves a detailed theoretical study.

In this work we have performed theoretical *ab initio* calculations to determine the equilibrium surface atomic geometry of the GaAs(111)B−Sb(3×8) and GaAs(111)B−Sb(1×3) surfaces. The electronic band structure of these surfaces has been studied, within and around the fundamental band-gap region. We have calculated the relative stability of the GaAs(111)B−Sb(3×8) and GaAs(111)B−Sb(1×3) surfaces, as a function of the concentration of the Sb-adatoms. Theoretically simulated STM images for the occupied states clearly show the formation of Sb-trimers and Sb-chains on the GaAs(111)B−Sb(3×8) surface, and of only Sb-chains on the GaAs(111)B−Sb(1×3) surface.

II. METHOD

Our calculations were performed in the framework of the density functional theory,[11] within the local density approximation (LDA) using the Ceperley-Alder correlation[12] as parametrized by Perdew and Zunger.[13] The electron-ion interaction was treated by using norm-conserving, *ab initio*, fully separable pseudopotentials.[14] The wave functions were expanded in a plane wave basis set with a kinetic energy cutoff of 10 Ry. The theoretical equilibrium lattice constant of 5.62 Å was used for the GaAs. In order to simulate the surfaces, we used the repeated slab method,[11] with a supercell containing six atomic layers and a vacuum region equivalent to twice the bulk lattice constant of the respective compound. To avoid the artificial electrostatic field, which arises from the application of the periodic boundary condition to the polar slab, we used a dipole correction as proposed by Neugebauer and Scheffler.[15,16] Our calculations indicate that the change of the total energy, due to dipole correction, is less than 1 meV. A layer of fractionally charged hydrogen atoms was used to saturate the cation dangling bonds at the bottom layer of the slab. Due to the large surface unit cell, and in order to keep the calculations computationally reasonable, the electronic charge density was calculated at the center of the surface Brillouin zone. The four topmost layers were fully relaxed to within a force convergence criterion of 25 meV/Å.

III. RESULTS AND DISCUSSIONS

A. GaAs(111)B−Sb(3×8) surface

The structural model and the total valence charge density of the GaAs(111)B−Sb(3×8) surface are shown in Fig. 1, hereafter referred to as the (3×8) surface. This surface presents rows of Sb chains pairs along the $[\bar{1}10]$ direction that are separated by 10.31 Å. On the surface unit cell, as shown in Fig. 1(a), between two chain-pairs there are two Sb trimers adsorbed on the T_4 sites and three unbonded (or rest) As atoms (three-fold coordinated), and between a chain-pair there is a ''line'' of unbonded (or rest) As atoms. The bond lengths between Sb atoms on the trimers and on the chains are very similar, 2.89 Å and 2.86 Å, respectively. Experimental works suggest a bond length in the range of 2.72 Å–2.90 Å.[1,2] The formation of covalent bonds between the Sb adatoms is clearly verified. However, the Sb bonds on the chains are slightly more covalent than on the trimers. The formation of covalent bonds between the adsorbed Sb atoms and the sublayer As atoms is shown in Figs. 1(b) and 1(c), where the total valence charge density is more concentrated on the As atoms, in agreement with the larger electronegativity of As. The vertical distance, along the z direction, between the top layer Sb and the second layer As atoms is almost the same (≈ 2.54 Å) for both trimers and chains. Due to the formation of the trimers and chains on the top layer, the GaAs bonds between the third and fourth layers, which are below the trimers or chains, are compressed by ≈ 0.05 Å relative to the GaAs bulk (2.43 Å). On the other hand, the bonds that are aside the trimers or chains are stretched by ≈ 0.07 Å. Thus the induced stress in the bulk region is almost the same below both the trimers and chains. As expected, the Sb–Sb bond angle is 60° in the trimers, but it is nearly 90° in the chains. As proposed by Moriarty *et al.*,[1–3] the relative stability of the chains is attributed to the local geometric similarities between the Sb chains and Sb in the solid crystalline phase. Our calculated results support this statement, since the bond length (2.86 Å) and bond angle ($\approx 88°$) of the chains are very similar to the bond length and bond angle in the crystalline phase (rhombohedral structure) of Sb. Relative to the third-layer Ga, the unbonded As atoms are at two different and significantly higher displacements (1.06 Å and 1.14 Å) than the GaAs vertical displacement (0.81 Å), as shown in Figs. 1(b) and 1(c), respectively.

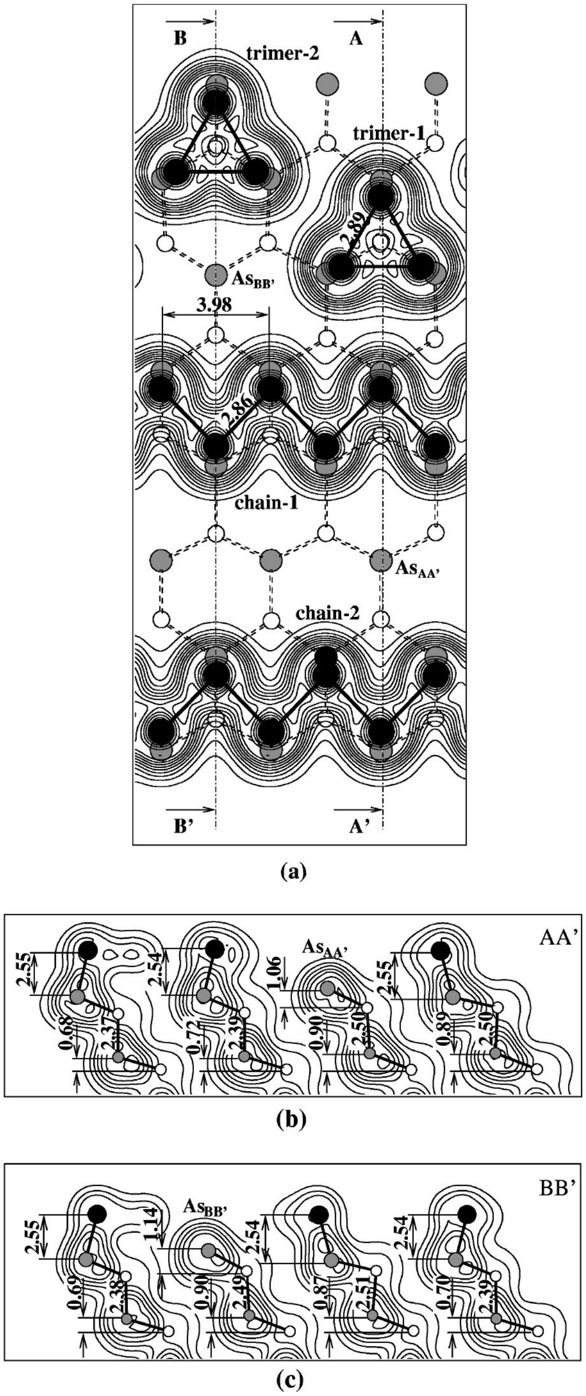


FIG. 1. Atomic positions and the total charge density on the GaAs(111)B−Sb(3×8) surface: (a) top view, (b) side view passing through the plane AA', and (c) side view passing through the plane BB'.

Our electronic structure calculations indicate that the (3×8) surface presents a semiconductor character, with the bulk energy band gap of 1.40 eV at the Γ-point calculated within the LDA at the theoretical lattice constant. Figure 2(a) presents the electronic band structure near the fundamental gap along the ΓX and ΓY directions, parallel and perpen-

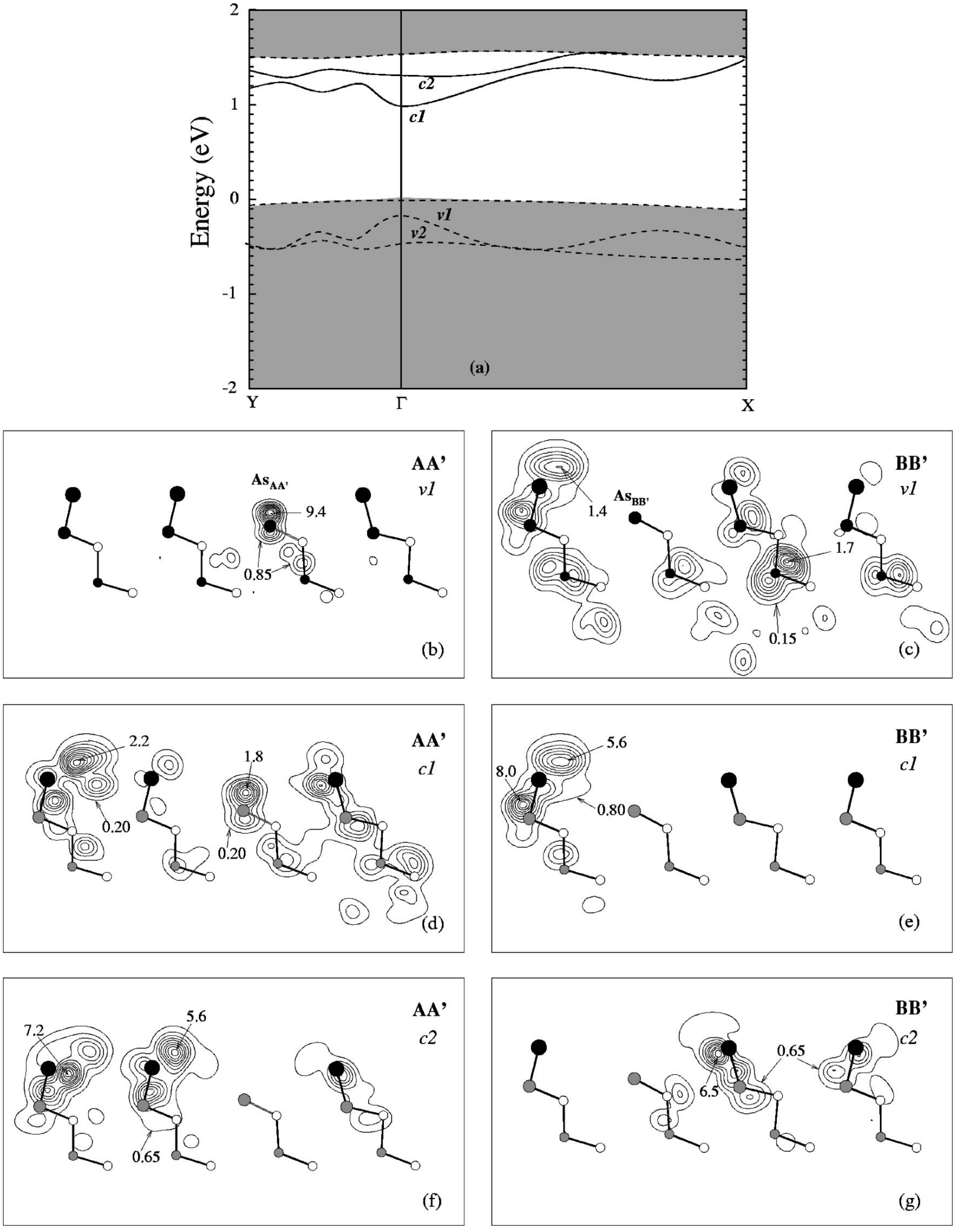


FIG. 2. (a) Electronic band structure of the GaAs(111)B−Sb(3×8) surface, near the bulk fundamental gap. Partial electronic charge density at the Γ-point for the *v1* state passing through (b) AA' plane and (c) BB' plane, for the *c1* state passing through (d) AA' plane and (d) BB' plane, and for the *c2* state passing through (e) AA' plane and (f) BB' plane. Unit: 10^{-3} electrons per (a.u.)^3.

dicular to the Sb chains, respectively. The two highest occupied states, *v1* and *v2*, are resonant with the GaAs bulk states, and are localized at 0.2 eV and 0.5 eV below the GaAs valence band maximum at the Γ-point. Figures 2(b) and 2(c) present the charge density of the *v1* band, passing through the planes AA' and BB' indicated in the Fig. 1(a). Clearly the *v1* band is mainly contributed from the lone p_z orbitals localized on the unbonded As atoms between the two chains, with two additional small contributions from: (i) π-like orbitals localized on the trimer-2, and (ii) second and fourth layer As atoms below the chains. However, the unbonded As atoms between the trimers and chains (i.e., within the trimer region, As$_{BB'}$) do not contribute to the formation of the *v1* band. The *v2* band, similar to *v1*, is formed by the

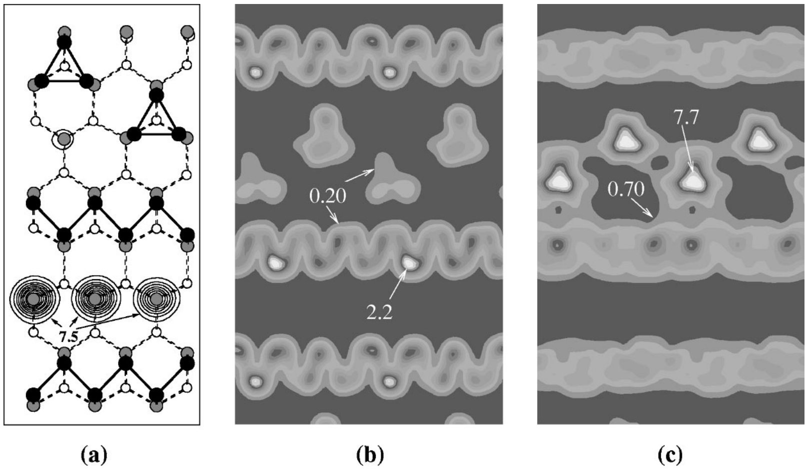


FIG. 3. (a) Partial electronic charge density for the GaAs(111)B$-$Sb(3$\times$8) surface at the Γ-point, plotted 1.2 Å above the unbonded As atoms within an energy interval of 0.4 eV below the bulk valence band maximum. Partial electronic charge density at the Γ-point, plotted 1.2 Å above the top-layer Sb atoms within an energy range: (b) 0.4 eV below the bulk valence band maximum and (c) 0.4 eV above the lowest unoccupied surface state. Unit: 10^{-3} electrons per (a.u.)^3.

lone p_z orbitals of the unbonded As atoms between chains. Different from the *v1*, the *v2* band is also localized on the unbonded As atoms between trimers and chains. Two unoccupied surface states, *c1* and *c2*, are found to be localized below the GaAs bulk conduction band minimum. Figures 2(d)–2(g) present the charge densities of these states. Essentially, these states arise due to the lone p_z orbitals of the Sb atoms forming the trimers. We find that the *c1* band is additionally contributed by the Sb$^{\text{trimer}}$–As backbonds, the Sb$^{\text{chain}}$–As backbonds, as well as from the unbonded As atoms between chains [cf. Figs. 2(d) and 2(e)]. The *c2* band has a strong contribution from the Sb$^{\text{trimer}}$–As backbonds and the Sb chains [cf. Figs. 2(f) and 2(g)].

The charge density distribution of the higher-lying occupied states, within an energy interval of 0.4 eV below the bulk valence band maximum and at 1.2 Å above the unbonded As atoms, is shown in Fig. 3(a). A dominant contribution from the unbonded As atoms between chains, $\text{As}_{AA'}$, is clearly seen. Figure 3(b) presents the charge density of the higher-lying occupied states within the an energy interval of 0.4 eV below the bulk valence band maximum and 1.2 Å above the top-layer Sb atoms. This figure represents a possible STM simulation at a constant height (1.2 Å from the Sb top-layer) and with a suitable bias voltage that allows imaging of the filled bands of the GaAs(111)B$-$Sb(3$\times$8) surface to within -0.4 eV below the bulk valence band maximum. The formation of the Sb chains is clearly observed. Figure 3(c) shows the charge density of the unoccupied surface states at 1.2 Å above the Sb top-layer, within an energy interval of 0.4 eV from the lowest unoccupied state. There is a high concentration of states on the trimers, and only a small contribution from the chains. Figure 3(c) also can be interpreted as a possible STM image of the unoccupied states for a tip height of 1.2 Å from the surface and with a bias voltage of 0.4 V above the lowest unoccupied state. Our theoretical simulations of the STM images for the occupied and unoccupied surface states are similar to the constant current STM images obtained by Moriarty *et al.*[1–3]

B. GaAs(111)B$-$Sb(1$\times$3) surface

Reduction in the coverage of Sb adatoms on the GaAs(111)B surface, from 3/4 ML to 2/3 ML, leads to the formation of the GaAs(111)B$-$Sb(1$\times$3) surface, as has been observed in the STM images.[2] The STM images indicate that upon an increased annealing treatment a transition from the (3$\times$8) reconstruction (characterized by locally ordered Sb chain pair and trimers) to a (1$\times$3) reconstruction (characterized by a long range order formed by a uniform coverage of Sb chains) has taken place. Our calculations indicate that the valence charge density distribution and the atomic geometry of the chains on the (1$\times$3) and (3$\times$8) surfaces are very similar, as shown in Fig. 4. Relative to the

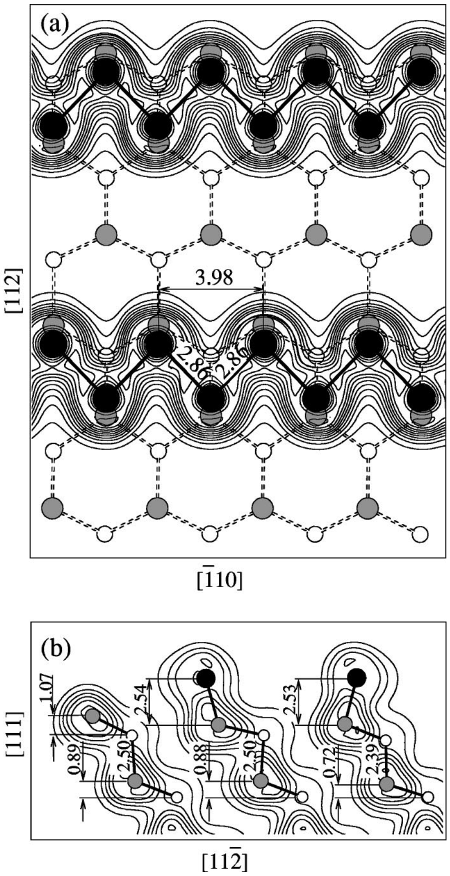


FIG. 4. Atomic positions and the total charge density of the GaAs(111)B$-$Sb(1$\times$3) surface: (a) top view, (b) side view.

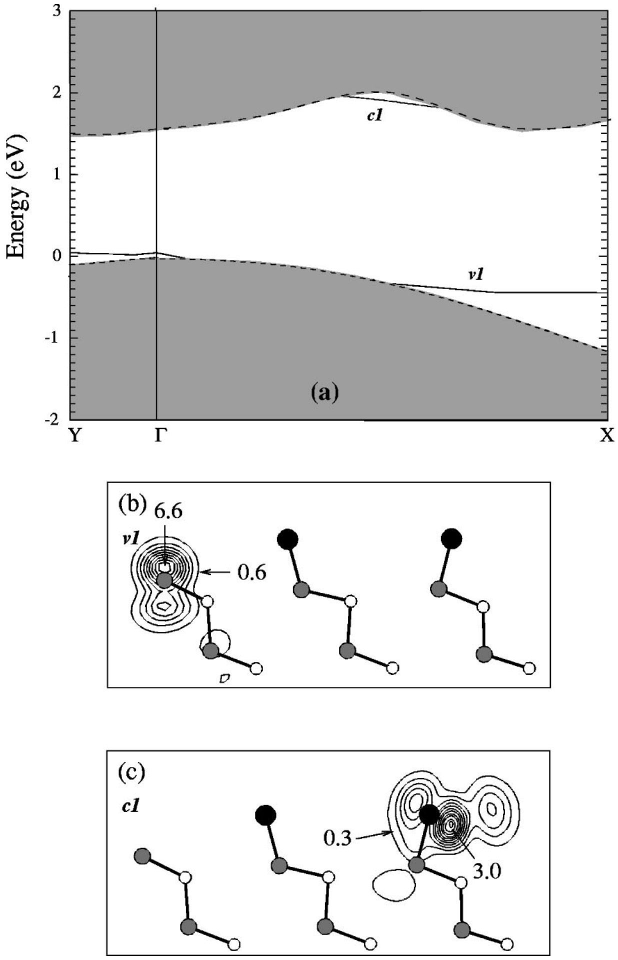
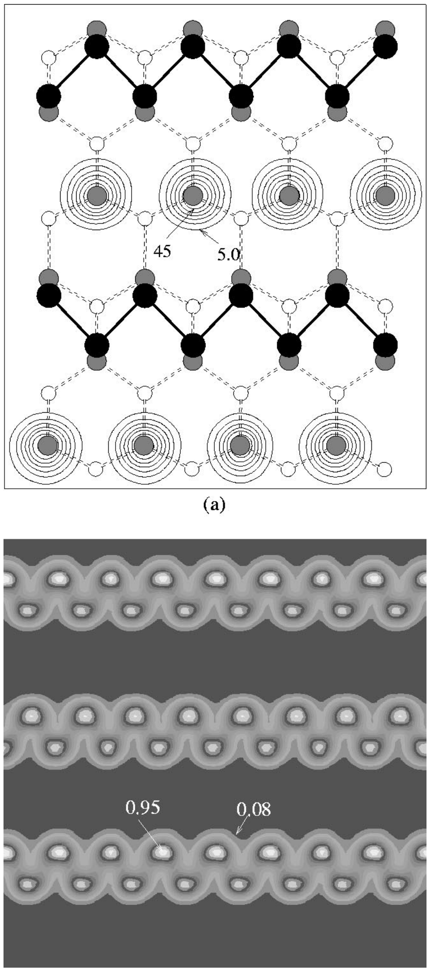


FIG. 5. (a) Electronic band structure of the GaAs(111)B−Sb(1×3) surface, near the fundamental gap. The Fermi level E_F lies slightly above the bulk valence band maximum, and is considered as the energy zero. Partial electronic charge density at the X' point: (b) *v1* band and (c) *c1* band. Unit: 10^{-3} electrons per (a.u.)^3.

bulk bond length, the Ga-As bonds below the chain are compressed by ≈0.05 Å, and the Ga-As bonds aside the chain are stretched by ≈0.07 Å. The unbonded As atoms are displaced upward by 0.26 Å relative to their ideal positions in the GaAs bulk. Thus the elastic stress on the GaAs substrate, due to the formation of Sb-chains, is very similar for both the (3×8) and (1×3) structures.

Figure 5 presents the calculated electronic band structure near the GaAs bulk fundamental band gap, along the ΓX and ΓY directions, parallel and perpendicular to the Sb chains, respectively. Two surface states have been identified in the bulk band-gap region. The band *v1*, near the valence band maximum, is dispersionless along the ΓY direction (perpendicular to the Sb chain), but shows a weak dispersion along the chain (the ΓX direction). The highest occupied state (the Fermi level) lies almost at the valence band maximum, making the *v1* band partially filled: it is completely filled along ΓX and completely empty along ΓY. This state is completely localized on the unbonded As atoms and can be identified as the lone p_z orbital; see Fig. 5(b). The band *c1* is completely empty and falls into the band-gap region halfway along the ΓX direction. It is mainly contributed by the lone p_z orbitals on the Sb chain atoms [see Fig. 5(c)], a situation somewhat similar to that found for the (3×8) surface [cf. Fig. 2(d)].



(a)

(b)

FIG. 6. (a) Partial electronic charge density of the GaAs(111)B−Sb(1×3) surface, plotted 1.2 Å above the unbonded As atoms within an energy range of 0.4 eV below the Fermi level E_F. (b) Partial electronic charge density, plotted 1.2 Å above the top-layer Sb atoms within an energy range of 0.4 eV below E_F. Unit: 10^{-3} electrons per (a.u.)^3.

Our results are in complete agreement with the suggestion forwarded by Moriarty *et al.*[2] that the (1×3) surface does not obey the ECR. Despite some charge transfer from the Sb-chains to the As rest atoms, the latter remain partially occupied. The small electronegativity difference, and the large distance between Sb and the As rest atoms, are insufficient for a complete charge transfer from Sb to As. Our results suggests that this reconstruction is stabilized by a strain relieving mechanism within the Sb-chains. We will discuss this point in Sec. III C.

Figure 6 presents the charge density distribution of the higher-lying occupied states, within an energy interval of the 0.4 eV below the calculated Fermi level, and on the surface plane located at 1.2 Å above the unbonded As atoms. Similar to the (3×8) surface, we observed a high charge concentration on the unbonded As atoms. Within the same energy interval (0.4 eV below the Fermi level), at 1.2 Å above the top layer Sb atoms, the charge density is distributed along the chains. However, the charge concentration on the chains is about 50 times smaller than the charge density on the unbonded As atoms [cf. Fig. 6(b)].

C. Relative stability of the GaAs(111)B−Sb(3×8) and GaAs(111)B−Sb(1×3) surfaces

The relative stability of the Sb atoms, forming chains or trimer structures on the GaAs(111)B surface, can be inferred by investigating total energy differences. We first consider the total energy difference, expressed as

$$\Delta E(3\times 8)=E_{\mathrm{trimer}}-E_{(3\times 8)},$$

where E_{trimer} represents the total energy of the GaAs(111)B surface covered only by Sb trimers (with six trimers per unit cell, 3/4 ML), and $E_{(3\times 8)}$ represents the total energy of the GaAs(111)B−Sb(3×8) surface (containing two trimers, 1/4 ML, and two chains per unit cell, 1/2 ML). These two structures are stochiometrically equivalent with respect to the concentration of the Sb atoms, and both models satisfy the ECR. We have used the same calculational procedure to calculate both E_{trimer} and $E_{(3\times 8)}$, including the same size of the supercell. Our calculations indicate that the (3×8) model is energetically more favorable than the trimer model by 0.55 eV/(3×8) or 0.14 eV per trimer. This indicates that the equilibrium configuration of the (3×8) surface prefers four trimers per 3×8 unit cell to be converted into the chain geometry. The energetic stability of the Sb chains, with respect to the Sb trimers, was proposed by Moriarty *et al.*,[2] and our calculations confirm this experimental proposition.

We next calculated the energetic stability of the (1×3) model, with respect to the (3×8) and *trimer* models. As these structures present different concentrations of Sb atoms, we have to include the chemical potential μ_{Sb} of the Sb element. With this, the total energy difference can be written as

$$\Delta E_i(\mu_{\mathrm{Sb}})=E_i-E_{(1\times 3)}-2\mu_{\mathrm{Sb}},$$

where $i=(3\times 8)$ or trimer and $E_{(1\times 3)}$ represents the total energy of the GaAs(111)B−Sb(1×3) surface. The variation in the chemical potential μ_{Sb} must be considered subject to its maximum value being the chemical potential of Sb solid ($\mu_{\mathrm{Sb}}^{\mathrm{bulk}}$):

$$\mu_{\mathrm{Sb}}\leqslant\mu_{\mathrm{max}}^{\mathrm{Sb}}\equiv\mu_{\mathrm{Sb}}^{\mathrm{bulk}}.$$

The chemical potential $\mu_{\mathrm{Sb}}^{\mathrm{bulk}}$ was calculated using the same calculational procedure and similar technical details, as used for the surface calculations. The result of the $\Delta E_i(\mu_{\mathrm{Sb}})$ and $\Delta E(3\times 8)$ are shown in Fig. 7. The values of μ_{Sb} are relative to $\mu_{\mathrm{Sb}}^{\mathrm{bulk}}$. Our results indicate that for high concentration of Sb, viz. in the limit $\mu_{\mathrm{Sb}}\rightarrow\mu_{\mathrm{Sb}}^{\mathrm{bulk}}$, the (3×8) model (with 3/4 ML coverage of Sb) is energetically more favorable than the (1×3) model: $\Delta E_{(3\times 8)}(\mu_{\mathrm{Sb}})<0$. However, for $\mu_{\mathrm{Sb}}\leqslant\mu_{\mathrm{Sb}}^{\mathrm{bulk}}-0.22$ eV the (1×3) model (with 2/3 ML coverage of Sb) becomes energetically more stable: $\Delta E_{(3\times 8)}(\mu_{\mathrm{Sb}})>0$. Our calculations also indicate that the formation of the GaAs(111)B surface covered only by Sb-trimers, the *trimer* model, is energetically less favorable than the GaAs(111)B surface covered only by Sb-chains, viz. the (1×3) model: $\Delta E_{\mathrm{trimer}}(\mu_{\mathrm{Sb}})>0$, even for high concentration of Sb.

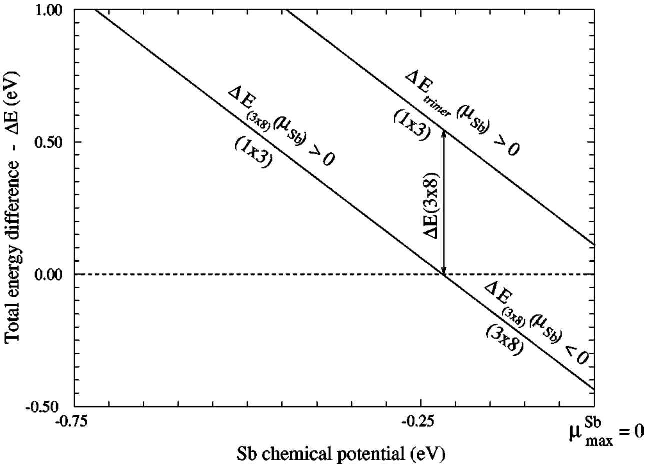


FIG. 7. Phase diagram for the GaAs(111)B surface covered by Sb atoms, forming GaAs(111)B−Sb(3×8) and GaAs(111)B −Sb(1×3) surfaces, and Sb-trimers only.

Thus our total energy results support a possible (3×8) →(1×3) structural transition as a function of the Sb coverage. It is found that the structural transition (3×8)→(1×3) is favored by two contributions: (i) by the relative increase in the density of Sb-chains for the (1×3) structure and (ii) by a desorption process that reduces the density of Sb atoms. The stability of the (3×8) model with respect to the trimer model is due to the conversion of some of the Sb-trimers into the Sb-chains. The Sb-chains configuration somewhat mimics the crystalline phase of the Sb solid, providing a strain relief mechanism. The same strain relief mechanism is achieved during the (3×8)→(1×3) transition. However, this transition is not accompanied by the conservation of Sb adatoms. While a high density of Sb atoms favors the (3×8) model over the (1×3) model, desorption of Sb atoms from the Sb-trimers is expected to eventually favor the (1×3) model over the (3×8) model.

The above results can also help to construct a picture of the adsorption process and structural transition of Sb on the GaAs(111)B surface. During the initial process of the deposition of Sb adatoms on the GaAs(111)B-(2×2) surface, the top layer As atoms (forming As-trimers) are replaced by Sb, giving rise to Sb-trimers on the (2×2) reconstructed surface.[1–3] However, the STM images indicate that the Sb-trimers are very poorly ordered, which is attributed to the bond distortion of the Sb adatoms forming trimers on the GaAs(111)B surface. After an annealing process at ≈375 °C, a number of surface reconstructions have been observed (predominantly the (3×8) model), formed by Sb-trimers and -chains. Our result of $\Delta E(3\times 8)$ is in quite good agreement with this structural transition: Sb-trimers (2×2) reconstructed→Sb-trimers and -chains (3×8) reconstructed. On the other hand, as we have previously commented, the annealing process at ≈475 °C of the (3×8) surface induces

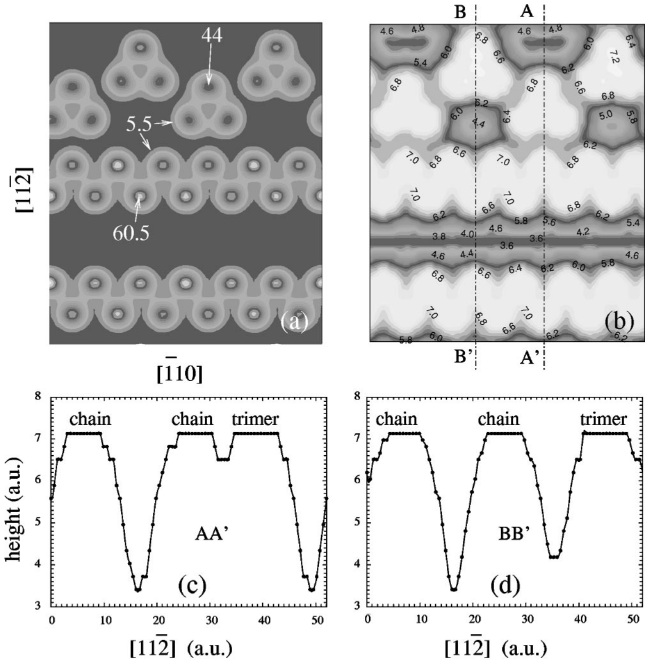


FIG. 8. Theoretical STM simulation for the GaAs(111)B$-$Sb(3×8) surface, within the energy range of 3 eV below the bulk valence band maximum: (a) constant height mode (1.2 Å above the top-layer Sb atoms) and (b) constant current mode. The numbers indicate the vertical distance (in atomic units) from the top layer Sb atoms. Surface corrugation: (c) in the AA' plane and (d) in the BB' plane. Charge density unit: 10^{-3} electrons per (a.u.)^3.

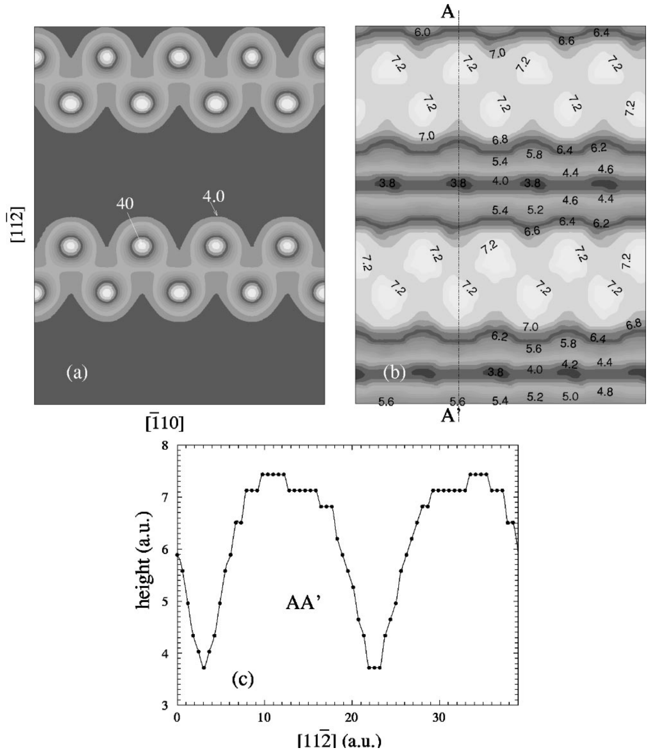


FIG. 9. Theoretical STM simulation for the GaAs(111)B$-$Sb(1×3) surface: (a) constant height mode (1.2 Å above the top-layer Sb atoms) and (b) constant current mode. Energy interval of 3 eV below the E_F. The numbers indicate the vertical distance (in atomic units) from the top layer Sb atoms. (c) Surface corrugation in the AA' plane. Charge density unit: 10^{-3} electrons per (a.u.)^3.

a desorption process of the Sb atoms from the surface, giving rise to the (1×3) surface formed only by Sb chains (Sb coverage of 2/3 ML). Our calculated results of the $\Delta E_{(3\times8)}(\mu_{\mathrm{Sb}})$ indicates that the (1×3) model becomes energetically more favorable than the (3×8) model with the reduction of the Sb coverage on the GaAs(111)B surface, which also confirms the experimental findings.

D. STM simulation of the GaAs(111)B$-$Sb(3×8) and GaAs(111)B$-$Sb(1×3) surfaces

Finally, we have extended our STM simulation of the (3×8) and (1×3) surfaces in two different modes: (i) constant-height ($\approx$1.2 Å above the top layer Sb atoms) and (ii) constant-current. In the both cases, we have considered the occupied states within an energy interval of the 3 eV below the highest occupied slab state. (This choice corresponds to typical bias voltages applied for obtaining occupied state images in experimental STM investigations.) The STM images for the constant-current mode were obtained by calculating the constant charge density contour plot, considering different heights above the surface (up to 4.26 Å from the top layer Sb atoms). The results for the constant-height mode are shown in Fig. 8(a) for the (3×8) surface and 9(a) for the (1×3) surface. For the (3×8) surface the charge localization on the trimers and chains is clearly verified, with a higher charge concentration on the chains. On the (1×3) surface the formation of chains is also clearly verified. Figures 8(b) and 9(b) present the results of the STM simulation in the constant-current mode. In Fig. 8(b) we can verify the formation of trimers and chains on the (3×8) surface. The values presented in the figure indicate the vertical position with respect to the Sb top layer. The minimum value of the vertical position ($\approx$3.4 a.u.) occurs between the chains, i.e., along the ''channel'' formed by unbonded As atoms, and the maximum ($\approx$7.4 a.u.) occurs on the chains and trimers. Figures 8(c) and 8(d) present the vertical position along the AA' and BB' lines, as indicated in Fig. 8(b). From these values we can estimate a surface corrugation of 2.12 Å, which is very close to the calculated vertical distance between the top layer Sb (forming trimers or chains) and the sublayer unbonded As atoms ($\approx$2.10 Å). The result for the STM simulation of the (1×3) surface in Fig. 9(b) clearly shows the chain formation, with the minimum height ($\approx$3.7 a.u.) along the ''channel'' occurring at the unbonded As atoms, and the maximum ($\approx$7.4 a.u.) occurring on the chains. The resulting surface corrugation is equal to 1.97 Å [see Fig. 9(c)], which is also very close to the calculated height difference between Sb chains and unbonded As atoms (2.07 Å). Our simulated STM images are in good agreement with the real STM images observed by Moriarty *et al.*,[1–3] for (3×8) and (1×3) surfaces, taken in the constant-current mode with similar bias voltage.

IV. CONCLUSIONS

In conclusion, we have performed a detailed theoretical study of the atomic geometry, stability, and electronic structure of the GaAs(111)B$-$Sb(3×8) and GaAs(111)B$-$Sb(1×3) surfaces. The electronic structure calculations of the (3×8) surface indicate that this structure is semiconducting in nature. The highest occupied surface state lies approximately 0.2 eV below the bulk valence band maximum, and the corresponding wave function is primarily localized on the unbonded surface As atoms. The lowest unoccupied surface state, calculated within the LDA, lies approximately 0.5 eV below the bulk conduction band minimum and is primarily localized on the Sb trimers and chains. The atomic geometry of the (1×3) surface presents a number of similarities with respect to the (3×8) structure, e.g., the geometry of the Sb chains and the unbonded As atoms are almost identical. The (1×3) structure is stabilized by a strain relieving mechanism in the Sb-chains but does not satisfy the ECR, giving rise to partially occupied states which are localized on the unbonded As atoms. The Fermi level, passing through the partially occupied band, lies slightly above the bulk valence band maximum.

Our total energy calculations indicate that the chain formation of Sb adsorbate atoms is energetically more favorable, compared to Sb trimer formation, for the same coverage of Sb on the GaAs(111)B surface. It is predicted that the (3×8) and (1×3) reconstructions are relatively more favorable for higher and lower Sb coverages, respectively, in complete agreement with the $(3\times8)\rightarrow(1\times3)$ structural transition illustrated by experimental STM data obtained in the work by Moriarty *et al.*[2] Our STM simulations indicate the formation of trimers and chains for the (3×8) model, and the formation of only trimers for the (1×3) model. For both structures our simulated images are in good agreement with the experimental STM results. With the limited size of the vacuum region used in our STM simulations, we have determined the surface corrugation for both models, which agree very well with the calculated surface atomic topology.

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