

Method of linear combination of structural motifs for surface and step energy calculations: Application to GaAs(001)

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First-principles calculations of the atomic structure and formation energies of semiconductor surfaces and surface steps are often complicated by the existence of complex structural patterns. We suggest here a simpler, algebraic -not differential! approach that is based on two observations distilled from previous first-principles calculations. *First*, a relatively large collection of equilibrium structures of surfaces and bulk point defects can be built from a limited number of recurring local “structural motifs,” including for GaAs tetrahedrally bonded Ga and As and miscoordinated atoms such as threefold-coordinated pyramidal As. *Second*, the structure is such that band-gap levels are emptied, resulting in charged miscoordinated atoms. These charges compensate each other. We thus express the total energy of a given surface as a sum of the energies of the motifs, and an electrostatic term representing the Madelung energy of point charges. The motif energies are derived by fitting them to a set of pseudopotential total-energy calculations for *flat* GaAs-001! surfaces and for point defects in *bulk* GaAs. This set of parameters is shown to suffice to reproduce the energies of *other* -001! surfaces, calculated using the same pseudopotential approach. Application of the “linear combination of structural motif” -LCSM! method to flat GaAs-001! surfaces reveals the following: -i! The observed $h\text{-}2\times 3!$ surface may be a disordered $c\text{-}8\times 6!$ surface. -ii! The observed $\alpha\text{-}2\times 6!$ surface is a metastable surface, only 0.03 eV/ $1\times 1!$ higher than the $a\text{-}2\times 4!$ surface having the same surface coverage. -iii! We confirm the recent suggestion by Hashizume *et al.* that the observed $g\text{-}2\times 4!$ phase of the $\alpha\text{-}2\times 4!$ surface is a mixture of the $b2\text{-}2\times 4!$ and $c\text{-}4\times 4!$ surfaces. In particular, we examined an 8×7 surface structure which has a lower energy than the earlier proposed $g\text{-}2\times 4!$ structure. Application of the LCSM method to prototype *steps* on the GaAs-001!- $\alpha\text{-}2\times 4!$ surface is illustrated, comparing the LCSM results directly to pseudopotential results.

I. INTRODUCTION: THE BASIC IDEA

With the advent of scanning tunneling microscopy -STM! and spectroscopy techniques, it is now possible to examine in detail the adequacy of the theoretically proposed atomic-scale structures of surfaces. While it is possible to directly calculate from first principles the total energies of various flat surface structures, and in some simple cases even the relative energies of the structurally more complex surface steps,¹ these first-principles calculations suggest a simpler, approximate approach to such time-consuming calculations. Two central observations are pertinent here: *First*, in a relatively large collection of proposed structures of III-V -001! surfaces²⁻⁴ -Figs. 1-3!, as well as in calculated structures of bulk point defects,²⁻⁵ the cation and anion atoms assume only a small number of local structures, to be named here “structural motifs.” For example, all the local-density approximation -LDA! derived GaAs-001! surface structures in Figs. 1-3 can be thought of as being built from different combinations of the seven structural motifs in Fig. 4: Denoting the local coordination number by superscripts, these motifs include tetrahedrally bonded $\text{Ga}^{\sim 4!}$

ergies are presented -Sec. III!; -ii! additional reconstruction models for GaAs-001! that are too computer intensive for current pseudopotential LDA calculations -Sec. IV!; -iii! prototypical steps on GaAs-001!- 2×4 ! surface -Sec. V!. We find that the LCSM method provides good quantitative estimates of the formation energies and, at the same time, distills essential features from complex LDA calculations.

II. THE METHOD OF LINEAR COMBINATION OF STRUCTURAL MOTIFS

Based on the discussion in the Introduction, we postulate that the total energy of a system \mathbf{S} -=bulk point defects, surfaces, or steps! can be written as

$$E_{\mathbf{S}, m_{\mathcal{R}}} = E_{\text{LCSM}}(\mathbf{S}) + E_{\text{Mad}}(\mathbf{S}) + E_{\mathcal{R}}(\mathbf{S}, m_{\mathcal{R}}), \quad (1)$$

where

$$E_{\text{LCSM}}(\mathbf{S}) = \sum_M V_M$$

nearest-neighbor shell to a given central site can vary, e.g.,
threefold Ga^{3+} can have either 3As, or $\text{Ga}^{4+}+2\text{As}$, or
 $\text{As}^{4+}+2\text{Ga}$ neighbors. While the one-site motif energy
 $e_M @ \text{Ga}^{3+}$

so in Eq. 5! $DN_{\text{Ga}}=1$ and $DN_e=-3$. We assume that the system \mathcal{S} is also in equilibrium with *bulk* GaAs,¹⁰ leading to the constraint

$$m_{\text{Ga}} + m_{\text{As}} = m_{\text{GaAs}} = -DH, \quad (8)$$

where $DH = \mu_{\text{Ga}}^{\text{solid}} + \mu_{\text{As}}^{\text{solid}} - \mu_{\text{GaAs}}^{\text{bulk}} = 0.92$ eV is the heat of formation of bulk GaAs calculated using LDA.³ Equation 8! then allows us to eliminate a single variable, i.e., m_{As} , and to express the reservoir energy as $DE_{\mathcal{R}}(\mathcal{S}, m_{\text{Ga}}, m_e)$. This gives

DE

here reproduce well the sequence of stable surface energies over the entire physical range of m_{Ga} . We see that they do: Going from As rich to Ga rich, the sequence $c-4 \times 4!!$ $b2-2 \times 4!!$ $a-2 \times 4!!$ $b2-4 \times 2!$ is reproduced. We further see that the LCSM method also reproduces reasonably well the order of energies and the “crossing point” chemical potentials of the LDA calculation.

Experimentally, three distinct STM surface phases -i.e., a ,

tifs \tilde{e}_M - m !. The transformation is not unique; however, this does not matter since $S_M V_M e_M$

E@b2-2×4!#

stable surface. Unfortunately, following the octet rule, we see that this surface is not charge compensated -note the charge assignment at the bottom of Fig. 6!, so this structure cannot be stable. Here, we modify the model of Gomyo *et al.* to achieve surface charge compensation. This is done by removing some of the surface As-As dimers. The resulting $c\text{-}8\times 6!$ structure, containing 24 atoms per unit cell @see Fig. 6-b!#, differs from the original model of Gomyo *et al.*, by having a missing As-As dimer for every eight dimers in a row. We suggest that the experimentally observed 2×3 surface could be a $c\text{-}8\times 6!$ surface, which appears in the RHEED as 2×3 , due to disorder of the missing dimers. The $c\text{-}8\times 6!$ surface structure is stabilized -see Table III! by a high density of As-As adatom dimers on an As-terminated surface. Our LCSM calculation indicates that the ensuing $c\text{-}8\times 6!$ structure has only slightly higher formation energies than the stable $c\text{-}4\times 4!$ surface in the chemical-potential range surrounding the $c\text{-}4\times 4!$ $b2\text{-}2\times 4!$

1×1 cell 7×1 ; only a small percentage of the surface has $5 \times$, while smaller open areas are absent.

To see whether a structure resembling the mixed phase can have a lower energy than the $g\text{-}2 \times 4$ surface structure of Fig. 1, we constructed, starting from the two models suggested in Ref. 17, an 8×7 ≈ 56 atoms per cell surface structure with an open area of $7 \times$ (see Fig. 9-a). The 8×7 cell contains three $c\text{-}4 \times 4$ surface cells and four $b2\text{-}2 \times 4$ surface cells. While each $c\text{-}4 \times 4$ cell has three As adatom dimers and one missing dimer as shown in Fig. 2, the $b2\text{-}2 \times 4$ cells are deformed to fill the space left by the $c\text{-}4 \times 4$ cells. This 8×7 structure is not the only structure that can be made from the $b2\text{-}2 \times 4$ and $c\text{-}4 \times 4$ surfaces. We can also make 8×9 , 8×11 , and similar structures. The smallest charge compensated supercell is the 8×5 cell, where the As-As dimers of the $b2\text{-}2 \times 4$ cells in the open area in Fig. 9-a become surface nearest neighbors. The 8×5 surface has a higher surface energy, due to Coulomb repulsion among these dimers. The motif frequencies for the 8×7 surface are shown in Table II, line 19 and in Table III, line 15. These motifs are, in fact, the average of the motif frequencies of three $c\text{-}4 \times 4$ and four $b2\text{-}2 \times 4$ surface cells. Thus, the energy difference between the 8×7 surface and the average of $c\text{-}4 \times 4$ and $b2\text{-}2 \times 4$ surfaces lies in the Madelung energy difference, which is higher for the 8×7 surface by about $0.026 \text{ eV}/1 \times 1$. This is expected, since we must sacrifice the Madelung energy in order for a complete space filling in the 8×7 surface. The energy of the 8×7 structure vs m_{Ga} is shown in Fig. 7: It is lower than that of the $g\text{-}2 \times 4$ structure. In particular, at the chemical potential corresponding to the $c\text{-}4 \times 4$ $b2\text{-}2 \times 4$ transition, the calculated energy of the 8×7 structure is about $0.06 \text{ eV}/1 \times 1$ lower. This confirms the work of Hashizume *et al.* Since the real 8×7 structure is disordered, its energy will be further lowered at finite temperatures, due to an entropy term. This may explain its apparent stability at growth temperatures.

The 8×7 surface has the As-As dimers on the top surface, while the As-As adatom dimers are all in the open area (see Fig. 9-a). An alternative of the mixed surface structure can have, instead, the As-As adatom dimers on the top surface,

of the structural motifs of Fig. 4 -extension to many more surface steps will be discussed elsewhere²⁴. We further identify only those step structures that satisfy the charge-compensation octet rule. These are reasonable assumptions, since the nominally flat GaAs-001 surfaces that were used to extract the LCSM parameters involve local troughs, whose facets -see Figs. 1-3 are miniforms of the -001 surface monolayer steps and the bilayer steps discussed here.

The GaAs-001 surface is a polar surface with an atomic stacking sequence... Ga/As/Ga/As. The step height h in unit of monolayer spacing $=a/4$, where a is the bulk lattice constant can thus only be a multiple of 2, i.e., $h=2t$, where $t=1,2,\dots$. This ensures that the upper and lower terraces are identical, made, in this case, of the As-terminated 2×4 surfaces. Furthermore, the -001 surface has two orthogonal, inequivalent surface orientations $\sim 110^\circ$ and $\sim 1\bar{1}0^\circ$. This leads to two types of basic steps: the *A* step, with edges parallel to surface As-As dimers along the $\sim 110^\circ$ direction, and the *B* step, with edges perpendicular to the dimers.

Steps created as a pure geometric construct, for example, the primitive *AI*, *AII* steps on a $b2\text{-}2\times 4$

predicted LCSM formation energy of the *BII*-1 step from the $b\text{-}2\times 4!$ surface -per unit step! is

$$E_{@BII} - 1$$

formation energies of the *AI*-1 step for $m_{\text{Ga}} < -0.21$ eV. No LDA calculation was performed here.

B. The *BII*-1 step

This is a *B* step on a $b\text{-}2\times 4!$, not the $b2\text{-}2\times 4!$, surface (Fig. 11-b)!. This step is stabilized with respect to *BII* by forming one As^{-3!} vacancy for every four *BII* step units. The

The LDA total-energy calculation showed that near the band gap, the electronic structure of the DBA $\sqrt{3}\times\sqrt{3}$ step is quite similar to that of the $\sqrt{2}\times\sqrt{2}$ surface: both are semi-conducting. The LDA step formation energy for the DBA $\sqrt{3}\times\sqrt{3}$ step -per unit step- is

E

two Ga-As bonds. The bulk Ga^{-4!} atom contributes, however, only $\frac{3}{4}$ electrons to the Ga^{-3!}-Ga^{-4!} bond. The Ga^{-3!} atom, thus, needs to contribute $\frac{5}{4}$ electrons to completely fill the Ga^{-3!}-Ga^{-4!}

$$\begin{aligned} E_{\mathbf{S}} - E_{\mathbf{S}_0} &= \epsilon E_{\mathbf{S} + \mathbf{S}_{b1}} - \epsilon E_{\mathbf{S}_0 + \mathbf{S}_{b2}} \\ & - \epsilon E_{\mathbf{S}_{b1}} + \epsilon E_{\mathbf{S}_{b2}}, \end{aligned} \quad \text{-B5}$$

where \mathbf{S}_{b1} and \mathbf{S}_{b2} are two different back surface configurations. Different from the front surfaces, the back surfaces

are only intermediate steps towards the final results. They can, thus, be made as simple as possible, i.e., the 1×1 step and 1×1 surface. These allow us to use standard rectangular-shaped cells, with much larger step separations to evaluate accurately the second term in Eq. -B5.

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