

## Energetics of GaAs(100)-(2×4) and -(4×2) Reconstructions

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Formation energies for a variety of GaAs(100) surface structures have been calculated as a function of the atomic chemical potentials using the first-principles pseudopotential density-functional approach. We find that the surface transforms through four phases as the chemical potential varies across its accessible range. As the Ga chemical potential increases the surface transforms from an As-rich  $c(4\times 4)$  through two distinct  $(2\times 4)$  structures and finally to a Ga-rich  $(4\times 2)$  phase. The predicted structures account for most scanning tunneling microscopy observations for the  $c(4\times 4)$ ,  $(2\times 4)$ , and  $(4\times 2)$  phases.

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The GaAs(100) surface exhibits a large number ( $\sim 7$ ) of reconstructions which occur as the stoichiometry of the surface is varied. Starting with the most As-rich phase, which has a  $c(4\times 4)$  symmetry, it has been observed that as As is driven from the surface by heating the surface undergoes a sequence of structural transitions: from the  $c(4\times 4)$  through several different  $(2\times 4)$  phases, through the “ $(3\times 1)$ ” and to “ $(2\times 6)$ ” phases (which are not well ordered), and finally to the Ga-rich  $(4\times 2)$  phase [1–5]. It is generally accepted that in each reconstruction of the GaAs(100) surface, the valence electrons are accommodated in low energy states: either in Ga-As, As-As, or Ga-Ga bonds, or in As dangling-bond orbitals. This view is supported by previous total energy and electronic structure calculations [6–8]. Even so, our present knowledge of the GaAs(100) surface structures is incomplete, and the relative importance of energetics and kinetics in determining surface structure is unclear. We show here that most of the well ordered structures observed on GaAs(100) may be understood within a thermodynamic model in which the relative surface energy of the structures changes as the chemical potential varies within its allowed range.

In this work we address the structure problem from the standpoint of equilibrium energetics by calculating surface energies for a variety of possible structures. A commonly used ansatz for constructing low energy surface structures is to require, under conditions of charge neutrality, that all the As dangling bonds are filled and that all Ga dangling bonds are empty. This hypothesis, which is sometimes referred to as the electron counting rule, limits the number of possibilities but does not lead to a unique structure. We have, with one exception, restricted our study to models which satisfy the electron counting rule.

To compare energies of structures with differing stoichiometries we have determined the surface energies as a function of the Ga chemical potential ( $\mu_{\text{Ga}}$ ). For each value of  $\mu_{\text{Ga}}$  within its allowed range we determine the structure having the lowest formation energy. We find evidence for the existence of at least two different equilibrium  $(2\times 4)$  reconstructions: one with three As di-

mers and one with two As dimers per cell. This result is consistent with reflection high energy electron diffraction (RHEED) [1], scanning tunneling microscope (STM) [2,3], and reflectance-difference spectroscopy experiments [4]. The calculations also predict that the Ga-rich  $4\times 2$  phase exhibits a bilayer structure proposed by Biegelsen *et al.* [2] which has two Ga dimers in the top layer and one Ga dimer in the third layer. In addition we have examined the recent proposal of Falta *et al.* [5], who on the basis of ion scattering experiments proposed that the surfaces contained more Ga than is present in the most widely discussed models. We examined two structures obtained by replacing As atoms with Ga, but in both cases we found that the replacement did not lead to thermodynamically stable structures.

The calculational method employed here is based on the plane-wave pseudopotential method [9–11]. As in previous work [12–14], total energies and forces are calculated within the local density approximation [15] for supercell structures representing the GaAs surfaces. The plane-wave cutoff ( $E_{\text{cut}}$ ) is typically 8 or 10 Ry, and 2 or 4  $k$  points are employed in the Brillouin zone integrations. These are sufficient to obtain an accuracy of  $\pm 0.01$  eV/( $1\times 1$ ) for the relative values of the surface energies.

The relative stability of two structures having different numbers of Ga and As atoms depends on the reservoir with which the atoms are exchanged in the structural transition. Questions of thermodynamic stability are therefore posed within the context of the atomic chemical potentials ( $\mu_{\text{Ga}}$  and  $\mu_{\text{As}}$ ). The surface energy  $\sigma$  may be expressed as

$$\sigma A = U - n_{\text{Ga}}\mu_{\text{Ga}} - n_{\text{As}}\mu_{\text{As}},$$

where  $U$  is the total energy of a GaAs film and  $A$  is the surface area of the film. The sum of the chemical potentials is constrained to be equal to the energy per cell of bulk GaAs:  $\mu_{\text{Ga}} + \mu_{\text{As}} = E_{\text{GaAs(bulk)}}$ . Consequently the surface energy may be written as a function of a single variable, which we will take to be  $\mu_{\text{Ga}}$ . In this case the surface energy per  $(1\times 1)$  unit cell,  $\sigma_{1\times 1}$ , may be written

$$\sigma_{1\times 1} = \sigma_{\text{Ga(ri ch)}} + \Delta n(\mu_{\text{Ga}} - \mu_{\text{Ga(bulk)}}),$$

TABLE I. Stoichiometries ( $\Delta n$ ) and relative energies for GaAs(100) surfaces. For each structure  $\Delta E$  is the energy relative to that of the most stable structure with the same  $\Delta n$ .

Structure	$\Delta n$	$\Delta E$ [eV/(1×1)]
$c(4\times 4)$	$\frac{5}{4}$	
$\gamma(2\times 4)$	$\frac{2}{4}$	
$\beta(2\times 4)$	$\frac{1}{4}$	
$\alpha(2\times 4)$	0	0.0
$\alpha_{\text{sym}}(2\times 4)$	0	0.07
$\alpha_{\text{Ohno}}(2\times 4)$	0	0.26
$\alpha(4\times 2)$	0	0.15
$c(2\times 2)$	0	0.05
$\beta 2(4\times 2)$	$-\frac{1}{4}$	0.0
$\beta(4\times 2)$	$-\frac{1}{4}$	0.03
$\beta_{\text{rep}}(2\times 4)$	$-\frac{1}{4}$	0.13
$2\times 2$ (buckled Ga dimers)	$-\frac{2}{4}$	0.0
$\beta_{\text{rep}}(4\times 2)$	$-\frac{2}{4}$	0.05

where  $\Delta n$  is the difference ( $n_{\text{As}} - n_{\text{Ga}}$ ) per (1×1) unit cell, and  $\sigma_{\text{Ga(rich)}}$  is the surface energy in the Ga-rich limit.  $\Delta n$  is defined such that it is equal to  $\frac{1}{2}$  for the (1×1) As-terminated surface and  $-\frac{1}{2}$  for the (1×1) Ga-terminated surface. Values of  $\Delta n$  for various GaAs(100) surfaces are listed in Table I. The maximum value for  $\mu_{\text{Ga}}$  corresponds to  $\mu_{\text{Ga}} = \mu_{\text{Ga(bulk)}}$ , and the minimum value corresponds to  $\mu_{\text{Ga}} = \mu_{\text{Ga(bulk)}} - \Delta H$ , where  $\Delta H$  is the heat of formation of bulk GaAs from Ga and As. From calculations of the total energies of the condensed phases of Ga, As, and GaAs we find  $\Delta H = 0.92 \pm 0.03$  eV, which is in good agreement with the experimental value; 0.85 eV [16].

In all we have calculated the relative energies for fourteen different GaAs(100) surfaces. Schematic representations for some of these surfaces are shown in Fig. 1, and their energies are given in Fig. 2 and Table I. The  $\beta(2\times 4)$  model shown in Fig. 1(a) consists of three symmetric As dimers per (2×4) unit cell. This dimer-vacancy model, proposed by Chadi [6], has become the standard model for the (2×4) reconstruction. In each unit cell there are three As dimers in the first layer and four Ga dangling bonds in the second layer. Three electrons are transferred from the Ga to As dangling bonds, which results in a semiconducting surface. We find that this structure is stable in a limited range of chemical potential. As shown in Fig. 2, under As-rich conditions the  $\beta(2\times 4)$  becomes unstable with respect to the  $c(4\times 4)$  structure. The model employed here for the  $c(4\times 4)$  structure [Fig. 1(e)] consists of three As ad-dimers on top of a complete As monolayer [2,17]. We have also examined the stability of the  $\gamma(2\times 4)$  structure [Fig. 1(d)] which is obtained by adding an As ad-dimer to the  $\beta(2\times 4)$ . Previous work [7] suggested that the  $\gamma(2\times 4)$  structure might be stable under As-rich conditions. However, we find that the  $\gamma(2\times 4)$  is unstable with respect to dissociation into the  $\beta(2\times 4)$  and  $c(4\times 4)$  structures [18].

Removal of an As dimer from the  $\beta(2\times 4)$  model, fol-

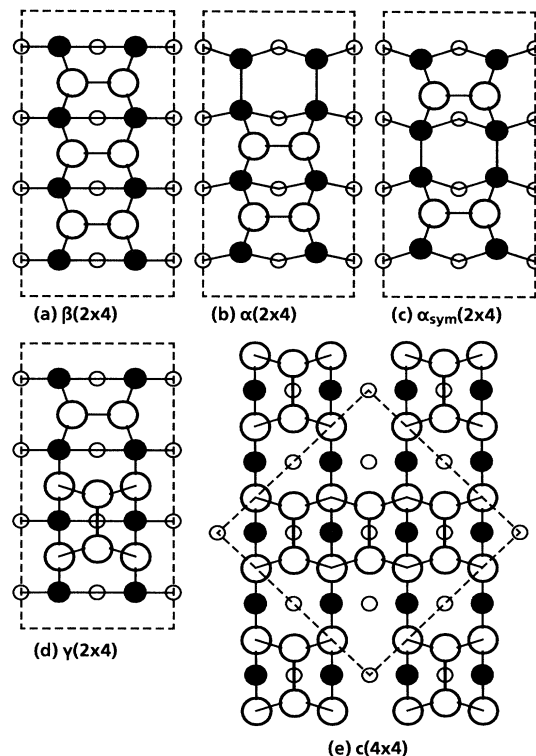


FIG. 1. Schematic representations of possible As-terminated reconstructions of the GaAs(100) surface. Filled (open) circles denote Ga (As) atoms. Dashed lines indicate the boundaries of the unit cells.

lowed by significant atomic displacements, leads to the  $\alpha(2\times 4)$  model shown in Fig. 1(b). Without large lateral shifts, which are indicated schematically in Fig. 1(b), the surface would exhibit twofold coordinated Ga atoms in the second layer. However, the top two layers undergo lateral displacements which vary between 0.4 and 1.2 Å from the ideal positions, and these displacements allow

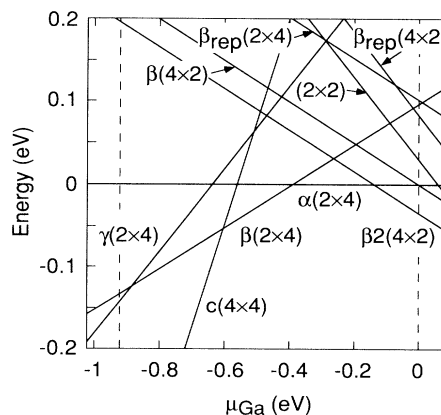


FIG. 2. Formation energy per (1×1) unit cell for GaAs(100) surfaces as a function of  $\mu_{\text{Ga}}$  over the thermodynamically allowed range:  $-0.92 \text{ eV} < \mu_{\text{Ga}} - \mu_{\text{Ga(bulk)}} < 0$ .

the formation of second layer Ga-Ga bonds. A structure with this topology has been suggested by Farrell and Palmström [1] on the basis of RHEED data. A symmetric variation of the  $\alpha(2\times 4)$  surface shown in Fig. 1(c) is not as stable. As shown in Fig. 2, we find that for  $\mu_{\text{Ga}} > \mu_{\text{Ga(bulk)}} - 0.40$  eV, the  $\alpha(2\times 4)$  model is stable with respect to the  $\beta(2\times 4)$  model. However, for higher  $\mu_{\text{Ga}}$  the  $\alpha(2\times 4)$  surface becomes unstable with respect to the more Ga-rich surfaces.

According to Ohno [7], the second layer Ga-Ga bonding described above should not occur in the  $\alpha(2\times 4)$  model. In contrast, we find that the structure obtained by Ohno actually corresponds to a saddle point of the total energy surface and that forming the Ga-Ga bonds lowers the energy by 0.26 eV/(1 $\times$ 1). Moreover, the rebonded  $\alpha(2\times 4)$  is found to be the lowest energy structure within a restricted range of chemical potential and may correspond to the two As-dimer structure observed in STM experiments [2,19–21].

If the remaining two As dimers are removed from the  $\alpha(2\times 4)$  unit cell one may form a (1 $\times$ 2) surface completely terminated by Ga dimers [Fig. 3(a)]. Such a surface has an excess of 1 electron per Ga dimer. Consequently, the surface electronic structure is metallic, exhibits partial occupation of the Ga dangling-bond states, and therefore violates the electron counting principle. It is possible to create a semiconducting surface by allowing the Ga dimers to buckle and tilt: The result is a (2 $\times$ 2) structure with one “up” atom and three “down” atoms in each cell [12]. The two excess electrons in each (2 $\times$ 2) cell fill a band of Ga dangling-bond states on the up

atom. Nevertheless, the calculations show that this surface is unstable for any physically allowed value of the chemical potentials. The electron counting rule, which would prohibit this structure, is thereby corroborated in this case.

Removal of  $\frac{1}{2}$  monolayer of Ga from the ideal Ga-terminated surface allows the formation of a  $c(2\times 2)$  surface comprised of twofold coordinated Ga atoms [22]. In this structure, which is indicated schematically in Fig. 3(b), the Ga atoms relax into the plane of the second layer As atoms so that the As-Ga-As bond angles are close to 180°. Each Ga atom contributes  $\frac{3}{4}$  electrons to each of its two bonds with As, and donates  $\frac{3}{4}$  electrons to each of the threefold coordinated As atoms in the unit cell. Thus, the As dangling bonds are fully occupied and the nonbonding Ga  $p$  orbitals are empty. The energy of this structure, although surprisingly low, is still 0.05 eV/(1 $\times$ 1) higher than the  $\alpha(2\times 4)$  surface.

Removing 1 out of 4 Ga dimers from the (1 $\times$ 2) surface leads to the  $\beta(4\times 2)$  dimer vacancy structure shown in Fig. 3(c). In this case the three excess electrons on the Ga dimers are transferred to the four As dangling bonds created by the vacancy formation. Because this results in a semiconducting surface there is no driving force for dimer tilting and the Ga dimers are symmetric. Since each Ga dimer is in an  $sp^2$  bonding configuration seeking a planar nearest neighbor geometry, there is a small lateral displacement of the underlying As in the direction away from the Ga dimers. Our calculations indicate that this structure, which is commonly assumed to be appropriate for the (4 $\times$ 2)/ $c(8\times 2)$  reconstruction, is actually unstable with respect to the  $\alpha(2\times 4)$  surface even in the most Ga-rich environment. Consequently, we must search for another model to explain the (4 $\times$ 2)/ $c(8\times 2)$  reconstruction. Ultimately we found that the model proposed by Biegelsen *et al.* [2] on the basis of STM experiments, denoted  $\beta 2(4\times 2)$  in Fig. 3(d), is the most stable structure in extreme Ga-rich conditions. An  $\alpha(4\times 2)$  model having two Ga dimers in the top layer and rebonded As in the second layer, was found to be energetically unfavorable.

As seen in Fig. 2, a transition from the  $\alpha(2\times 4)$  structure to the  $\beta 2(4\times 2)$  model occurs for  $\mu_{\text{Ga}} > \mu_{\text{Ga(bulk)}} - 0.13$  eV. This transformation involves the loss of both Ga and As atoms. The net loss is two As atoms per (4 $\times$ 2) unit cell and so  $\Delta n$  changes from zero to  $-\frac{1}{4}$ . We emphasize, however, that experiment shows the existence of intermediate structures having poorly ordered “(3 $\times$ 1)” and “(2 $\times$ 6)” symmetry which occur between the  $\alpha(2\times 4)$  and the  $\beta 2(4\times 2)$ . We suggest that these intermediate structures should have stoichiometries between that of the  $\alpha(2\times 4)$  surface and the  $\beta 2(4\times 2)$  surface, i.e., between  $\Delta n = 0$  and  $\Delta n = -\frac{1}{4}$ . For example, in the (2 $\times$ 6) structure proposed by Biegelsen *et al.* [2],  $\Delta n = 0$ .

To explain their ion scattering data, Falta *et al.* [5] proposed models in which the Ga concentration in the

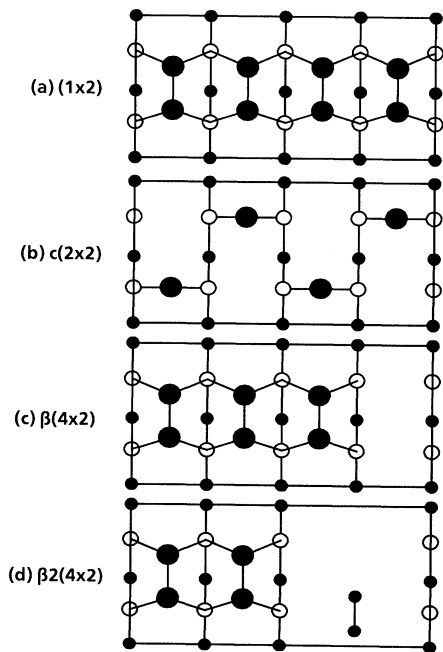


FIG. 3. Schematic representation for possible (4 $\times$ 2) reconstructions (Ga-terminated) of the GaAs(100) surface. Filled (open) circles denote Ga (As) atoms.

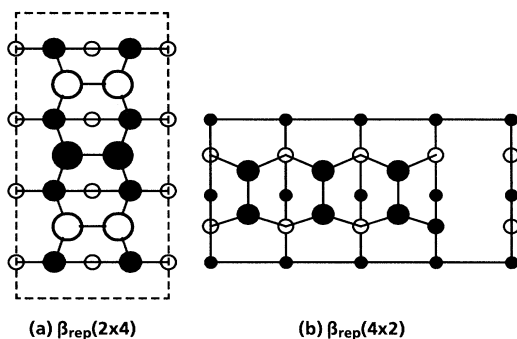


FIG. 4. Models obtained by replacing first or second layer As atoms with Ga. Filled (open) circles denote Ga(As) atoms.

first or second layer is increased by replacing As with Ga atoms. The electron counting rules do not distinguish between structures in which a threefold coordinated As atom, which has a doubly occupied dangling bond orbital, is replaced by a Ga atom, which has an empty dangling bond [2]. Because each Ga atom contributes two fewer electrons than each As atom to the valence band, the doubly occupied As dangling-bond state is replaced by an empty Ga dangling-bond state. This replacement, however, changes the stoichiometry and the nature of the bonds: Ga-As bonds are replaced by Ga-Ga bonds. Consequently the formation energies of the two structures will be very different and have different dependencies on the chemical potential. We calculated the formation energies for two of these models. In the first case we replaced the central As dimer of the  $\beta(2 \times 4)$  surface with a Ga dimer as shown in Fig. 4(a). The resulting energy, denoted  $\beta_{\text{rep}}(2 \times 4)$  in Fig. 2, is much higher than those for stable structures. In the second case we replaced 1 of the 4 threefold coordinated As atoms in the second layer of the  $\beta(4 \times 2)$  surface with a Ga atom [Fig. 4(b)]. The energy of this structure, denoted  $\beta_{\text{rep}}(4 \times 2)$  in Fig. 2, is increased by 84 meV per  $(1 \times 1)$  in the Ga-rich limit. Therefore the minimum energy cost is 0.67 eV for each such As-Ga replacement.

In summary we have presented total energy calculations which, in the context of a thermodynamic model, account for most of the well ordered GaAs(100) surfaces. In the As-rich limit we find a  $c(4 \times 4)$  structure to be the most stable. For intermediate chemical potentials, both the three As-dimer  $\beta(2 \times 4)$  and the two As-dimer  $\alpha(2 \times 4)$  surfaces are predicted to be stable. In contrast to a previous study [7] we find that second layer Ga-Ga bonds stabilize the  $\alpha(2 \times 4)$ . Finally, in the Ga-rich limit we find that the  $\beta(4 \times 2)$  surface, which has two Ga dimers in the top layer and a third Ga dimer in the third layer is the most stable structure.

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- [18] The reaction  $\gamma(2 \times 4) \rightarrow \frac{3}{4}\beta(2 \times 4) + \frac{1}{4}c(4 \times 4)$  is exothermic:  $\Delta E = 0.06 \text{ eV}/(1 \times 1)$ . Our result for the relative energies of the  $\beta(2 \times 4)$  and  $\gamma(2 \times 4)$  surfaces is slightly different from that obtained in Ref. [7]. We find that the chemical potential for which these two surfaces have equal formation energies is much closer to the As-rich limit than reported in Ref. [7]. Our result, that the formation energies are very similar in the As-rich limit, can be understood by noting that the local bonding environment of the As atoms is not significantly altered when As is removed from a bulk As reservoir and added to the  $\beta(2 \times 4)$  surface to form the  $\gamma(2 \times 4)$ .
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- [22] The energy for a  $(2 \times 1)$  ordering of the Ga atoms is slightly higher [by 0.02 eV  $(1 \times 1)$ ] than the  $c(2 \times 2)$ . The  $(2 \times 1)$  ordered structure is stable with respect to a dimerization of the Ga atoms which would create a  $(2 \times 2)$  structure.