

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

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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 $c\text{-}4\times 4! \rightarrow b2\text{-}2\times 4! \rightarrow a\text{-}2\times 4! \rightarrow b2\text{-}4\times 2!$ 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 $c\text{-}4\times 4!\rightarrow b2\text{-}2\times 4!$

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 $c\text{-}4 \times 4 \rightarrow b2\text{-}2 \times 4$ 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

$$\begin{aligned}
 E_{@BII-1} - E_{@b\text{-}2\times 4!} &= -\frac{3}{8}\tilde{e}\text{-}M1! + \frac{7}{16}\tilde{e}\text{-}M2! \\
 &\quad - \frac{3}{16}\tilde{e}\text{-}M3 + d'_{As\text{-}As}! + \frac{1}{16}\tilde{e}\text{-}M5! \\
 &\quad + DE_{Mad} = 0.14 - \frac{1}{8}m_{Ga}\text{-eV}!. \tag{-17!}
 \end{aligned}$$

We see that the formation of the *BII*-1 step results in a $\frac{3}{8}$ decrease of the *M1* motif $@\tilde{e}(M1)=0.0\text{ eV}\#$, but with a large, $\frac{7}{16}$ increase of the *M2* motif $@\tilde{e}(M2)=1.37\text{ eV}\#$. In comparison, the $-\frac{3}{16}$ change in the $\text{-}M3 + d'_{As\text{-}As}!$ motif and the $\frac{1}{16}$ change in the *M5* motif are relatively small. The high density of the *M2* motif alone increases the formation energy by 0.6 eV, thus destabilizing the *BII*-1 step with respect to the $b\text{-}2\times 4!$ surface. The large, positive energy of motifs of $0.52 - \frac{1}{8}m_{Ga}\text{ eV}$ here is only partially offset by the decrease in the Madelung energy of 0.38 eV -see Table II, line 22!.

Our LDA calculation showed that the *BII*-1 step is semi-conducting with a band gap of ; 1 eV. The highest occupied states are the dangling-bond states of the step edge $As^{-3!}$ atoms and the lowest unoccupied states are the dangling-bond states of the $Ga^{-3!}$ atoms surrounding the $As^{-3!}$ vacancy. We obtain an LDA step formation energy -per unit step! of

$$E_{LDA@BII-1} - E_{LDA@b\text{-}2\times 4!} = 0.16 - \frac{1}{8}m_{Ga}\text{-eV}!, \tag{-18!}$$

close to the LCSM prediction @Eq. -17!#.

C. The double A(S50) step on $b2(234)$

The primitive *AI* step $-Q_{AI}=+0.25!$ and *AII* step $-Q_{AII}=-0.25!$ of Fig. 10 can be combined into charge-compensated surface structures, since Q ,776

formation energies of the *AI*-1 step for $m_{Ga} < -0.21\text{ eV}$. 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 bond. The dangling bond of the Ga⁻³ atom, thus, contains only $\frac{1}{4}$ electron. The Ga⁻³ atom is, therefore, a $\frac{1}{4}$, not a $\frac{3}{4}$, electron donor. Similarly, an As⁻³ atom with two Ga and one As⁻⁴ nearest neighbors @viz., the rebonded As⁻³ atoms in the $a\text{-}4\times 2$ surface in Fig. 2# is a $\frac{1}{4}$, not a $\frac{3}{4}$, electron acceptor. This gives lines 7 and 8 of Table I.

-v! *Rebonded Ga⁽³⁾*

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

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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