Stoichiometry and Surface Reconstruction: An *Ab Initio* Study of GaAs(100) Surfaces

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Ga- and As-terminated GaAs(100) surfaces are studied through first-principles density-functional pseudopotential calculations of the energies of surfaces with different stoichiometries and reconstructions. We predict structural transitions as a function of Ga and As chemical potentials within an experimentally accessible range which is shown to be fixed by the bulk energies of Ga, As, and GaAs. The bulk energies are determined accurately by the *ab initio* calculations. The predicted surface stoichiometries are in good agreement with experimental data.

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Despite the importance of the GaAs(100) surface in technological applications, e.g., in the areas of crystal growth and heteroepitaxy, the understanding of this surface is still at a preliminary stage, both theoretically and experimentally. Since the surface exhibits a rich variety of structures as a function of surface stoichiometry and temperature,[1-4] the challenge for theory is to determine stable surface structures taking into account variations in Ga and As coverage, or equivalently variations in Ga and As chemical potentials.

In this Letter we report on a systematic study of the stoichiometry, atomic reconstruction, and surface energy of 1×1, 2×1, 1×2, and 2×2 Ga- and As-terminated Ga(100) surfaces.[5] The effects of larger unit cells on the surface energies and atomic structures are studied by tight-binding calculations. An important aspect of this work is to establish the appropriate chemical potentials. We show that the range of chemical potentials allowed for each element under equilibrium conditions are fixed by that of the elemental bulk phases and we carry out *ab initio* calculations of the energies of bulk Ga, As, and GaAs at $T=0$. To test the accuracy of these calculations, we compute the heat of formation of GaAs and find it to be in exceptionally good agreement with experiment. Using the theoretical limits on the chemical potentials we determine the GaAs(100) surface energy as a function of Ga and As coverage and atomic structure.

Our calculation is based on the self-consistent density-functional approach of Hohenberg, Kohn, and Sham,[6] with the Ceperley-Alder form[7] for the exchange-correlation energy in the local density approximation (LDA). A momentum-space formalism is applied.[8] *Soft* norm-conserving nonlocal atomic pseudopotentials[9] for Ga and As were generated and tested against hard potentials by the examination of several bulk properties of GaAs as described elsewhere.[5,10,11] Our surface calculations use a basis set consisting of plane waves with an energy cutoff of 6 Ry ($\simeq 1130$ plane waves for a 2×2 periodicity), which our tests[5,10,11] have shown is accurate for the present soft pseudopotentials. Eight (four) special sampling points in the primitive surface Brillouin zone were taken in the energy summations for the 2×1 (2×2) cells. For each surface reconstruction, we start from an initial surface atomic geometry and carry out self-consistent pseudopotential calculations to evaluate the Hellmann-Feynman forces[8] on the atoms. The atoms are moved and new forces are calculated until the minimum of the energy and the optimum atomic configurations are obtained.

The total energy comparisons between different structures on the Ga- and As-terminated (100) surfaces with different surface Ga or As coverages make it necessary to consider the energies of the appropriate atomic reservoirs involved in the exchange of atoms with the surface. We determine the stable structures by using standard thermodynamic quantities such as the Gibbs free energy and the chemical potential μ_i of each type of atom i which takes into account the fact that the numbers of atoms are conserved in reactions at the surface. The chemical potential μ_i is defined to be $\mu_i = dG/dn_i$ where $G=E+PV-TS$ is the Gibbs free energy. Since the most common sources in molecular-beam epitaxial growth of GaAs are bulk metallic Ga and As_2 or As_4 gas, we must derive the proper chemical potentials for these sources to include in our calculations. For condensed states considered here the Gibbs free energy can be approximated by the internal energy at $T=0$, since the PV term is very small and the TS term tends to cancel in the desired energy differences. However, for a gaseous phase the effect of T and P on μ_i cannot be ignored. [At this point our analysis is qualitatively different from that of Kaxiras and co-workers,[12-14] who studied the (111) surface. The differences are discussed elsewhere.[15]] For an ideal gas, μ_i has a simple dependence on P, T, and the atomic or molecular mass,[16] but in general, the dependence of $\mu_i(P,T)$ on P and T is complicated. Nevertheless, without a detailed knowledge of $\mu_i(P,T)$ we still can set rigorous limits on its range of values as long as the system is in equilibrium. In particular, each μ_i must satisfy $\mu_i \leq \mu_i^{\text{bulk}}$, since when $\mu_i = \mu_i^{\text{bulk}}$ the gas phase condenses to form the elemental bulk phase. In addition, since pairs of Ga and As atoms can be exchanged with bulk GaAs, equilibrium requires

$$\mu_{\text{Ga}} + \mu_{\text{As}} = \mu_{\text{GaAs}}^{\text{bulk}} = \mu_{\text{Ga}}^{\text{bulk}} + \mu_{\text{As}}^{\text{bulk}} - \Delta H_f,$$

where ΔH_f is the heat of formation. These two conditions together determine the upper and lower limits for the chemical potentials μ_i of the elemental reservoirs at a surface in equilibrium with its surroundings. They are

$$\mu_{\text{As}}^{\text{bulk}} - \Delta H_f \leq \mu_{\text{As}} \leq \mu_{\text{As}}^{\text{bulk}}, \tag{1a}$$

$$\mu_{\text{Ga}}^{\text{bulk}} - \Delta H_f \leq \mu_{\text{Ga}} \leq \mu_{\text{Ga}}^{\text{bulk}}, \tag{1b}$$

i.e., under epitaxial growth conditions the ranges of the chemical potentials are set by the corresponding *bulk* states.

We have calculated carefully the total energies of bulk Ga, As, and GaAs because accurate energies are crucially important in the comparison of surface energies of Ga- or As-terminated GaAs(100) surfaces with different stoichiometries. The calculations for the elements, described in detail in Ref. 11, are for Ga and As in their bulk metallic structures, which are respectively orthorhombic with eight atoms per cell and trigonal with two atoms per cell, with parameters chosen to minimize the total energies. For GaAs we use the theoretical lattice constant 5.52 Å, 2% smaller than the experimental value. The accuracy of these *ab initio* results is attested by the heat of formation ΔH_f, which we find to be 0.73 eV per GaAs pair, in excellent agreement with the experimental value[17] of 0.74 eV.

For our *ab initio* surface calculations we have considered three different surface stoichiometries. They correspond to surface coverages of $\theta_{\text{Ga}}=1$, $\theta_{\text{As}}=1$, and either $\theta_{\text{Ga}}=\frac{1}{2}$ or $\theta_{\text{As}}=\frac{1}{2}$. The latter two are different half-filled surfaces both of which have the same stoichiometry as the bulk. Unit cells with 1×1, 2×1, 1×2, and 2×2 periodicities were examined. Ga- (As-) terminated surfaces were modeled with a 5- (6-) layer slab plus a 3- (2-) layer vacuum. To avoid charge-transfer problems and to decouple the two ends of the slab, we imposed fractional charges on one end of the slab. In the present calculation we chose pseudo Ga surface atoms with a valence charge of 3.5 instead of 3 (for the As case the valence charge would be 4.5 instead of 5) for computational reasons. The other end of the slab was used to examine a variety of surface reconstructions. This arrangement allows us to calculate the total energies for the different slabs with exactly the same k points in the primitive Brillouin zone so that the relative energies can be determined with minimal systematic errors. The determination of the surface energy requires an additional calculation. After the Ga(100)-1×2 surface with $\theta_{\text{Ga}}=\frac{1}{2}$ is completely relaxed, we form a five-layer slab with a half-monolayer Ga coverage at both sides and no fractionally charged atoms. The two surfaces are the same except for a 90° rotation. Since this surface has bulk stoichiometry (8 Ga+8 As for a 2×2 structure), its surface energy can be compared directly with the bulk energy so that the absolute energy is established. The total energies for other surfaces can be obtained from their energies relative to this surface, with results given in Figs. 1 and 2.

The primary results are as follows: (1) For each surface the lowest energy is achieved when the surface atoms *dimerize*. Each Ga (As) dimer reduces the energy by 1.7 eV (0.7 eV) from the ideal unrelaxed geometry. However, for $\theta_{\text{Ga}}=\frac{1}{2}$ and $\theta_{\text{As}}=\frac{1}{2}$ missing-row surfaces, the *relaxed* surfaces have only slightly higher energies than the dimerized ones because of a large relaxation effect. (2) In Fig. 1 appropriate reservoirs are indicated between surfaces with different stoichiometries and energy differences are given when atoms are exchanged with these reservoirs. These bulk reservoirs set the limits for the most Ga-rich ($\mu_{\text{Ga}}=\mu_{\text{Ga}}^{\text{bulk}}$) and As-rich ($\mu_{\text{As}}=\mu_{\text{As}}^{\text{bulk}}$) environments. This same information is given graphically by the points in Fig. 2(a). There we also show parabolic curves fitted through these points to represent possible interpolation for other fractional coverages. In addition, the shaded areas of Fig. 2 indicate the range for intermediate chemical potentials. (3) We can see that the energy (per atom) decreases in going from a filled to a half-filled surface, i.e., the energy decreases in the addition of Ga to an As-terminated surface ($\theta_{\text{Ga}}=0$) or As to a Ga-terminated surface ($\theta_{\text{As}}=0$) is larger than if we go from a half-filled to a filled surface (e.g., adding Ga to a $\theta_{\text{Ga}}=\frac{1}{2}$ to make a $\theta_{\text{Ga}}=1$ surface, etc.). This indicates that there is a net repulsive energy as more atoms are added to the surface, so that the surfaces are likely to stabilize with fractional coverage. (4) Our tight-binding calculations[18] for the As-terminated surface with larger unit cells show that the energy can be lowered for more complex reconstructions. For $\theta_{\text{As}}=\frac{1}{2}$, the surface energy of As(100)-2×4 structure is 0.3 eV per 1×1 cell lower than that of As(100)-2×2 structure. The energy reduction arises almost entirely from a rehybridization of

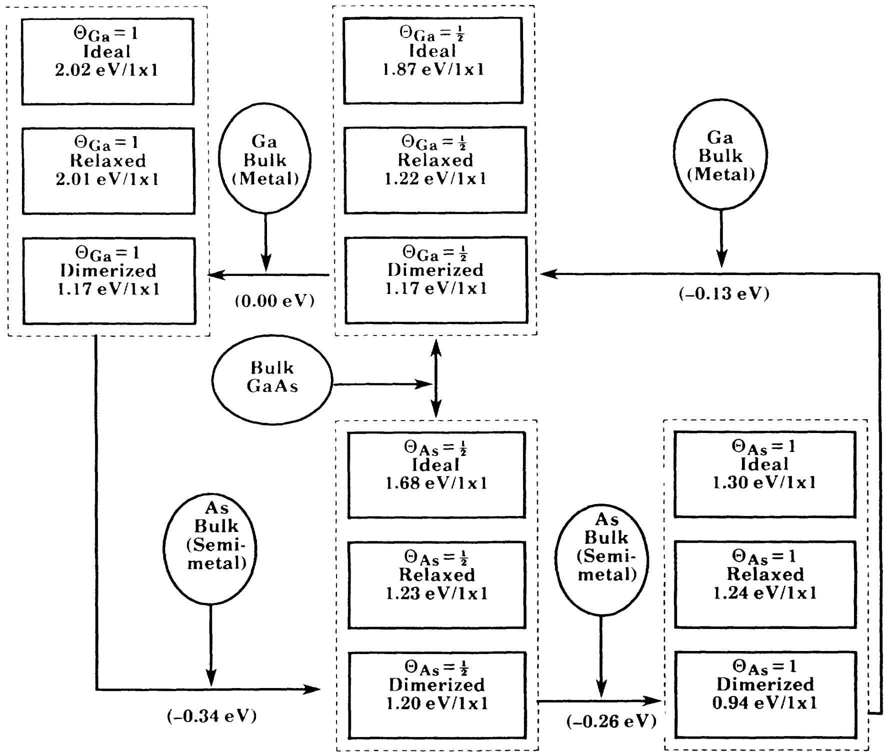

FIG. 1. The surface energy for GaAs(100) surface with different stoichiometries, where θ represents the surface coverage of the element which appears in the subscript. The energies of the stoichiometric $\theta = \frac{1}{2}$ surfaces are absolute energies for creation of the surface from bulk. For the other surfaces, the energy differences with chosen reservoirs are given in parentheses for each arrow. We also assign total energies to these surfaces with the convention that the energy gained in going from $\theta_{\mathrm{As}} = 1$ ($\theta_{\mathrm{Ga}} = 1$) to $\theta_{\mathrm{Ga}} = \frac{1}{2}$ ($\theta_{\mathrm{As}} = \frac{1}{2}$) surfaces is the difference in energies minus $\Delta H_f/2$. Note that the energy gain in a complete cycle is the heat of formation (0.73 eV).

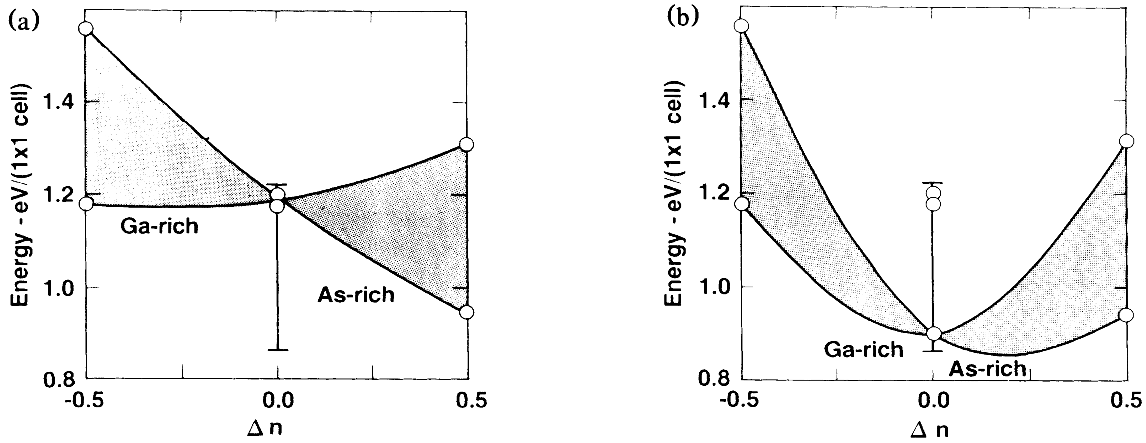

FIG. 2. Energy $E_{\mathrm{surface}}(n_i) - \sum_i \mu_i n_i$ (per surface atom) as a function of $\Delta n = n_{\mathrm{As}} - n_{\mathrm{Ga}}$. (a) The density-functional and (b) density-functional plus tight-binding results. The points are calculated values from Fig. 1 for the limiting case of "Ga-rich" and "As-rich" chemical potentials. The curves are parabolas fitted through the points as a suggestion of the energies of possible other structures with different stoichiometries. The shaded areas represent the continuous family of curves for intermediate chemical potentials. The two points at $\Delta n = 0.5$ and $\Delta n = -0.5$ define the limits of the surface energies for these stoichiometries. The difference of these two limits is one-half of the heat of formation of bulk GaAs as described in the text. The minima in (b) suggest that the most stable surface will be intermediate between half and full coverage. The vertical line at $\Delta n = 0$ and its two limits indicate the expected range of the GaAs(100) surface energy with $\theta = \frac{1}{2}$ as explained in the text.

second-layer dangling-bond orbitals on *twofold* coordinated Ga atoms which is possible in a 2×4 cell but not in a 2×2 one where the Ga atoms are constrained to be *threefold* coordinated. This energy is included in Fig. 2(b) together with the energies from our *ab initio* calculations. With these results for $\theta=\frac{1}{2}$ our parabola fits indicate that most stable surfaces have fractional coverage and one would not get full coverage for any chemical potentials consistent with equilibrium. (5) The energies of $\theta_{\text{Ga}}=\frac{1}{2}$ and $\theta_{\text{As}}=\frac{1}{2}$ can be compared directly with that of the (110) surface[10] since each has the same bulk stoichiometry. (This may be easily seen from the fact that slabs for each of these cases have the same number of Ga and As atoms per cell.) Since (110) is the cleavage surface, it is expected to have the lowest surface energy per unit area; i.e., it sets a lower bound for the $\theta=\frac{1}{2}$ (100) surface energy. On the other hand, it also sets an upper bound above which the $\theta=\frac{1}{2}$ (100) surface would be unstable to making (110) facets. These two limits are plotted in Fig. 2, linking with a vertical line which indicates the expected range of surface energy for the GaAs(100) surface with $\theta=\frac{1}{2}$. We can see from Fig. 2(a) that our *ab initio* results for 2×2 reconstruction is barely below the upper limit, and from Fig. 2(b) that the tight-binding results for 2×4 (or 4×2) reconstruction are barely above the lower limit.

In conclusion, our first-principles calculations on the 1×1, 1×2, 2×1, and 2×2 Ga- or As-terminated GaAs(100) surfaces gives the surface energy as a function of the surface stoichiometry as well as the chemical potential. The limits of the chemical potential are shown to be set by the elemental bulk phases and equilibrium conditions. For each surface, dimer or dimer-plus-vacancy structure is found to be the lowest energy state. As a function of chemical potentials, the most stable surfaces are found to change from Ga rich to As rich, with coverage θ_{Ga} or θ_{As} in the range $\frac{1}{2}<\theta<1$, which is in good agreement with experimental data.[4]

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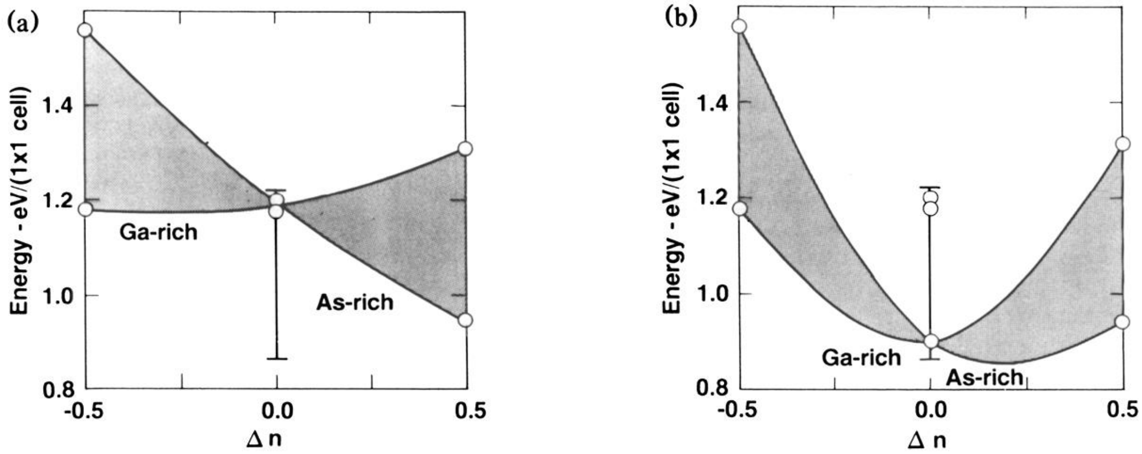

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