RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 50, NUMBER 3 15 JULY 1994-I

Structure of GaAs(001) surfaces: The role of electrostatic interactions

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(Received 9 February 1994; revised manuscript received 11 May 1994)

We report first-principles total-energy calculations for the GaAs(001) surface. Our results indicate that the 2×4 reconstruction corresponds to the $\beta2(2\times4)$ structure, which exhibits two As dimers in the top layer and a third As dimer in the third layer. This structure has a lower surface energy than the $\beta(2\times4)$ model, which has three As dimers in the top layer. We also find that a model recently proposed by Skala *et al.* [Phys. Rev. B **48**, 9138 (1993)] for the structure of the Ga-rich 4×2 phase is energetically unfavorable. From our results we conclude that electrostatic interactions between the charged building blocks of polar semiconductor surfaces play an important role in determining the equilibrium structure. We introduce a simple model for estimating these interactions.

It is widely accepted that the surfaces of polar semiconductors reconstruct in a manner which forces the anion dangling bonds to be filled and the cation dangling bonds to be empty. This is referred to as the electron-counting principle. On the (001) surface of GaAs—a zinc-blende semiconductor with tetrahedral coordination in the bulk—satisfaction of the electron-counting principle requires transfer of charge from the threefold-coordinated Ga atoms to threefold-coordinated As atoms. Formally, this leaves As atoms negatively charged and Ga atoms positively charged. We argue here that the interactions between the charges will in many cases determine the structure of the surface. We estimate the interaction energy from a very simple calculation of the Madelung energy, and demonstrate the efficacy of the model by comparison to first-principles total-energy calculations for $c(4\times4)$, 2×4, and 4×2 reconstructions of the GaAs(001) surface.

Molecular-beam-epitaxial growth of GaAs(001) is usually carried our under conditions of temperature and flux which lead to a 2×4 reconstruction. Such surfaces have been studied with a variety of experimental techniques including reflection high-energy electron diffraction,[1] scanning tunneling microscopy (STM),[2–9] reflectance difference spectroscopy,[10] and medium-energy ion scattering.[11,12] Nevertheless, a clear picture of the atomic structure and stoichiometry of the 2×4 structure has not been obtained. An important question is whether there exists more than one instrinsic 2×4 reconstruction. Indeed, three plausible 2×4 structures have been discussed in the literature.[1–15] These structures are denoted $\beta(2\times4)$, $\alpha(2\times4)$, and $\beta2(2\times4)$ and are indicated schematically in Fig. 1. The simplest model is the $\beta(2\times4)$ structure formed by removing one out of every four As dimers from the fully dimerized surface. This results in a structure in which there are three As dimers in the surface layer and four threefold Ga atoms in the second layer of each unit cell. Some early STM images[2,3] have been interpreted in terms of this $\beta(2\times4)$ model, but more recent data[3–9] indicate that a structure with only two As dimers in the top layer is more prevalent. Two models which are compatible with these STM images are the $\alpha(2\times4)$ and $\beta2(2\times4)$ structures shown in Figs. 1(b) and 1(c).

We have recently performed a set of first-principles total-energy calculations for the GaAs(001) surface in which we examined structures spanning the range of stoichiometries from the As-rich $c(4\times4)$ to the Ga-rich 4×2 structures.[15] The energetics of the $\alpha(2\times4)$ and $\beta(2\times4)$ structures were calculated as part of that study, but no calculations were performed for the $\beta2(2\times4)$ structure. Previous work, due to Ohno,[14] indicated that the $\beta2(2\times4)$ reconstruction was higher in energy than the $\beta(2\times4)$ model by 0.02 eV/(1×1). However, considerations of the effect of electrostatic interactions on the energetics of GaAs(001) surfaces suggest that the $\beta2(2\times4)$ structure could in fact be energetically favorable with respect to the $\beta(2\times4)$ structure. We therefore decided to perform our own total-energy calculations for the $\beta2(2\times4)$ surface. As in our previous work,[15] the calculations of the surface energies are performed with the first-principles pseudopotential method and the local-density-functional approximation. From various tests, we believe the calculated energy differences are reliable to within 0.01 eV/(1×1).

A transformation from the $\beta(2\times4)$ to the $\beta2(2\times4)$ structure can be achieved by removing two As and two Ga

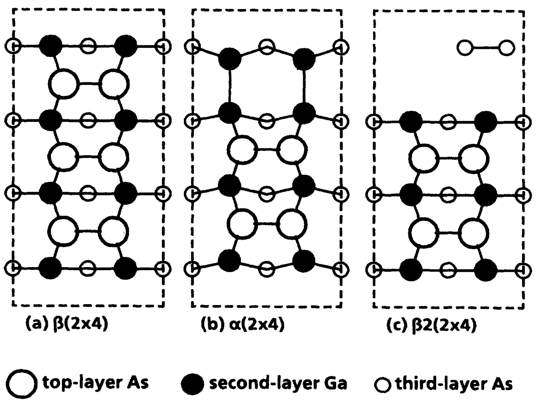
(a) β(2x4) (b) α(2x4) (c) β2(2x4)

FIG. 1. Structural models for the (a) $\beta(2\times4)$, (b) $\alpha(2\times4)$, and (c) $\beta2(2\times4)$ model for the GaAs(001) surface.

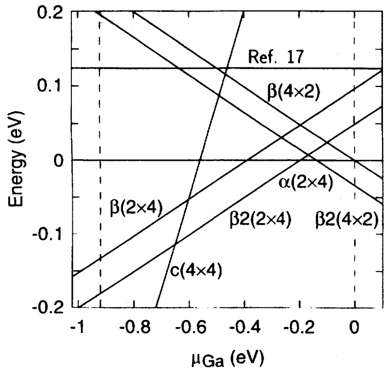

FIG. 2. Formation energy per 1×1 unit cell for GaAs(001) surfaces as a function of $\mu_{\rm Ga}$ over the thermodynamically allowed range: $-0.92<\mu_{\rm Ga}-\mu_{\rm Ga(bulk)}<0$ eV.

atoms from each 2×4 unit cell and incorporating them into a bulk environment. Therefore, the energy difference between the two structures depends only on the sum of the As and Ga chemical potentials: $\mu_{\rm Ga}+\mu_{\rm As}$. Under the usual assumption of equilibrium with the bulk, this sum is a constant equal to the energy per cell of bulk GaAs; in other words, the relative formation energy of the two structures is independent of chemical potential. The $\alpha(2\times 4)$ and $\beta2(2\times 4)$ structures have different stoichiometries, so the energy difference between the two depends on the atomic chemical potentials.[15,16]

The calculated surface energies are shown in Fig. 2 together with results obtained in our previous work. We find the $\beta2(2\times 4)$ structure to be more stable than the three-dimer $\beta(2\times 4)$ structure by 0.05 eV/(1×1). *We may therefore rule out the $\beta(2\times 4)$ model as a possible equilibrium phase.* As we will discuss below, the origin of the greater stability of the $\beta2(2\times 4)$ structure can be traced to the difference in electrostatic interactions between charged subunits which make up the two structures. The inclusion of the $\beta2(2\times 4)$ structure not only eliminates the $\beta(2\times 4)$ as a possible equilibrium phase, but it also greatly reduces the chemical potential window in which the $\alpha(2\times 4)$ surface could be stable. Because experiments[3,10] indicate the presence of ordered structures with stoichiometries intermediate between those of the 2×4 and 4×2 phases, it now seems likely to us that the $\alpha(2\times 4)$ structure is not an equilibrium phase.

Recently Skala *et al.*[17] performed STM experiments for the Ga-rich 4×2 reconstruction and interpreted their results in terms of the model shown in Fig. 3. This model is quite different from the $\beta2(4\times 2)$ model proposed by Biegelsen *et al.* on the basis of earlier STM experiments.[3] The model proposed by Skala *et al.* satisfies the electron counting rule, but requires that electrons are transferred from Ga dimers in second-layer terraces to rows of As dimers in the first layer. One may anticipate that this lateral and vertical charge transfer, which occurs over a distance of approximately 5 Å, is energetically costly. Our first-principles calculations indicate that the model of Skala *et al.* is energetically unfavorable as shown in Fig. 2. Further analysis is needed to determine if the $\beta2(4\times 2)$ structure, which we found to be lowest in energy in the Ga-rich limit,[15] is compatible with the available STM data for the Ga-rich $4\times 2/c(8\times 2)$ surface,[3,17] or whether a completely new model is required.

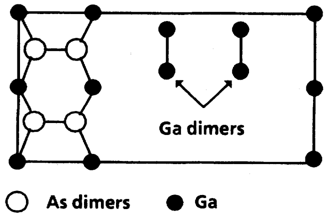

FIG. 3. Model proposed by Skala *et al.* (Ref. 17) for the $4\times 2/c(8\times 2)$ reconstruction of GaAs(001). The model has two As and two Ga dimers in each unit cell.

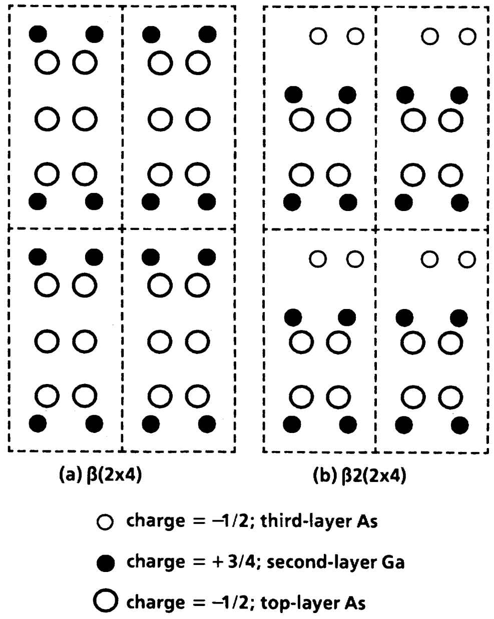
(a) β(2x4) (b) β2(2x4)

FIG. 4. Schematic representation of charge distributions implied by the electron-counting model for the $\beta(2\times 4)$ and $\beta2(2\times 4)$ structures. The charge distribution corresponding to the $\beta2(2\times 4)$ structure has a lower electrostatic energy.

Both the $\beta(2\times 4)$ and $\beta2(2\times 4)$ structures satisfy the electron-counting principle. In addition, the local bonding environment of each atom in the two structures is essentially identical. Therefore the question arises: What is the factor which determines the relative stability of the two structures? Since the energy of the Ga dangling-bond states is much higher than the As lone-pair orbitals, there is a transfer of charge which leaves the As lone-pair bands filled and the Ga-derived bands empty. Formally we may assign a charge of $-\frac{1}{2}$ to each of the six As atoms in the cell and a charge of $+\frac{3}{4}$ to each of the four threefold-coordinated Ga atoms. The total charge in the unit cell is zero. The assignment of charges to the As and Ga atoms is the same for the $\beta(2\times 4)$ and $\beta2(2\times 4)$ structures, but the arrangement of charge within the unit cell is different as shown in Fig. 4. To compute the energy arising from the Coulomb interactions between these subunits, we first perform a Madelung summation for the periodic array of charges on the surface,

$$S=\tfrac{1}{2}\sum q_i q_j/|\mathbf{R}_i-\mathbf{R}_j|.$$

The vectors $\mathbf{R}_i$ are the positions of the atoms having charge q_i. As might be anticipated by inspection of Fig. 4, we find the Madelung energy to be lower for the $\beta2(2\times4)$ structure. To obtain a quantitative estimate of the energy difference, we must take screening into account. We do this crudely by dividing S by the static dielectric constant of GaAs, which we take to be ~13, and thereby obtain for the difference in screened Madelung energies $(\Delta S/\varepsilon)$ a value of ~0.05 eV/(1×1). This value is similar to the result of the *ab initio* calculation and supports our view that the greater stability of the $\beta2(2\times4)$ structure originates from more favorable electrostatic interactions.

The relative stability of the $\beta(2\times4)$ and $\beta2(2\times4)$ structures has also been examined previously by others. Employing the tight-binding approximation (TBA), Chadi found that the two structures had the same energy.[13] Because the TBA neglects the kind of electrostatic interactions which we suggest stabilizes the $\beta2(2\times4)$ structure, it is not surprising that it does not distinguish between the two structures. On the other hand, we do not understand why the local-density calculations performed by Ohno predict the $\beta(2\times4)$ structure to be lower in energy than the $\beta2(2\times4)$ structure.[14]

One may wonder whether the concurrence between our first-principles calculations and the electrostatic model is a coincidence or whether the model has a wider applicability. To answer this question we have considered several additional cases where the model may be applied, and we find that in all cases it gives the correct sign for the energy difference. (Because of its simplicity, we cannot expect the model to give quantitatively precise energy differences.) First of all we note that the 4×2 surfaces, which exhibit Ga dimers in the top layer and threefold-coordinated As atoms in the second layer, may occur in either the $\beta(4\times2)$ or $\beta2(4\times2)$ varieties.[15] The electrostatic model predicts that the $\beta2(4\times2)$ structure is lower by 0.07 eV/(1×1) whereas the *ab initio* calculations give a result of 0.03 eV/(1×1). As another example, consider the two possible structures shown in Fig. 5 in which twofold-coordinated Ga atoms are arranged on a complete layer of As. The Ga atoms may be arranged in either a $c(2\times2)$ or 2×1 pattern. Within the electron-counting model, there is a charge transfer of 1.5 electrons from the Ga to the As lone pairs. The screened Madelung energy difference is 0.06 eV/(1×1) compared to the *ab initio* result of 0.02 eV/(1×1). A similar competition arises between 2×1 and $c(2\times2)$ order on the ZnSe(001) surface and again the simple model predicts the energy difference correctly.[18] On the basis of these results, we believe that electrostatic interactions are the driving force for ordering on many polar semiconductor surfaces and that the model may be applied to predict correctly the type of ordering which is observed.

As another example, consider the $c(4\times4)$ phase observed under extreme As-rich conditions. The accepted structural model for this phase consists of an additional $\frac{3}{4}$ ML of As dimers on top of a complete As layer. The As dimers in the surface layer can be ordered in either a $c(4\times4)$ arrangement or in a 4×2 pattern without changing the local bonding environment of any atoms. Consideration of the bonding leads to the conclusion that charge is transferred laterally from fourfold-coordinated As atoms to threefold-coordinated As atoms in the second layer. The resulting electrostatic energy favors the $c(4\times4)$ ordering as observed experimentally[3] and also as predicted by total-energy calculations. The first-principles calculations predict an energy difference of 0.05 eV/(1×1) whereas the model predicts an energy difference of 0.04 eV/(1×1).

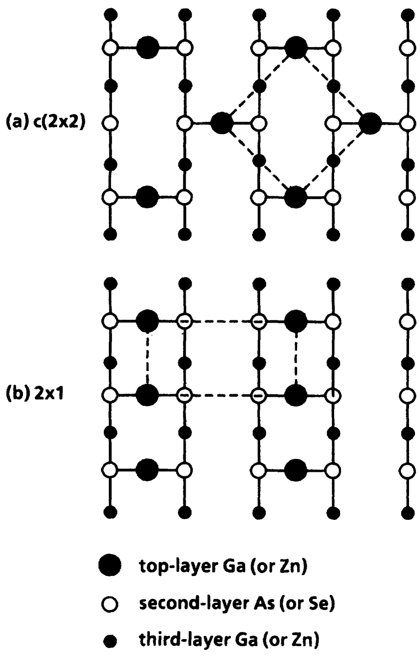

FIG. 5. (a) $c(2\times2)$ and (b) 2×1 arrangements of twofold-coordinated Ga (or Zn) structures. The electrostatic interaction energy is lower in the $c(2\times2)$ arrangement. For GaAs (ZnSe), 1.5 (1.0) electrons are transferred from the Ga (Zn) to the two threefold-coordinated As (Se) atoms in each cell.

Finally we note that the electrostatic interactions would favor a $c(4\times4)$ ordering of the β structures in contrast to the observed 2×4 [or $c(2\times8)$] order.[19] On the other hand, the $\beta2$ structures cannot form $c(4\times4)$ structures because of bond topological constraints. Thus the observed 2×4 [or $c(2\times8)$] order is more naturally explained in terms of the $\beta2$ structure.

In summary, we have shown that the most likely explanation for the 2×4 ordered reconstruction of the GaAs(001) surface is the $\beta2(2\times4)$ structure. Based on our results, we must rule out the $\beta(2\times4)$ structure as a possible equilibrium phase. We have introduced a simple model based on electrostatic interactions that clarifies the origin of the reconstructions observed on GaAs(001). The model is simple to apply and is likely to be applicable to many of the surfaces of III-V and II-VI semiconductors.

Work at NREL was supported by DOE Contract No. DE-AC02-83CH10093. Work at PARC was supported in part by ONR Contract No. N00014-92-C0009.

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[16] The surface energy may be expressed as follows: $\sigma_{1\times 1} = \sigma_{\mathrm{Ga(rich)}} + \Delta n(\mu_{\mathrm{Ga}} - \mu_{\mathrm{Ga(bulk)}})$, where Δn is the difference $(n_{\mathrm{As}} - n_{\mathrm{Ga}})$ per 1×1 unit cell, and $\sigma_{\mathrm{Ga(rich)}}$ is the surface energy in the Ga-rich limit. Δn is defined such that it is equal to zero for the $\alpha(2\times 4)$ surface and $\frac{1}{4}$ for the $\beta(2\times 4)$ and $\beta 2(2\times 4)$. The maximum value for μ_{Ga} corresponds to $\mu_{\mathrm{Ga}} = \mu_{\mathrm{Ga(bulk)}}$, and the minimum value corresponds to $\mu_{\mathrm{Ga}} = \mu_{\mathrm{Ga(bulk)}} - \Delta H$, where ΔH 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.

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