

Atomic Structure of the GaAs(001) – $c(4 \times 4)$ Surface: First-Principles Evidence For Diversity of Heterodimer Motifs

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(Received 14 May 2004; published 27 September 2004)

The GaAs(001) – $c(4 \times 4)$ surface was studied using *ab initio* atomistic thermodynamics based on density-functional theory calculations. We demonstrate that in a range of stoichiometries, between those of the conventional three As-dimer and the new three Ga-As-dimer models, there exists a diversity of atomic structures featuring Ga-As heterodimers. These results fully explain the experimental scanning tunneling microscopy images and are likely to be relevant also to the $c(4 \times 4)$ -reconstructed (001) surfaces of other III-V semiconductors.

DOI: 10.1103/PhysRevLett.93.146102

PACS numbers: 68.47.Fg, 68.35.Bs, 68.35.Md, 71.15.Mb

For semiconductor surfaces and their reconstructions, it is commonly believed that the main contribution to the surface free energy is governed by the breaking of bulk chemical bonds and possibly making of new surface bonds. Entropic contributions are typically ignored. Here, we will present an example of a semiconductor surface, the GaAs(001) – $c(4 \times 4)$ surface, where configurational entropy contributes significantly to the surface free energy. So far, the atomic structure of the GaAs(001) – $c(4 \times 4)$ surface has not been fully clarified, despite the fact that it is a frequently encountered surface in epitaxial growth of III-V semiconductor heterostructures: For example, in epitaxial growth of InAs on (001)-oriented GaAs surface—the prototypical system used to manufacture self-assembled quantum dots [1]—the substrate displays a $c(4 \times 4)$ reconstruction. We also note that the issue of configurational entropy has a bearing for reconstructed semiconductor surfaces in general, for the following reason: While the unit mesh of a reconstruction is usually well known from diffraction experiments, determining the atomic arrangement *within* the unit mesh often poses a vexing problem. It is well conceivable that several atomic patterns are very close in energy (to within the thermal energy $k_B T$). In this case, while still displaying translational symmetry, the reconstruction at finite temperature must be characterized by the coexistence of diverse structural motifs within the unit cell, and configurational entropy, so far neglected in the analysis, becomes a notable factor in determining its thermodynamic stability.

In this Letter, we combine accurate first-principles calculations using density-functional theory (DFT) for a multitude of possible atomic structures of the GaAs(001) – $c(4 \times 4)$ reconstruction with a thermodynamic stability analysis. The $c(4 \times 4)$ reconstruction, which is the principal reconstruction of the GaAs(001) surface at low temperatures and/or under high arsenic pressures, undergoes a phase transition to a (2×4) reconstruction at higher temperatures and/or lower As pressures. Our thermodynamic analysis shows that the

transition temperature and pressure are shifted due to the presence of a diversity of structural motifs within the $c(4 \times 4)$ unit cell, as compared to the previously accepted structural model for the $c(4 \times 4)$ surface. This can be understood as an effect of configurational entropy favoring the (structurally diverse) $c(4 \times 4)$ situation. In addition to this fundamental issue, understanding this phase transition is also of practical importance because it is often used by crystal growers to calibrate their temperature measurements.

The first observation of the GaAs(001) – $c(4 \times 4)$ reconstruction dates back to early experiments on homoepitaxial growth of GaAs [2–4], with the first theoretical attempts for structural identification made more than two decades ago [5]. Subsequent experimental studies [6,7] gave evidence for a double-layer structure consisting of As-As dimers, with the dimer bond along the [110] direction, adsorbed on a full As monolayer. A few possible geometries have been initially proposed, containing from one to three As dimers per surface unit cell. The scanning tunneling microscopy (STM) experiment by Biegelsen *et al.* [8] and first-principles surface-energy calculations [9,10] gave credibility to the three-dimer model shown in Fig. 1(a). This widely accepted model can be described as rows of As dimers (bond length from X-ray diffraction studies [7] ≈ 2.6 Å) running in the $[\bar{1}10]$ direction, with blocks of three As dimers interrupted by a dimer vacancy, resulting in a $c2mm$ planar space group.

The high As coverage of the conventional three-dimer model [Fig. 1(a)], however, is in noticeable conflict with the varying, but usually lower As coverage deduced in different experimental studies [3,4,11]. Moreover, STM images [12,13] of the actual GaAs(001) – $c(4 \times 4)$ surface indicate various deviations from the ideal six As atom termination of the $c(4 \times 4)$ unit mesh depending on preparation conditions: missing corner As atoms, strings of only two or three As atoms, etc. As a particular rationale, Ohtake *et al.* [14] have recently proposed a structural model, consisting of three buckled Ga-As “heterodimers” (hd) [Fig. 1(b), hereafter referred to as

$c(4 \times 4)$ -hd], on the basis of STM and spectroscopic measurements.

Our atomistic analysis of the GaAs(001) $- c(4 \times 4)$ surface starts from DFT total-energy calculations of the surface energies for numerous structures. For a compound material such as GaAs, a meaningful discussion of the thermal stability of surface reconstructions needs to take into account thermal equilibrium between a gas phase and the GaAs bulk. We apply *ab initio* atomistic thermodynamics [15]: The gas phase is taken into account through a variable arsenic chemical potential $\mu_{\text{As}}(T, p_{\text{As}})$, p_{As} being the As partial pressure and T the temperature. In an extension of the standard approach, we explicitly include contributions due to configurational entropy to the surface reconstruction in a second step, by calculating the surface partition function [16].

The DFT calculations [17] employ norm-conserving pseudopotentials [18] in conjunction with a plane-wave basis set (cutoff energy of ten Ry), and the local-density approximation to electronic exchange and correlation energy. Surfaces were represented, within the supercell approximation, by slabs of seven (or eight) atomic layers

whose bottom (cation-terminated) surface was passivated by pseudohydrogen atoms ($Z_{\text{H}} = 1.25$). Brillouin zone (BZ) integration was carried out using a set of special \mathbf{k} points equivalent to 64 points in the 1×1 surface BZ. A set of calculations is performed for a slab with two hydrogen-passivated surfaces, which is used to subtract the contribution of the bottom surfaces of the reconstructed slabs to be investigated. As a first step, surface free energies at $T = 0$ K are then calculated from the total energies E_{tot} according to the expression [10]

$$\gamma^0(\mu_{\text{As}}) = \frac{1}{A}(E_{\text{tot}} - N_{\text{Ga}}E_{\text{GaAs}}^{\text{tot}}) - \frac{\Delta n}{A_{1 \times 1}}[\mu_{\text{As}} - \mu_{\text{As}(\text{bulk})}], \quad (1)$$

where $E_{\text{GaAs}}^{\text{tot}}$ is the total energy per Ga-As pair in a bulk Ga As reservoir, $\mu_{\text{As}(\text{bulk})}$ is the chemical potential of rhombohedral bulk As metal, N_k the number of atoms of species k , A the area of the surface unit cell, and $\Delta n = \Delta N/8 \equiv (N_{\text{As}} - N_{\text{Ga}})/8$ the surface stoichiometry per 1×1 unit cell, with the stoichiometric $\alpha 2$ surface defining $\Delta N = 0$. Slab geometries were fully relaxed, keeping the bottom layer and passivating pseudohydrogen atoms fixed, until the residual forces were ≤ 0.025 eV/Å. These settings result in an accuracy of surface-energy differences better than 1–2 meV/Å².

Next, we note that replacing one or both of the As atoms in the As dimers with Ga atoms keeps the surface compliant with the electron counting heuristics [19], as any three-dimer block on top of a complete As monolayer generates three extra electrons which satisfy the needs of the four As dangling bonds due to one dimer vacancy. This observation leads us to expect that the surface energies of some structures could be very close, resulting in several realizations of the reconstruction with the same $c(4 \times 4)$ periodicity coexisting at elevated T . There are three As dimers and thus 2^6 combinations with stoichiometries $\Delta n \in [-\frac{1}{4}, \frac{5}{4}]$, the limiting cases being three Ga-Ga and three As-As dimers, respectively. We find interactions between configurations in different $c(4 \times 4)$ unit cells to be negligibly small on the scale of our DFT calculations (< 1 meV/Å²). Therefore, thermal equilibrium for given T and μ_{As} can be described by a partition function Z defined independently for each unit cell of area A ,

$$Z = \sum_{i \in S} Z_i, \quad Z_i = g_i \exp[-\gamma_i^0(\mu_{\text{As}})A/k_{\text{B}}T], \quad (2)$$

where g_i is a symmetry-determined degeneracy factor, and k_{B} the Boltzmann constant. The surface free energy, including contributions from configurational entropy, is then given by

$$\gamma(T, p_{\text{As}}) = -(k_{\text{B}}T/A) \ln Z[\mu_{\text{As}}(T, p_{\text{As}})] \quad (3)$$

Generally, in calculating the partition function Z , the set of structures S in Eq. (2) should include all 64 combina-

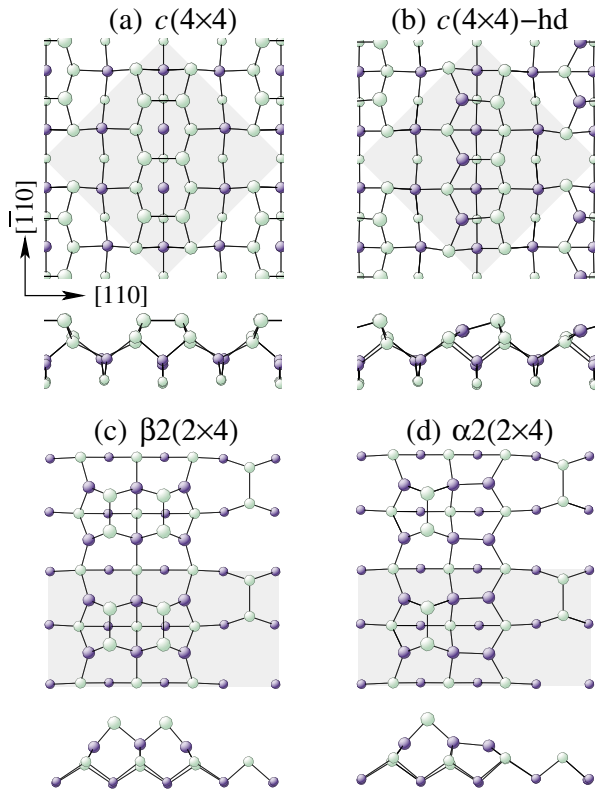


FIG. 1 (color online). Low-energy reconstructions of the GaAs(001) surface for moderate-to-As-rich growth conditions [Ga: dark (blue) circles, As: bright (green) circles]. Shaded rectangles indicate the surface unit cell. All top views represent surface area A equivalent to two unit cells, $A = 16A_{1 \times 1} \equiv 8a_0^2$, a_0 being the bulk lattice constant of GaAs. Side views along the $[\bar{1}10]$ direction are given in the lower panels.

tions for the $c(4 \times 4)$ unit cell as well as all other possible $(n \times m)$ reconstructions, e.g., the less As-rich (2×4) and Ga-rich (4×2) reconstructions. Under As-rich conditions, however, the $c(4 \times 4)$ structures with $\Delta n < 0$ (and eventually the stoichiometric ones, $\Delta n = 0$) contribute negligibly to Z , and are therefore discarded. Indeed, we find, for instance, that a three-dimer configuration comprising a single Ga-Ga dimer (corresponding to $\Delta n = \frac{3}{4}$) is higher in energy compared to the conventional $c(4 \times 4)$ reconstruction by at least $10 \text{ meV}/\text{\AA}^2$ for $\mu_{\text{As}} = \mu_{\text{As}(\text{bulk})}$, while for two neighboring Ga-Ga dimers ($\Delta n = \frac{1}{4}$) this figure is greater than $20 \text{ meV}/\text{\AA}^2$ [cf. the highest-energy line in Fig. 2(a)]. For evaluation of Z under As-rich condition we have thus considered 14 symmetry-inequivalent $c(4 \times 4)$ structures, as well as the $\beta 2$ and $\alpha 2$ (2×4) reconstructions, Fig. 1(c) and 1(d). Surface free energies $\gamma^0(\mu_{\text{As}})$ of all structural models considered here, calculated from Eq. (1), are given in Fig. 2(a). The statistical probabilities c_i of a particular configuration i with surface energy γ_i^0 can be calculated from $c_i = Z_i/Z$, and are plotted in Fig. 2(b) for $T = 700 \text{ K}$. This figure unequivocally demonstrates that in the very As-rich limit the GaAs(001) surface forms exclusively a conventional, three As-dimer $c(4 \times 4)$ reconstruction, Fig. 1(a). With μ_{As} decreasing, initially one As atom in either of the edge dimers is substituted by a Ga atom yielding one buckled Ga-As heterodimer. At $\mu_{\text{As}} \approx \mu_{\text{As}(\text{bulk})} - 0.1 \text{ eV}$ this configuration constitutes roughly half of the surface area and remains dominant down to the $c(4 \times 4) \rightarrow (2 \times 4)$ transition. Shortly before the $\beta 2(2 \times 4)$ reconstruction appears, in the region $\mu_{\text{As}} \sim \mu_{\text{As}(\text{bulk})} - 0.2 \text{ eV}$, almost all $c(4 \times 4)$ units feature various combinations of Ga-As heterodimers. In the light of this, the $c(4 \times 4)$ -hd model, Fig. 1(b), is *just one* out of many possible structures. Moreover, if we define the phase transition $c(4 \times 4) \rightarrow \beta 2(2 \times 4)$ by requiring $c_{\beta 2} = 50\%$, taking into account the diversity of $c(4 \times 4)$ structures significantly shifts the transition point between these two reconstructions: From Fig. 2(b), we conclude that at $T = 700 \text{ K}$ the transition occurs at a μ_{As} by 65 meV lower than expected if only the conventional $c(4 \times 4)$ would be considered. This corresponds to a reduction in the predicted transition pressure p_{As} by about a factor of 10. A more detailed analysis would have to include the energy of phase boundaries, and the associated surface stress relaxation, which is beyond the scope of this Letter.

Since direct experimental evidence for the structure of the GaAs(001) $- c(4 \times 4)$ surface has been obtained mainly from STM, we next explore the implications of Fig. 2(b) for the *simulated* filled-state STM images of this surface. We consider a square region of 10×10 unit cells. In order to build the corresponding STM image first a square matrix of the same size is randomly populated with $c(4 \times 4)$ unit meshes, whose abundances (concentration) c_i correspond to Fig. 2(b). For each configuration

with $c_i \geq 1\%$ a constant-current mode STM image of a single unit cell is simulated within the Tersoff-Hamann scheme [20] using bias voltage $V_b = -2.5 \text{ V}$. The images map the “tip” height corresponding to isoelectron density $\rho_0(\mathbf{r}) = 5 \times 10^{-6} \text{ Bohr}^{-3}$ for the electron density $\rho(\mathbf{r})$ integrated over the energy range $[E_{\text{VB}}, E_{\text{VB}} + eV_b]$, with E_{VB} being the valence band maximum. Finally, the STM images shown in Fig. 3 are assembled by selecting the corresponding individual images. For symmetry-equivalent configurations the final unit mesh to be used is randomly selected from the subset of g_i structures. Simulated STM images for two different values of μ_{As} are shown in Fig. 3.

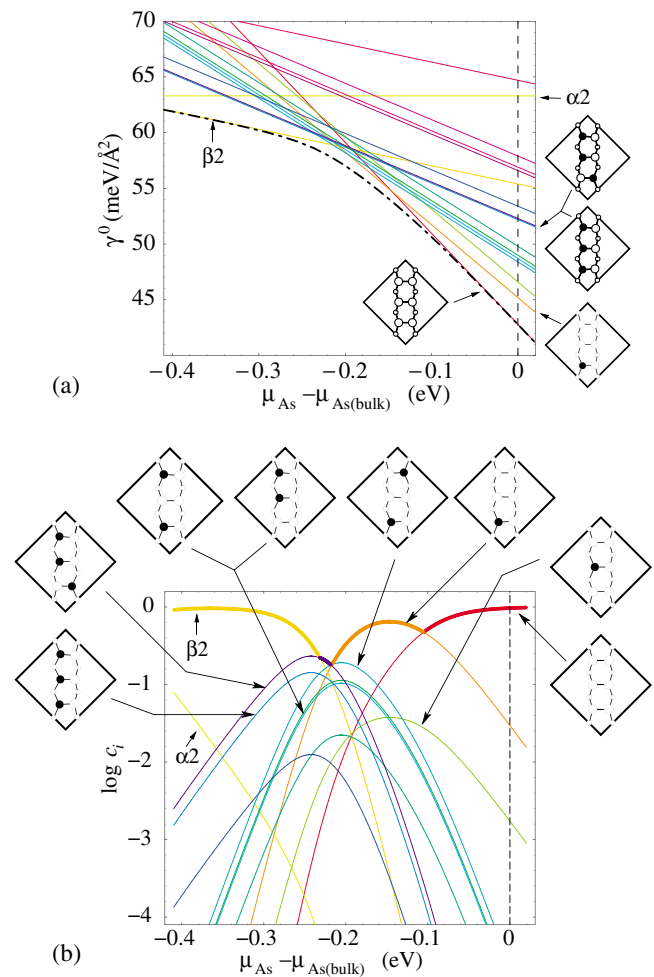


FIG. 2 (color). (a) Surface free energies γ^0 vs μ_{As} for all structural models considered, calculated according to Eq. (1). The lines labeled $\beta 2$ and $\alpha 2$ correspond to the (2×4) structural models shown in Fig. 1(c) and 1(d), respectively. The dash-dotted curve gives the surface free energy calculated at $T = 700 \text{ K}$, according to Eq. (3). (b) Equilibrium concentration of different structural units on the GaAs(001) surface at $T = 700 \text{ K}$. The $c(4 \times 4)$ structural units show the three-dimer block along with the supporting second-layer As atoms (Ga: black circles, As: empty circles).

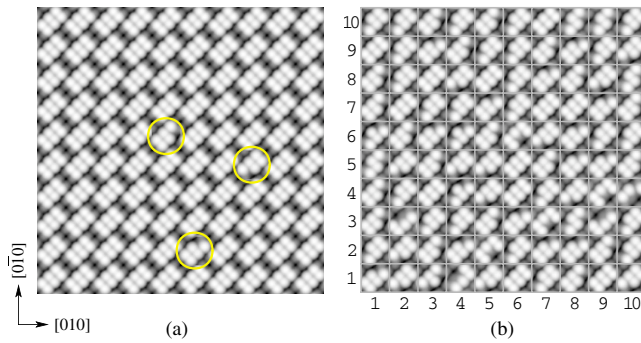


FIG. 3 (color online). Simulated filled-state STM images of GaAs(001)- $c(4 \times 4)$ (10×10 unit meshes) at $T = 700$ K, using abundances c_i from Fig. 2(b). (a) Nearly perfect conventional $c(4 \times 4)$ reconstruction for $\mu_{\text{As}} = \mu_{\text{As}(\text{bulk})}$. (b) For $\mu_{\text{As}} - \mu_{\text{As}(\text{bulk})} = -0.15$ eV heterodimers are found in $\approx 85\%$ of the unit cells.

As it can be expected from Fig. 2(b), the STM image in the extreme As-rich limit, Fig. 3(a), displays the familiar brickwork pattern of the conventional $c(4 \times 4)$ reconstruction, Fig. 1(a). Only in a tiny fraction of the unit meshes marked by circles one corner As atom is substituted by Ga. Under less As-rich conditions, Fig. 3(b), the simulated STM image reveals a rather diverse surface with local stoichiometry variations $\Delta n \in [\frac{1}{2}, \frac{5}{4}]$. Remarkably, virtually all motifs in this image have been observed in experimental STM images of the $c(4 \times 4)$ reconstruction, not only for the case of GaAs(001) [12–14], but also for InSb(001) [21]. We conclude that the T- and Γ -like motifs, as those in cells (3, 1) and (4, 1) in Fig. 3(b), are signatures of a block with two identical Ga-As heterodimers, which may be neighbors or separated by an As-As-dimer. Similarly, blocks with two Ga-As dimers having an inversion center appear as Z-like features, e.g., cell (8, 3) in Fig. 3(b). Finally, we identify the reported strings of two As atoms [13] to be, in fact, due to a three-heterodimer structural unit, similar to the $c(4 \times 4)$ -hd model, where the Ga and As positions in one of the edge dimers are swapped, e.g., cell (10, 4) in the same figure.

In summary, we have shown by *ab initio* thermodynamics that the structure of the GaAs(001) - $c(4 \times 4)$ surface under all experimentally relevant conditions features diverse combinations of As-As dimers and Ga-As heterodimers. These structures bridge the gap of stoichiometries between those of the conventional and the recently proposed $c(4 \times 4)$ -hd model [14]. Heterodimers are not a novelty in the structural chemistry of the (001) surface of III-V semiconductors [22,23], and have been shown to play an important role for nucleation on some surfaces [24]. GaAs(001) - $c(4 \times 4)$ is another example where heterodimers may be crucial for understand-

ing the process of GaAs homoepitaxial growth under As-rich conditions [25] as well as the $(2 \times 4) \leftrightarrow c(4 \times 4)$ phase transition [13,14,26].

This work was supported by the Deutsche Forschungsgemeinschaft within Sfb 296. E. P. would like to acknowledge fruitful discussions with Y. Temko.

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