Energetics of As Dimers on GaAs(001) As-Rich Surfaces

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The stabilities of GaAs(001) As-rich surfaces have been determined for the first time by state-of-the-art total-energy calculations. The As-rich surface is found to be inherently *rough*; it cannot exist thermodynamically in a complete As monolayer structure, but in a missing-As-dimer or a two-As-layered structure. The *steepening* relaxation of the As-dimer block is essential to the stability of the As-rich surface. The peculiar interaction between As dimers is obtained, which may play an important role in the growth mechanism. The validity of the electron counting model is discussed.

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The GaAs(001) surface manifests a sequence of reconstructions dependent on surface stoichiometry ranging from the As-rich $c(4\times4)$ structure to the Ga-rich $c(8\times2)$ reconstruction. Among them, the As-rich (2×4) surface is of the most technological interest since molecular-beam-epitaxy (MBE) growth usually begins and ends with this surface under As-rich growth conditions. The atomic structure of the (2×4) surface has been intensively investigated for several years [1–5]. It was reported that this symmetry exists over a range of surface stoichiometry [3–5]. The electron diffraction measurement actually showed three different phases (α, β, and γ, which are discussed below) [3], although it could not determine the structures definitely since the unit cell is relatively large.

The principal model for the (2×4) surface is the vacancy model [2, 3], which assumes that some As dimers are missing in a (2×4) unit cell. A tight-binding total-energy calculation has shown that the (2×4) unit cell with three As dimers and one missing dimer is energetically favorable [2]. This structure obeys the "electron counting model," which is a guiding principle popularly used to determine surface structures of compound semiconductors [2, 3]. The electron counting model requires that a surface structure is stable where the number of electrons per unit cell will exactly fill all As dangling bonds and empty all Ga dangling bonds. The existence of missing dimers has been confirmed by recent scanning-tunneling-microscope (STM) images [4, 5]. The resolution of the STM images, however, is not sufficient to determine the structure of individual dimers in detail. Furthermore, there has been no theoretical investigation on the structure of the (2×4) surface performed using *ab initio* methods. Our knowledge of the surface structures and their stabilities is still very limited. In this Letter, we have determined the detailed atomic structures and stabilities of As-rich surfaces by using state-of-the-art total-energy calculations. We also discuss some of the interesting features of the energetics of As dimers on these surfaces. In addition, the validity of the electron counting model is mentioned.

To determine the relative stabilities of GaAs(001) surfaces with different As coverages, we must calculate their formation energies, which depend on the As chemical potential $\mu_{\rm As}$. At zero temperature the formation energy Ω may be written as

$$\Omega = E - n_{\rm As}\mu_{\rm As}. \tag{1}$$

Here, E is the total energy and $n_{\rm As}$ is the number of As atoms. We assume that the surface is in equilibrium with GaAs bulk and the elemental reservoirs under MBE growth conditions. This assumption requires that the sum of the chemical potentials for Ga and As equals the bulk GaAs energy, and that the chemical potential for each element cannot be above that of the bulk elemental phase. From these two conditions, the upper and lower limits for $\mu_{\rm As}$ are determined [6],

$$\mu_{\rm As(bulk)} - \Delta H_f \le \mu_{\rm As} \le \mu_{\rm As(bulk)}, \tag{2}$$

where ΔH_f is the heat of formation of GaAs. We have determined the range of $\mu_{\rm As}$ by calculating the total energies of the bulk forms of Ga (orthorhombic), As (trigonal), and GaAs [6].

The total energy was calculated within the local density functional (LDF) approach. The total energy functional was minimized with respect to both the plane-wave coefficients of the occupied orbitals and the ionic degrees of freedom by using the conjugate-gradient technique [7]. In computing the total energy, we employed the Wigner form of the exchange-correlation energy and *ab initio* norm-conserving Kleinman-Bylander pseudopotentials [8]. The pseudo wave functions were expanded in terms of a plane-wave basis set corresponding to a kinetic-energy cutoff of 7.29 Ry [9]. Four special k points were employed to sample the primitive surface Brillouin zone. The surface was modeled using supercells containing six layers of GaAs and one layer of hypothetical hydrogen used for the surface termination [10]. The atoms were assumed to be in their fully relaxed positions when the forces on the ions were smaller than 0.15 eV/Å. To check for convergence, we performed calculations for the supercell containing eight layers of GaAs.

The fully separable *ab initio* pseudopotentials proposed by Kleinman and Bylander (KB) substantially reduce computing time. The study of large-size systems

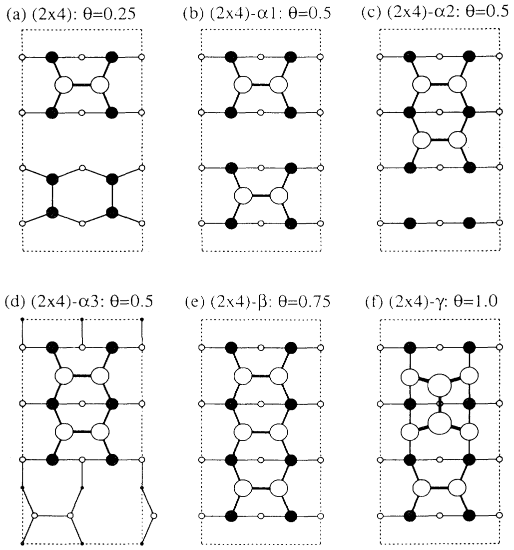

FIG. 1. Schematic atomic structures of GaAs(001)-As(2×4) surfaces whose As coverages θ are 0.25, 0.5, 0.75, and 1.0. Surface structures (a), (b), and (c) do not obey the electron counting model, whereas structures (d), (e), and (f) do obey it. The open (solid) circles represent As (Ga) atoms.

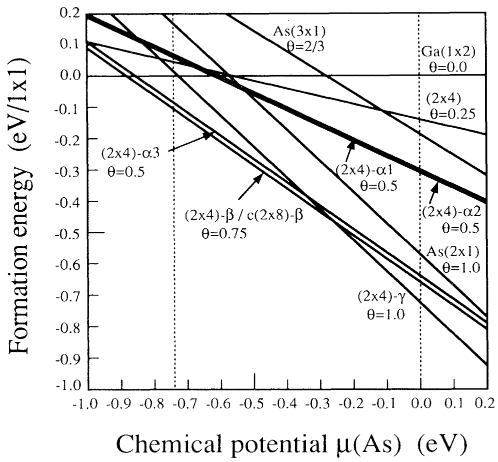

FIG. 2. Surface formation energies for the GaAs(001) As-rich surfaces. The vertical dashed lines indicate the range of the As chemical potential. The horizontal line at 0.0 eV is the surface energy of the GaAs(001)-Ga(2×1) surface. The origin of the As chemical potential is taken to be that of bulk As.

such as the GaAs(001)-(2×4) surface would be intractable without the KB potentials. It is known, however, that the separable pseudopotential does not work for some atoms, including Ga, since the logarithmic derivative is deviated from the all-electron calculation resulting in a spurious bound state (*ghost state*). We have constructed pseudopotentials from atomic calculations by using the method developed by Bachelet, Hamann, and Schluter [11]. The cutoff radius has been carefully chosen so as not to generate ghost states according to the recently proposed criterion [12]. The resulting KB pseudopotentials for Ga and As atoms are free from ghost states and reproduce the band structure of GaAs well.

In this Letter we consider several reconstruction models for GaAs(001) As-rich surfaces having (2×1), (2×2), (2×4), $c(2\times8)$, and (3×1) symmetries. The As coverage ranges from θ=0.25, through 0.5, 2/3, 0.75, and finally up to 1.0. The simplest model is a (2×1) structure consisting of a complete layer of As dimers (θ=1.0). Removing some of these As dimers leads to vacancy models for (2×4) reconstruction. The structure shown in Fig. 1(e) contains three As dimers and one missing dimer per (2×4) unit cell (θ=0.75), which is denoted as the β phase according to the notation in Ref. [3]. In this model the basic (2×4) units are in phase relative to one another. When they are arranged in antiphase along the missing-dimer rows, the structure has the $c(2\times8)$ symmetry.

When two As dimers are missing per (2×4) unit cell (θ=0.5), three structures are considered as shown in Figs. 1(b)–1(d). In 1(b), As dimers alternate with missing dimers forming an essentially (2×2) structure. In 1(c), two rows of As dimers alternate with two rows of missing dimers exposing second-layer Ga atoms, while in 1(d), the exposed second-layer Ga atoms are removed exposing the third-layer As atoms below them. Two-As-dimer (2×4) structures 1(b), 1(c), and 1(d) are denoted as the α_1, α_2, and α_3 phases, respectively. The one-As-dimer model is also considered in Fig. 1(a). The structure shown in Fig. 1(f) is generated by inserting an additional As dimer between two As dimers in the one-missing-dimer model. This model, denoted as the γ phase, has the same As coverage (θ=1.0) as the (2×1) surface. Furthermore, we consider the (3×1) structure in which one As atom is missing per unit cell and the remaining two As atoms are dimerized (θ=2/3).

The formation energies of As-rich surfaces are plotted in Fig. 2 as a function of the As chemical potential. In this figure the chemical potential is measured relative to $\mu_{\mathrm{As(bulk)}}$. The (2×4) β or $c(2\times8)$ β surface is the most stable structure in the range $-0.74 \leq \mu_{\mathrm{As}} \leq -0.27$ eV, having the same energy within 0.005 eV per (1×1) unit cell. This leads to the possibility of the coexistence of both structures, that is, the possibility that the basic (2×4) units are arranged both in phase and in antiphase.

The electron counting model also expects these surfaces to be stable [2, 3] since the basic (2×4) unit with one As dimer removed has the correct number of electrons required to fill all As dangling bonds and empty all Ga dangling bonds. Only removing one As dimer, however, cannot stabilize the β surface with respect to a complete As-monolayer (2×1) surface, without further surface relaxation.

The completely relaxed structure of the β surface is presented in Fig. 3. This surface has a dimer-block struc-

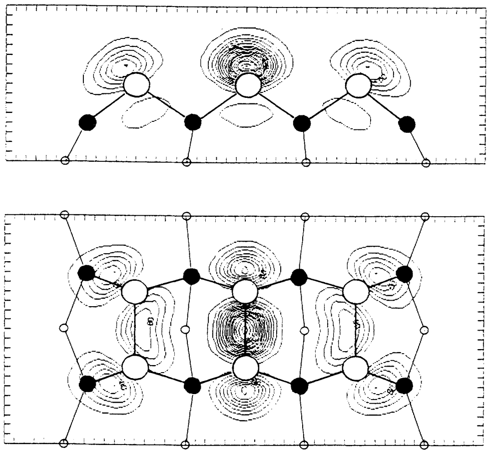

FIG. 3. Completely relaxed atomic structure and calculated charge density of the valence-band-maximum state of GaAs(001)-As(2×4) β surface. The open (solid) circles represent As (Ga) atoms.

ture consisting of three As dimers and eight second-layer Ga atoms. The most peculiar feature of the relaxed structure is that the threefold-coordinated Ga atoms move noticeably inside the dimer block and the As dimers move upwards from the surface, which causes the dimer block to steepen. This relaxation of surface Ga and As atoms is analogous to the buckling of the GaAs(110) surface [13]. We call this the *steepening* of the As-dimer block. The dimer-block steepening shifts the Ga dangling bonds higher and the As dangling bonds lower in energy, which widens the surface energy gap by about 1.0 eV, completes the charge transfer from the Ga dangling bonds to the As dangling bonds, and stabilizes the β structure by 0.31 eV per (1×1) unit cell. In this way, the steepening relaxation is of essential importance in the realization of the expectations of the electron counting model. The relaxed β surface exhibits nonmetallic character, consistent with the angle-resolved photoemission measurement [1]. The calculated charge density of the valence-band-maximum state, which is shown in Fig. 3, can also well explain the experimental STM images [4].

The α_2 phase is about 0.3 eV per (1×1) unit cell more unstable than the β phase. This surface exhibits a metallic character [14], which is contrary to the expectations from the tight-binding calculation [2] or the electron counting model [3]. These expectations were based on an assumption that the exposed second-layer Ga atoms would bond to the neighboring Ga atoms and become threefold coordinated. From *ab initio* calculations, however, the exposed Ga atoms are found to be not dimerized, being left twofold coordinated, which means that the above assumption is incorrect. In this way, the validity of the electron counting model is strongly dependent on how the surface atoms are relaxed or redimerized. The α_1 surface, having a higher energy by 0.01 eV per (1×1) unit cell than the α_2 surface, is also metallic. Thus, neither the α_1 nor the α_2 surface agrees with the photoemission measurement. On the other hand, the α_3 surface exhibits nonmetallicity since the third-layer As atoms can be redimerized. The steepening relaxation of two-As-dimer block stabilizes this surface by completing the charge transfer from Ga to As atoms. As a result, the α_3 phase is only 0.02 eV per (1×1) unit cell [15] higher in energy than the most stable β phase. It is not possible, however, to transform the α_3 phase into the β phase by just adding As atoms, because Ga atoms are also missing. Thus, the α_3 phase is not likely to appear during MBE growth, but will appear on annealed as-grown samples [5].

When $\mu_{\rm As}$ exceeds -0.27 eV, the (2×4) γ phase is stable with respect to the β structure. The γ surface has two As surface layers. The top As atoms are dimerized, and the second-layer As atoms and the third-layer Ga atoms are relaxed like in the dimer-block steepening of the β surface. Consequently, this surface is nonmetallic. It is noted that the As-monolayer (2×1) surface is much more unstable than the two-As-layered γ surface, in spite of both having the same As coverage (θ=1.0). The surfaces with higher As coverage, of course, have two-As-layered structures such as $c(4 \times 4)$ [16]. Thus, the As-rich surface cannot exist thermodynamically in the complete As monolayer structure, but it can in the missing-dimer or two-layered structures. This means that the As surface is an *inherently rough* surface. *Rough* surfaces have more possibilities for steepening relaxations to widen their energy gaps and lower their surface energies, compared with more *flat* surfaces. The realization of steepening relaxations is a driving mechanism responsible for the roughening of As-rich surfaces.

In practice, the surface during MBE growth is not usually in equilibrium with the As reservoir. The energetics and dynamics of As atoms play an important role in the growth mechanism. The energetics of As dimers is especially of interest since As dimers are thought to be a fundamental building unit of an As-rich surface. We can roughly estimate the interactions of As dimers on the surface from the calculated formation energies of various As-rich surfaces by assuming that the interaction between (2×4) unit cells is negligible. The obtained energetics [17] are

$$\begin{aligned} 1D + 1D &= 2D + 0.2\ \text{eV}, \\ 2D + 1D &= 3D + 1.6\ \text{eV}, \\ 3D + 1D &\le 4D - 1.8\ \text{eV}, \\ 3D + 1D &= 3D/1D - 0.6\ \text{eV}, \end{aligned} \tag{3}$$

where $1D$ denotes an isolated As dimer, nD denotes a block of n As dimers, and $3D/1D$ represents a two-layered block consisting of one top As dimer and three second-layer As dimers. The energy of a $4D$ block is assumed to be higher than that of a complete As-monolayer surface since the $4D$ block is supposed to gain no special stabilization energy similar to a $2D$ block. Equation (3) demonstrates the peculiar features of the interaction between As dimers. Isolated As dimers weakly attract one another to form a block of two dimers. Then, the two-dimer block strongly attracts another dimer, forming a three-dimer block. Once the three-dimer block is formed, it repels another dimer strongly. This means that three-dimer blocks are noticeably stable. Consequently, the As surface is constructed with blocks of three As dimers, leading to a (2×4) symmetry. When the As coverage θ exceeds 0.75 a two-As-layered structure is generated. The energetics of As dimers also has an influence upon the desorption process of As atoms from the surface. The energy required for an As dimer to desorb is dependent on the dimer-block structure on the surface. When $\mu_{\mathrm{As}} = \mu_{\mathrm{As(bulk)}}$, for example, the desorption energies of one As dimer from the surface are 1.2, 1.3, 2.8, and 0.5 eV, respectively, for dimer-block structures of $1D$, $2D$, $3D$, and $3D/1D$.

The interaction between (2×4) unit cells, which is neglected in deriving Eq. (3), may be important in some cases. For example, we can derive the following equation from Eq. (3): $3D + 3D \le 2D + 4D - 3.4$ eV. If both the $2D$ and $4D$ blocks exist in a (2×8) unit cell, the $2D + 4D$ structure satisfies the electron counting model due to a charge transfer between the $2D$ and $4D$ blocks. As a result, the $2D + 4D$ structure may become more stable than expected in the above equation. When the $2D$ and $4D$ blocks do not exist in the same (2×8) unit cell, however, the $2D + 4D$ structure cannot be stabilized since both the $2D$ and $4D$ blocks generate twofold-coordinated Ga atoms. Thus, the $2D+4D$ structure can be stabilized in only a few cases. During the formation of As-rich surfaces, these stabilizations due to the charge transfer between (2×4) unit cells are thought to be not so important. Thus, we have neglected the interaction between (2×4) unit cells.

In summary, we have investigated the stabilities of GaAs(001) As-rich surfaces using the state-of-the-art total-energy-calculation technique. The As-rich surface is found to be inherently *rough*; it cannot exist thermodynamically in the complete As monolayer structure, but it can in the one-missing-dimer or a two-As-layered structure. The *steepening* relaxation of the As-dimer block is essential to the stability of the As-rich surface. The interaction between As dimers has some peculiar features, which may play an important role in the growth mechanism of GaAs(001) surface. The validity of the electron counting model strongly depends on how the surface atoms are relaxed or redimerized.

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[15] The energy difference of 0.02 eV per (1×1) unit cell is meaningful because of the accuracy being about 0.1 eV per (2×4) unit cell [i.e., about 0.01 eV per (1×1) unit cell] in our calculations.
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[17] All of the reactions in Eq. (3) conserve the number of the surface As atoms, and hence the results are independent of the As chemical potential.