Structure of the GaAs(110) surface in As-rich conditions

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The dependence of the structure of the GaAs(110) surface on the As and Ga chemical potentials is explored. Total-energy calculations performed within the local-density-functional formalism using first-principles pseudopotentials indicate that in the extreme As-rich limit a 1×1 structure composed of As chains is slightly lower in energy than the Ga-As chain structure produced by cleaving. The 1×1 structure composed of Ga chains is found to be unstable with respect to Ga cluster formation. Calculations also indicate that the GaAs(110)1×1:Sb chain surface is stable with respect to Sb cluster formation.

Both GaAs($\bar{1}\,\bar{1}\,\bar{1}$) and GaAs(100) exhibit multiple reconstructions which arise from changes in the surface stoichiometry.[1] For example, the GaAs($\bar{1}\,\bar{1}\,\bar{1}$) surface exhibits a 2×2 reconstruction in As-rich conditions and a $\sqrt{19} \times \sqrt{19}$ reconstruction in Ga-rich conditions.[2] Within the context of equilibrium thermodynamics, the 2×2 reconstruction is stable when the chemical potential of As atoms (μ_{As}) is high whereas the $\sqrt{19} \times \sqrt{19}$ reconstruction is stable when the chemical potential of Ga atoms (μ_{Ga}) is high. In practice one obtains the As-rich surface following molecular-beam epitaxial (MBE) growth at low temperatures, and the Ga-rich surface can be obtained by annealing the growth surface in vacuum.[1] Such an annealing procedure preferentially desorbs As leaving the surface with an excess of Ga.

It is well known that the GaAs(110) surface exhibits a relaxed but otherwise unreconstructed 1×1 surface following cleaving in ultrahigh vacuum, and both the atomic and electronic structure of this surface are understood.[3-10] Cleaving results naturally in a surface having the same stoichiometry as bulk GaAs. In principle, a (110) surface produced by MBE growth under As- or Ga-rich conditions could be different in structure and stoichiometry than the cleaved surface. Thus, one may wonder if the GaAs(110) surface could exhibit multiple reconstructions depending on the chemical potentials of As and Ga. Here I examine this question by calculating the energetics of the GaAs(110) surface under the assumption that it is in equilibrium with reservoirs of Ga and As atoms and with bulk GaAs. First-principles total-energy calculations indicate that the GaAs(110) 1×1 cleavage surface is, in fact, thermodynamically stable over most of the range allowed chemical potentials of As and Ga, but is metastable in the *extreme limit* where the As chemical potential becomes equal to that of bulk As. In this limit a structure consisting of As-As chains is found to be slightly more stable.

Three possible GaAs(110) surface structures were examined including the structure formed by cleaving. A side view (schematic) of this structure is shown in Fig. 1(a). In this case the surface consists of Ga-As chains. Replacing the As atoms in the surface Ga-As chain by Ga atoms, we obtain the Ga-Ga chain surface shown in Fig. 1(b). Likewise if the Ga atoms are replaced by As,
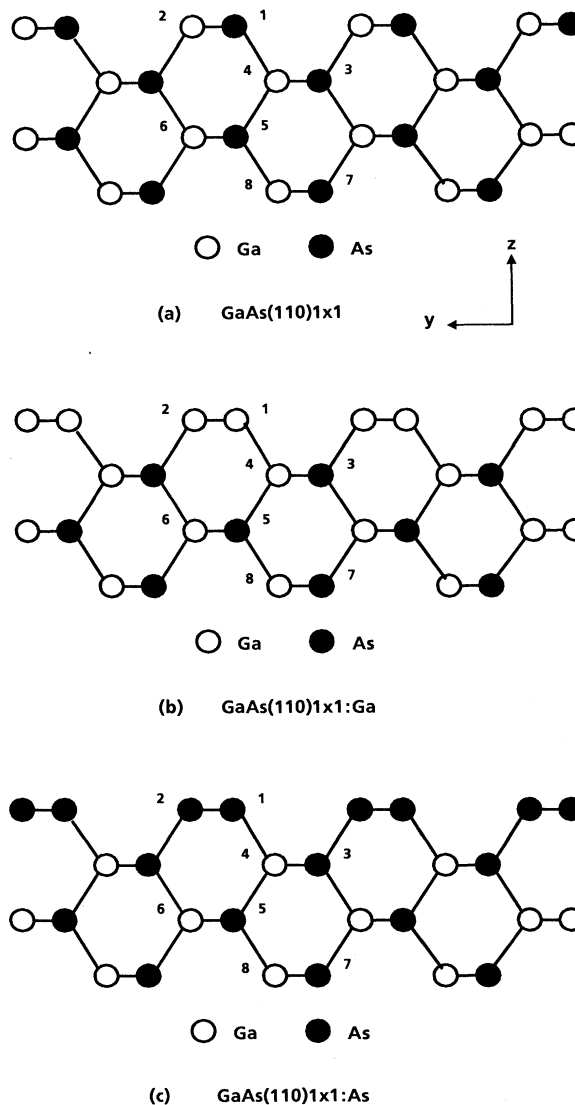

FIG. 1. Schematic side views of the three models studied in this work. (a) Ga-As chain; (b) As-As chain; (c) Ga-Ga chain. Calculated atomic displacements are listed in Tables I–III.

we obtain the As-As chain surface shown in Fig. 1(c). A structure of this type with Sb chains on the GaAs(110) surface has been studied extensively over the last decade.[11–15]

The relative formation energies of the these three surfaces were calculated within the local-density-functional approach[16] employing scalar relativistic norm-conserving pseudopotentials.[17] The Kohn-Sham equations were solved in the momentum space formalism.[18] The surface was modeled by a repeated slab geometry with supercells each containing 12 atomic layers. The plane-wave cutoff was taken to be 12 Ry and 6 k points were included in the irreducible Brillouin-zone summations for the total energy and forces.

The surface energy is defined in terms of the thermodynamic potential[19] $\Omega = U - TS - \sum_i n_i u_i$. The surface energy E_s is equal to Ω / A, where A is the surface area. In the expression for Ω, U is the total energy of the system. The entropy term, TS, is assumed to contribute very little to the difference in Ω for various structures and is neglected. The n_i are the numbers of ith constituents. The μ_i are the chemical potentials of the As and Ga atoms and are restricted to lie within a certain range determined by the constraints[20,21]: $\mu_{As} \leq \mu_{As(bulk)}$, $\mu_{Ga} \leq \mu_{Ga(bulk)}$, and $\mu_{Ga} + \mu_{As} = \mu_{GaAs(bulk)}$. Total-energy calculations for bulk As, Ga, and GaAs were performed in order to determine the allowed range of chemical potentials for As and Ga. With a plane-wave cutoff
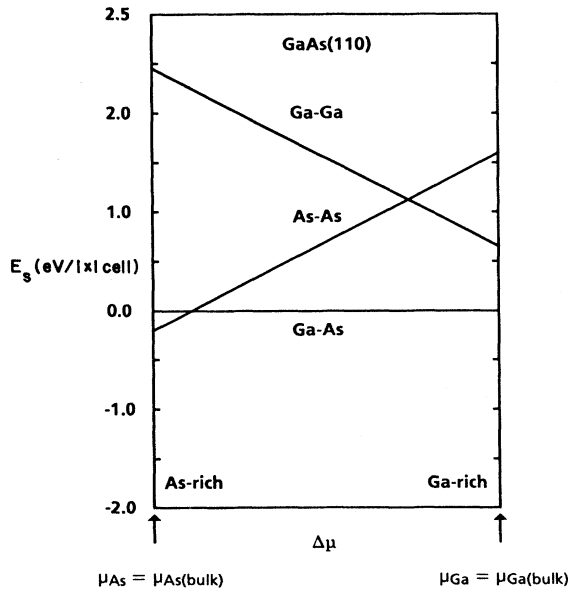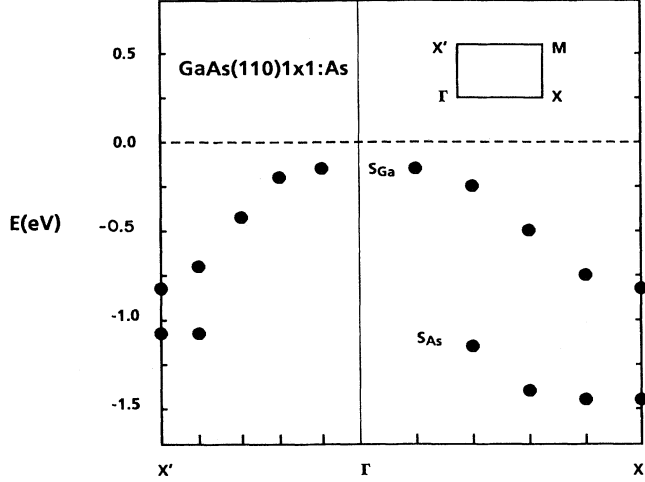

FIG. 3. Surface state dispersion for the As-As chain surface. The GaAs bulk valence-band maximum is located at 0.0 eV.

of 12 Ry the heat of formation of GaAs, $\Delta H = \mu_{As(bulk)} + \mu_{Ga(bulk)} - \mu_{GaAs(bulk)}$, is converged to within 0.02 eV.

Atomic coordinates for each of the three models were determined by an energy minimization process facilitated by force calculations and are given in Tables I–III. For the Ga-As chain surface the vertical displacement of the surface As and Ga atoms is 0.64 Å and the chain tilting angle relative to the (110) plane is 28.7°. Both of these structural parameters are in excellent agreement with previously determined experimental and theoretical values.[10] For both the Ga-Ga and the As-As chain surface the atoms comprising the surface chain are at nearly the same height and the chain tilting angle is nearly equal to zero. The intrachain As—As bond length is 2.55 Å, while that of the Ga atoms is 2.23 Å. The intrachain As—As—As bond angle is 103°. In the Ga-Ga chains the corresponding bond angle is 127°.

The relative surface formation energies are plotted in Fig. 2 as a function of the chemical potential difference between Ga and As: $\Delta\mu = \mu_{Ga} - \mu_{As}$. $\Delta\mu$ ranges from the As-rich limit $(\Delta\mu = \mu_{Ga(bulk)} - \mu_{As(bulk)} - \Delta H)$ to the Ga-rich limit $(\Delta\mu = \mu_{Ga(bulk)} - \mu_{As(bulk)} + \Delta H)$ where ΔH is

FIG. 2. Surface energy in eV/(1 × 1 cell) relative to the GaAs chain surface as a function of $\Delta\mu = \mu_{Ga} - \mu_{As}$. $\Delta\mu$ ranges from the As-rich limit: $\Delta\mu = \mu_{Ga(bulk)} - \mu_{As(bulk)} - \Delta H$, to the Ga-rich limit $\Delta\mu = \mu_{Ga(bulk)} - \mu_{As(bulk)} + \Delta H$. ΔH is the calculated heat of formation of bulk GaAs from bulk Ga and As. The calculations give $\Delta H = 0.89$ eV compared with the experimental value (Ref. 22) of 0.75 eV.

TABLE I. Displacements of the atoms from ideal positions for the Ga-As chain surface. Values are given in a.u. (1 a.u. = 0.529 Å). Atom numbers refer to Fig. 1(a).

Atom	Δx	Δy	Δz
1 As	0.0	−0.20	0.29
2 Ga	0.0	−0.66	−0.92
3 As	0.0	0.13	−0.05
4 Ga	0.0	0.14	0.08
5 As	0.0	0.05	−0.01
6 Ga	0.0	0.08	−0.01
7 As	0.0	0.03	−0.04
8 Ga	0.0	0.02	0.01

TABLE II. Displacements of the atoms from ideal positions for the Ga-Ga chain surface. Values are given in a.u. (1 a.u.=0.529 Å). Atom numbers refer to Fig. 1(b).

Atom	Δx	Δy	Δz
1 Ga	0.0	0.43	−0.41
2 Ga	0.0	−0.38	−0.35
3 As	0.0	−0.05	−0.05
4 Ga	0.0	−0.03	0.00
5 As	0.0	0.00	−0.05
6 Ga	0.0	−0.01	−0.02
7 As	0.0	−0.02	0.01
8 Ga	0.0	−0.03	0.00

TABLE IV. Displacements of the atoms from ideal positions for the GaAs(110)1×1:Sb chain surface. Values are given in a.u. (1 a.u.=0.529 Å). Atom numbers refer to Fig. 1(c), except that atoms 1 and 2 are Sb rather than As.

Atom	Δx	Δy	Δz
1 Sb	0.0	−0.57	0.56
2 Sb	0.0	0.50	0.56
3 As	0.0	−0.01	−0.17
4 Ga	0.0	0.00	−0.11
5 As	0.0	−0.01	−0.08
6 Ga	0.0	−0.04	−0.04
7 As	0.0	−0.02	0.01
8 Ga	0.0	−0.03	0.00

the calculated heat of formation of bulk GaAs from bulk Ga and As. The calculations give $\Delta H=0.89$ eV compared with the experimental value[22] of 0.75 eV. Over most of the range of allowed chemical potentials the Ga-As chain surface is the most stable. However, in the As-rich limit, the As-As chain surface becomes slightly more stable than the cleaved surface. In other words removing As atoms from a bulk As reservoir and adding them to the cleaved surface to form the As chains *lowers* the energy of the system (surface plus reservoir) by a small amount: 0.20 eV/(1×1 cell). On the other hand, even under the most extreme Ga-rich conditions, the Ga-As chain surface remains stable with respect to the Ga-Ga chain surface. Removal of Ga atoms from a bulk Ga reservoir and adding them to the cleaved surface to form the Ga chain reconstruction *increases* the energy of the system by 0.66 eV/(1×1 cell). The Ga-Ga chain surface is unstable with respect to Ga cluster formation.

Total-energy calculations were also performed for the GaAs(110)1×1:Sb surface for the purpose of testing the stability of the Sb monolayer chain structure with respect to Sb cluster formation. The calculations indicate that if Sb is removed from a large bulk Sb reservoir and added to the cleaved GaAs(110) surface to form the GaAs(110)1×1:Sb structure, the energy of the system is lowered by 0.42 eV/(1×1 cell). This result is consistent with the experimental fact that a well-ordered Sb chain surface forms on GaAs(110). The atomic structure deter-

TABLE III. Displacements of the atoms from ideal positions for the As-As chain surface. Values are given in a.u. (1 a.u.=0.529 Å). Atom numbers refer to Fig. 1(c).

Atom	Δx	Δy	Δz
1 As	0.0	−0.20	0.09
2 As	0.0	0.11	0.10
3 As	0.0	−0.05	−0.03
4 Ga	0.0	0.03	0.00
5 As	0.0	−0.05	0.01
6 Ga	0.0	−0.01	−0.02
7 As	0.0	−0.02	0.01
8 Ga	0.0	−0.03	0.00

mined from the energy minimization calculations (indicated in Table IV) is quite similar to the one obtained from low-energy electron diffraction (LEED) calculations.[12]

The surface state electronic structure associated with the As chains is shown in Fig. 3. The two bands shown there originate from the As dangling bonds. At the X point of the surface Brillouin zone the band labeled S_{Ga} has most of its weight on the As atom which is bonded to the second-layer Ga atom and the S_{As} band has its weight on the As atom which is bonded to the second-layer As atom. The existence and proposed structure of the As chain surface can be tested by comparing angle-resolved photoemission data with these results. It is interesting to note that the dispersion calculated here is similar to experimental[15] and theoretical[13−14] results obtained for GaAs(110)1×1:Sb.

There have been several experimental studies in which As has been deposited on the UHV cleaved GaAs surface held at room temperature. Kubler *et al.*[23] reported an arsenic rich surface with a 1×1 LEED pattern. They also found that the surface relaxation was removed as the As coverage was increased. Bachrach *et al.*[24] reported that the LEED pattern obtained on such a surface was 1×1 with a diffuse background. This could indicate that the deposited As does not order with the substrate held at room temperature. Chiang and Spicer[25] reported that the As saturation coverage was about 1 monolayer, and that annealing the surface at 300 °C drives off the excess As.

Recently there has been a renewal of interest in MBE growth on GaAs(110),[26,27] but there have apparently been no recent experimental attempts at a detailed characterization of such a surface. In light of the present results, it would be interesting to examine the surface atomic structure present following growth under various conditions. The present results suggest that up to 1 monolayer of As could be incorporated into the surface layer in extreme As-rich growth conditions.

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