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A density-functional based tight-binding approach to GaAs surface reconstructions

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Abstract. A density-functional-based non-orthogonal tight-binding (DF-TB) scheme is used to investigate models for the reconstructions of GaAs(110), (100) and (111) surfaces. The relative stabilities of the competing reconstructions are then determined as a function of the chemical potential, thus simulating a wide range of possible MBE growth conditions. We find a good agreement with recent experiments and *ab initio* calculations, and establish the validity of the scheme for large-scale applications.

1. Introduction

The characterization and understanding of surface reconstructions and their related electronic properties plays an important role in modern surface science. Unfortunately, most of the available experimental techniques, such as those of low-energy electron diffraction (LEED), surface-extended x-ray-absorption fine structure (SEXAFS) and high-energy-ion scattering, can only give indirect information concerning the atomic geometry. Moreover, the methods that do give direct surface information, such as scanning tunnelling microscopy (STM), often produce surface images of insufficient quality for definitive conclusions regarding surface structure to be reached. Additionally, STM can be ambiguous without a careful theoretical simulation.

There is therefore a clear need for predictive theoretical surface investigations. Of the theoretical tools available, the use of *ab initio* density-functional methods [1–4] gives the most reliable results. As these are computationally intensive and therefore time consuming, many interesting phenomena, such as the reconstructions of large surfaces including steps and extended defects, remain tantalizingly out of reach. With this in mind, a plethora of semi-empirical methods have evolved. Amongst these, the tight-binding methods [5–7] are a reliable alternative for determining the total energy and the geometrical structure of large systems. In many cases, the results obtained using these two-centre-oriented schemes deviate only slightly from those obtained using more sophisticated methods. However, the usual procedure of fitting the matrix elements necessary to calculate the band-structure energy to an input data set is rather complicated and somewhat arbitrary.

Our method, based on ideas of Seifert and Eschrig [8, 9], avoids the difficulties arising from an empirical parametrization. We calculate instead the Hamilton and overlap matrix elements from a local orbital basis within an LCAO scheme; these are derived by using density-functional theory and the local density approximation (DFT-LDA). The method can therefore be regarded as a density-functional-based tight-binding (DF-TB) scheme [10] and yields the same energy expression as common TB schemes. The crucial difference is that

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there is now a well defined procedure for the determination of the desired matrix elements. The method has been successfully applied to C, Si and BN [10–12] systems, where it has proved to be highly transferable across a broad spectrum of solid-state systems, ranging from small clusters to extended systems, such as surfaces containing several hundreds of atoms, giving results of comparable accuracy to that achieved by more sophisticated LDA calculations. In a previous publication [13], we have shown the DF-TB method to give correspondingly good results for bulk Ga, Al, As, GaAs and AlAs, as well as a wide range of possible clusters. This work describes the application of the method for investigating a variety of models for the reconstructions of the GaAs(110), (100) and (111) surfaces, and thus the establishing of the validity of the method for future use in large-scale growth simulations.

The paper is organized as follows. Section 2 briefly outlines the theoretical features of our method and describes the simulation regime. In section 3 we then examine various surface reconstructions and discuss the relative stabilities depending on the chemical potentials. Finally, in section 4, we summarize and discuss our results.

2. Methodology

We study the GaAs surfaces using a DF-TB molecular-dynamics (MD) method. The interatomic potentials and tight-binding Hamiltonians used have recently been shown to provide results for a wide class of different-scale GaAs systems [13], with an accuracy approaching that of fully self-consistent-field (scf) methods.

In contrast to the case for empirical TB schemes, the Hamiltonian and overlap matrix elements are obtained in a parameter-free way via the construction of pseudo-atomic orbitals and potentials. The corresponding contracted valence electron orbitals are used as a minimal basis set to represent the wavefunctions of the extended systems. Neglecting three-centre and crystal-field integrals, we calculate all necessary matrix elements using the LDA. After solving the general eigenvalue problem for the determination of the single-particle energies and eigenstates of the system in a non-self-consistent treatment, the total energy is written as a sum of occupied Kohn–Sham energies, the so-called 'band-structure' energy, plus a repulsive two-particle interaction. This repulsive energy is obtained as a universal short-range pair potential from the difference between scf-LDA cohesive energy curves versus distance and the corresponding band-structure energies of properly chosen reference systems (diatomics). Bulk properties were included by considering the experimental equilibrium crystal structures. For further details, we refer the reader to a recently published paper [10].

The surfaces were modelled by ten-monolayer-thick slabs with periodic boundary conditions in two dimensions. The first six monolayers were allowed to relax, while the remaining atoms were fixed to preserve the bulk lattice spacing. In order to prevent artificial charge transfer between the bottom of the slab and the surface, we saturate the dangling bonds on the bottom with pseudo-hydrogen. By demanding that the charge distribution in our slab model should not depend on whether we terminate our slab with an As or a Ga monolayer, we derive an equation for the charge contribution of the pseudo-hydrogen atoms, yielding 1.25 and 0.75 electrons per H atom, for the replacement of an As and a Ga atom respectively. These charges correspond to the charge per bond contributed from a tetrahedrally bound As or a Ga atom. As numerical tests have shown, the change in the surface energy is smaller than 0.5 meV $Å^{-2}$ if one monolayer is added to the slab, thus showing that our model is converged. We evaluate our surface energies for 16 k-points in the Brillouin zone. Again numerical tests show this k-point summation to be

converged.

The relative stabilities of two structures having different numbers of Ga and As atoms depends on the reservoir with which the atoms are exchanged in the structural transition. Questions of thermodynamic stability are therefore posed within the context of the atomic chemical potentials [14]. It can be shown [14] that the surface energy can be expressed as a function of the atomic chemical potential of one species, which we take to be μ_{Ga}. The allowed range of this chemical potential is then [14] $\mu_{\mathrm{Ga(bulk)}} - \Delta H_f \leqslant \mu_{\mathrm{Ga}} \leqslant \mu_{\mathrm{Ga(bulk)}}$, ranging from the Ga-rich ($\mu_{\mathrm{Ga}} = \mu_{\mathrm{Ga(bulk)}}$) to the As-rich environment. ΔH_f is the heat of formation for GaAs, which has been determined from enthalpy measurements to be 0.74 eV [15].

As in the work of Moll *et al* [1], we present the absolute surface energies for the (110) and (100) surface reconstructions in meV Å^{-2}. It is straightforward to generate these values by subtracting the energy of the bulk and the hydrogen surface from the total energy of the slab. The former can easily be obtained by computing the energy for a slab with both the top and bottom surfaces terminated with hydrogen.

Due to the fact that the (111) surface cannot be modelled with symmetric slabs (e.g. a slab with a (111) surface has a ($\bar{1}\bar{1}\bar{1}$) surface on the bottom), absolute surface energies cannot be obtained in the same simple manner as was employed for the other surface types. One must use instead an energy density formalism which, for scf-LDA schemes, has been described in detail by Chetty and Martin [16]. In the DF-TB method we define single atomic energies by performing a Mulliken charge analysis of the structure and weighting the contributing eigenstates with the corresponding eigenenergies. We apply this formalism to evaluate the absolute surface energies for the (111) surface. We divide the slab model by a boundary which passes through one double layer in such a way that each atom belonging to the boundary can be assigned to be 50% on the top and 50% on the bottom of the slab. This way of dividing the slab is achieved via pieces of (110) and (100) planes passing through one arbitrary double layer. Using this partition we can assign a total energy to the top of our slab, from which we evaluate the absolute surface energy by subtracting the corresponding bulk energy.

3. Reconstructions and relative stabilities of GaAs(110), (100) and (111) surfaces

3.1. The (110) surface

The (110) surface is the main cleavage surface of GaAs and has therefore been extensively studied [2, 17–19]. It is now well established that the relaxed (110) surface has (1×1) symmetry. The relaxation consists of a nearly bond-length-conserving rotation of the surface chains by a tilt angle of $\approx 30°$, where the As atoms in the surface layer rotate outwards and the Ga atoms move towards the bulk.

In our calculation, the tilt angle is found to be 28.5°. Since all As dangling bonds are filled, while the Ga dangling bonds are emptied, this surface fulfils the requirements of the electron-counting model and is therefore semiconducting.

We have also considered the Ga- and the As-terminated surfaces, where we have substituted for the As (Ga) atoms of the surface layer with Ga (As) atoms. On these non-stoichiometric surfaces, the atoms move very little from their lattice positions. For As termination, the surface As atoms have lone pairs. Since there are no Ga dangling bonds and the As lone-pair levels overlap with the valence band of bulk GaAs, the surface again becomes semiconducting. At the Ga-terminated surface, all dangling bonds are empty. However, the energy levels of the Ga–Ga bonds on the surface cross

the Fermi level, rendering the surface metallic. In figure 1, we show the absolute surface energies as a function of the chemical potential of Ga within the permitted range $\mu_{\mathrm{Ga(bulk)}} - \Delta_{H_f} \leqslant \mu_{\mathrm{Ga}} \leqslant \mu_{\mathrm{Ga(bulk)}}$ [14]. We find that the stoichiometric cleavage surface has a surface energy of 54 meV Å^{-2}, which is in agreement with the experimental surface energy of 54 ± 9 meV Å^{-2} determined from fracture experiments by Messmer and Bilello [20]. Theoretical values from *ab initio* calculations range from 52 meV Å^{-2} [1] to 57 meV Å^{-2} [17].

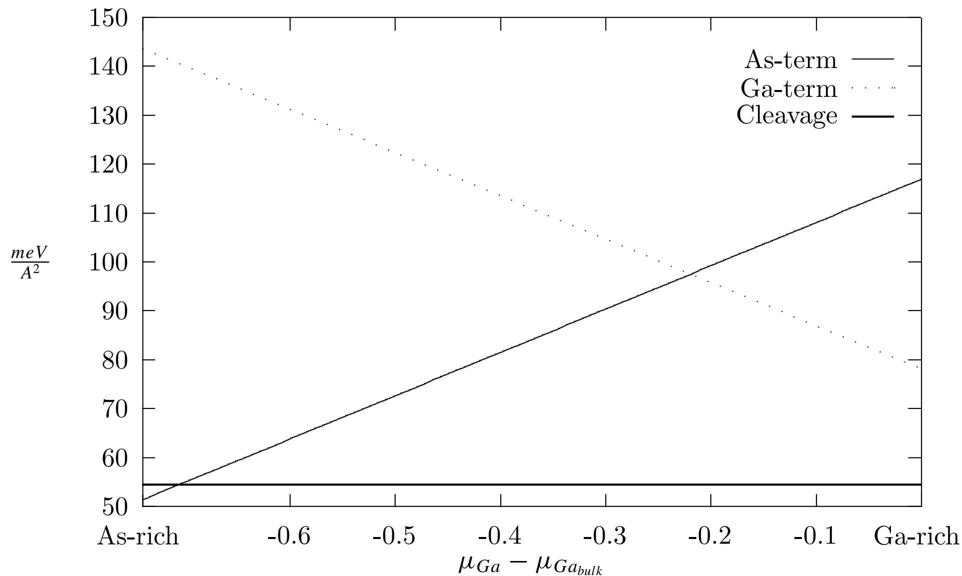

Figure 1. Surface energies in meV Å^{-2} of the GaAs(110) structures plotted versus $\mu_{\mathrm{Ga}} - \mu_{\mathrm{Ga(bulk)}}$.

In figure 1 we see that the As-terminated surface becomes stable in the extreme As-rich environment. This agrees with experiments of Kübler *et al* [18], who observed by means of LEED that for increasing As coverage the surface relaxation was progressively removed. Conversely, the Ga-terminated surface is not thermodynamically stable within the permitted range of the chemical potential. All of the results agree well with the scf-LDA predictions of Moll *et al* [1] and Northrup [2].

3.2. The (100) surface

The GaAs(100) surface manifests a sequence of stable reconstructions depending on the surface stoichiometry, ranging from the As-rich c(4×4) structure to the Ga-rich (4×2) reconstruction. These surfaces have been extensively investigated [1, 4, 21–23]. While the existence of missing dimers has been confirmed by recent STM images [23], the resolution of these images is often still not sufficient for determining the atomic arrangement in detail. Therefore, experimental knowledge of the different surface structures and their relative stabilities is still limited, making theoretical calculations necessary.

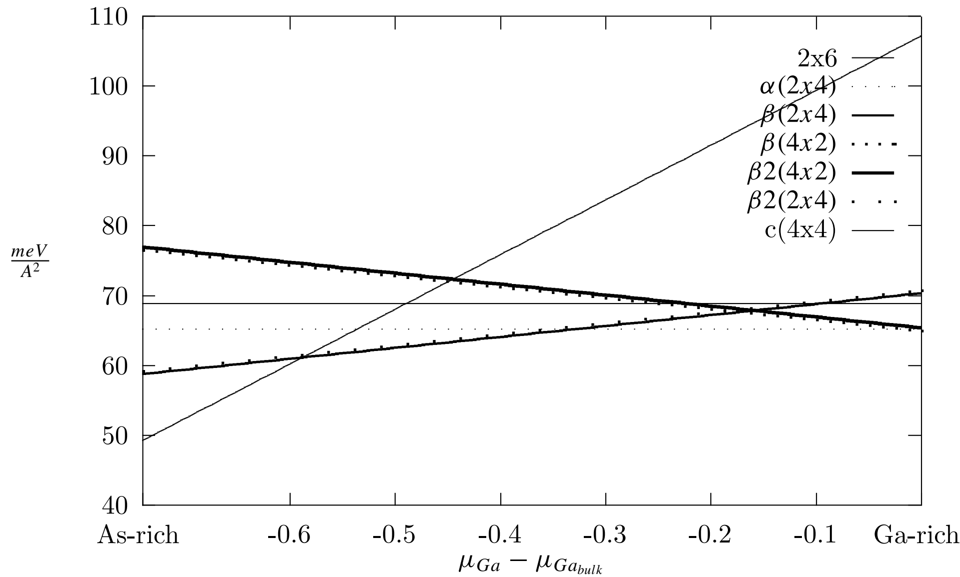

Figure 2. Surface energies in meV Å^{-2} of the GaAs(100) structures plotted versus $\mu_{\mathrm{Ga}} - \mu_{\mathrm{Ga(bulk)}}$.

Ohno [24], Northrup and Froyen [3] and Moll *et al* [1] carried out *ab initio* calculations for a variety of models and were able to establish that many of them are not equilibrium structures. We have performed calculations for all of the structures reported by Northrup and Froyen [4, 3]. In figure 2 we show the configurations which we find to be energetically most favourable.

A (4 × 2) periodicity is observed experimentally in a Ga-rich environment. However, even recent papers disagree on the predicted structure: while STM images obtained by Xue *et al* [25] indicate a two-dimer configuration, LEED intensity analysis by Cerdá *et al* [26] favours a three-dimer model. Northrup and Froyen [3] and Moll *et al* [1] find the two-dimer model to be slightly lower in energy. We determine the two surfaces, the $\beta(4 \times 2)$ (three Ga dimers per unit cell; see figure 3) and the $\beta\,2(4 \times 2)$ (two Ga dimers per unit cell; see figure 3), to be energetically almost degenerate.

The stoichiometric $\alpha(2 \times 4)$ surface consists of a 50% As coverage, arranged in two neighbouring dimers per cell (figure 3). In agreement with the already mentioned *ab initio* calculations, we determine this reconstruction to be the stable phase for the intermediate range of the chemical potential. The surface energy of 65 meV Å^{-2} is exactly the same as that reported by Moll *et al*.

Surfaces prepared under rather As-rich growth conditions exhibit (2 × 4) periodicity. In analogy to the Ga-rich (4 × 2) reconstruction, two structures have been proposed [24]: the $\beta(2 \times 4)$ model consisting of three As dimers per unit cell—see figure 3—and its counterpart, the $\beta\,2(2 \times 4)$ model (figure 4), having the same stoichiometry but only two As surface dimers. Again the calculated energies are very close, thus allowing the two structures to occur in thermodynamic equilibrium. *Ab initio* calculations by Ohno [24] and Northrup and Froyen [4] disagreed on the energetic ordering of these configurations. The two-dimer (2 × 4) reconstruction was subsequently observed using high-resolution STM experiments [27], thus confirming Northrup's result.

On cooling the sample under As-rich conditions, which could be provided by supplying

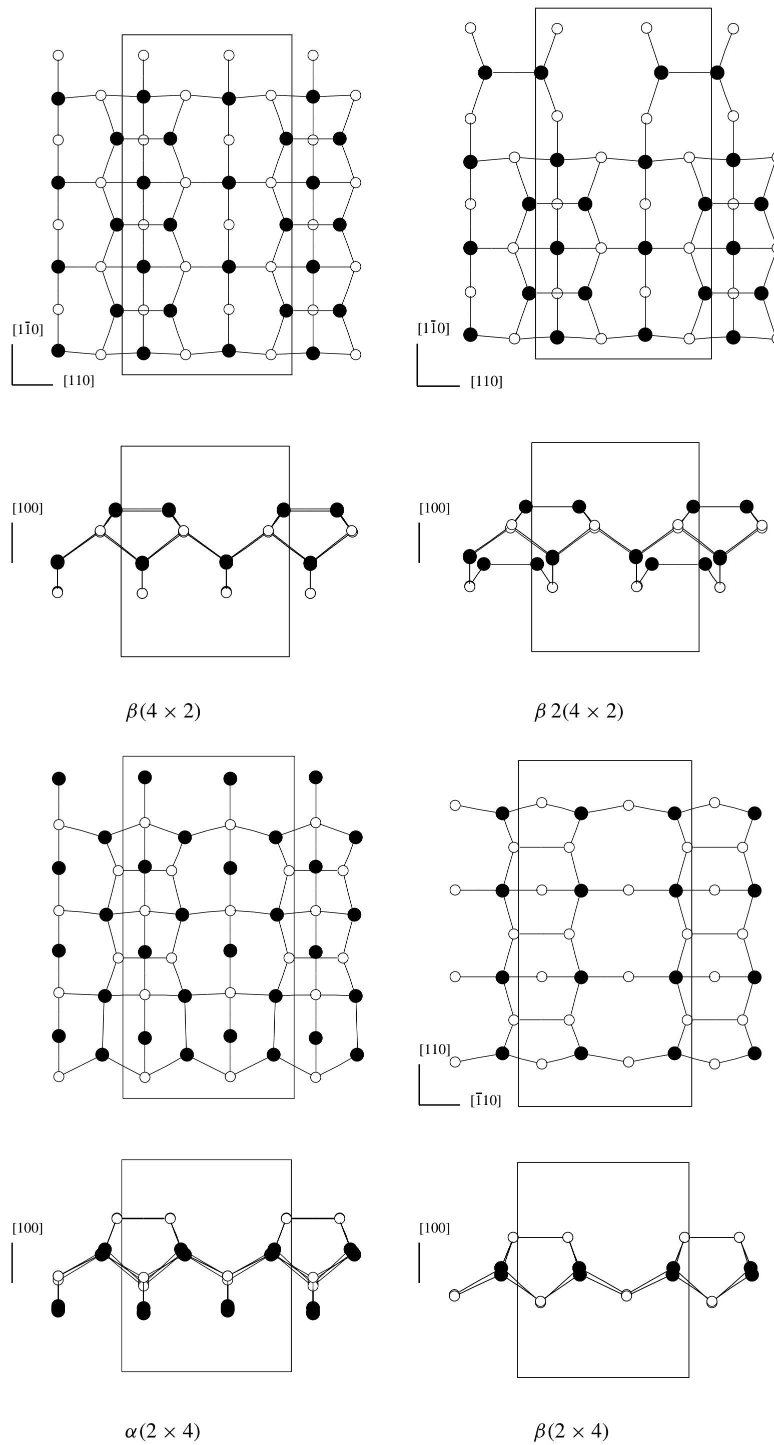

Figure 3. Top and side views of the relaxed (100) $\beta(4\times2)$, $\beta\,2(4\times2)$, $\alpha(2\times4)$, and $\beta(2\times4)$ structures. Filled circles represent Ga atoms, and empty represent circles As atoms.

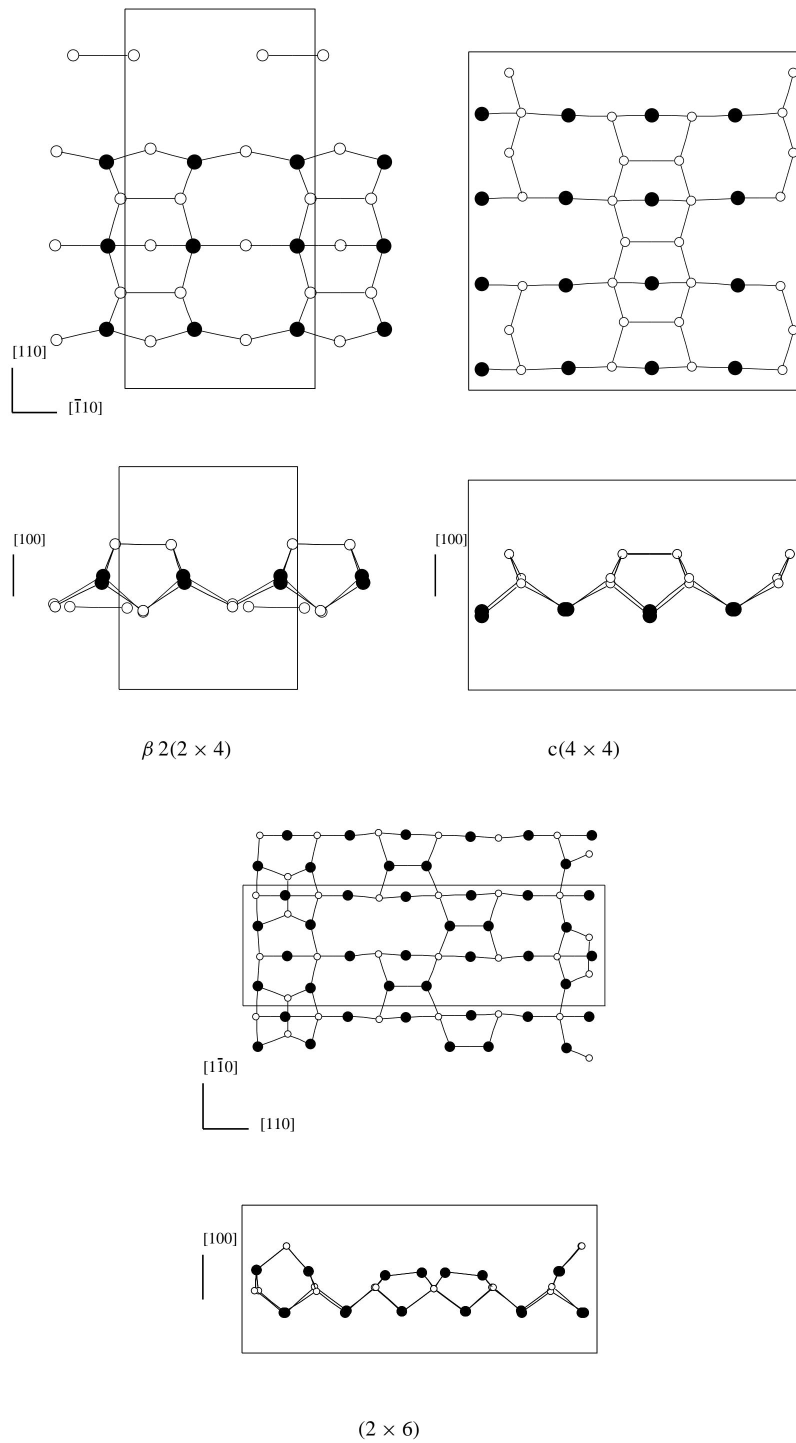

Figure 4. Top and side views of the relaxed (100) $\beta\,2(4 \times 2)$, c(4×4) and (2×6) structures. Filled circles represent Ga atoms, and empty circles represent As atoms.

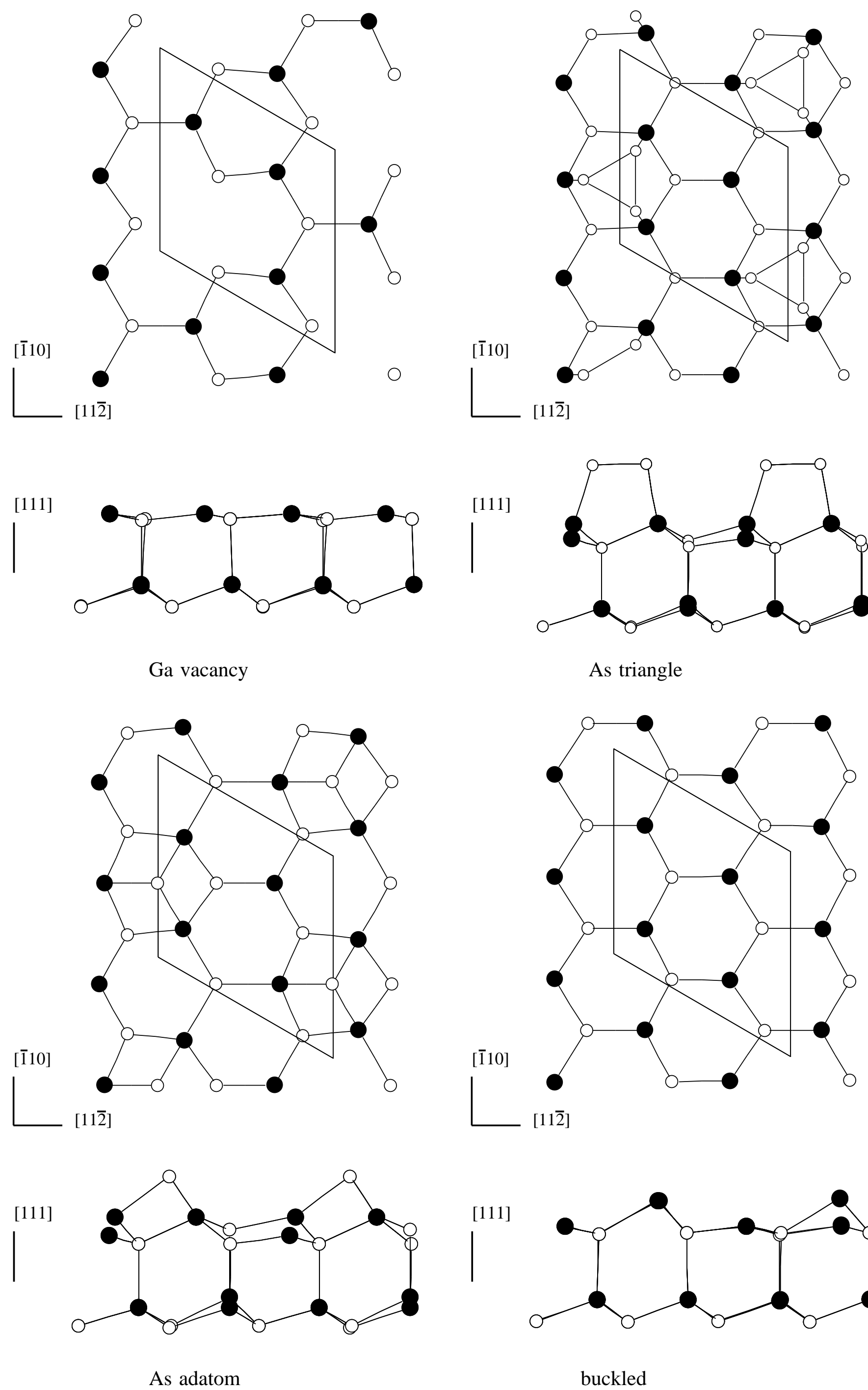

Figure 5. Top and side views of the relaxed (111) As adatom, As triangle, Ga vacancy and buckled structures. Filled circles represent Ga atoms, and empty circles represent As atoms.

either an As_4 or an As_2 flux, Biegelsen *et al* [23] observed a c(4×4) periodicity. Evaluating their STM images, they suggested a three-dimer phase, shown in figure 4. We agree with the *ab initio* result of Northrup and Froyen [4] and Moll *et al* [1] that this reconstruction becomes energetically favourable in the As-rich limit.

Finally, we have examined a structure with (2×6) periodicity—see figure 4—which has been proposed by Biegelsen *et al* [23] to account for their STM images. As far as we are aware, no *ab initio* calculations exist for this larger periodicity. We find that the energy of this surface lies slightly ($\approx$3 meV) above that of the $\alpha(2 \times 4)$ structure, which means that it could exist as a metastable phase.

For all of the structures of the (100) surface, the main relaxation mechanism consists of the formation of surface dimers which in all cases significantly reduced the surface energy. Comparing the As–As and Ga–Ga dimer lengths for the α- and β-structures with the LDA *ab initio* results [4, 1], the dimer lengths in the present calculations are slightly increased by $\approx$0.05 Å. This can be attributed to the fact that the GaAs lattice constant is usually slightly underestimated in LDA *ab initio* calculations, whereas the method employed here reproduces the bulk lattice constants with an error of less than 1%. For the c(4×4) reconstruction, we obtain As–As dimer lengths of 2.60 Å, while x-ray scattering experiments of Sauvage-Simkin *et al* [28] found the central and outer dimers to have lengths of 2.63 ± 0.06 Å and 2.59 ± 0.06 Å respectively.

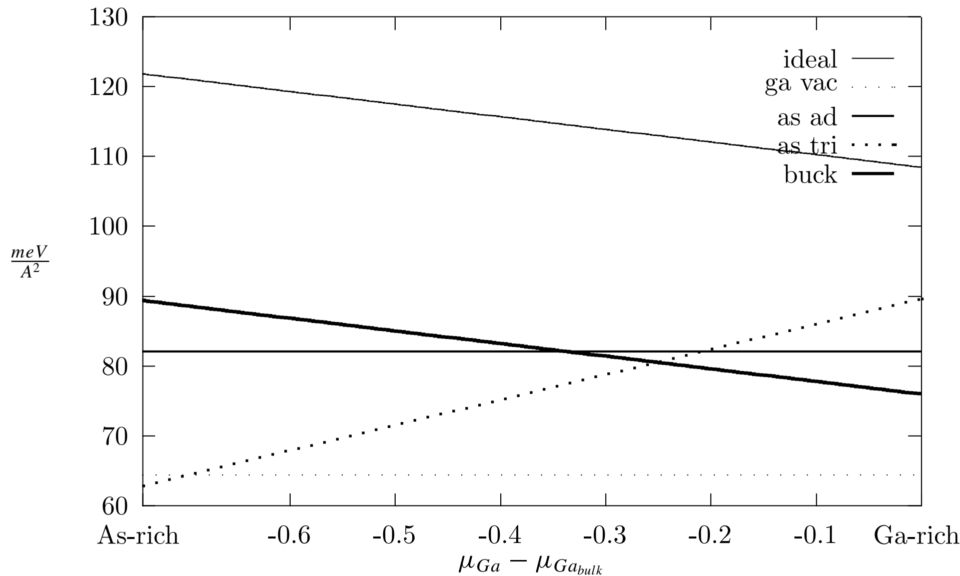

Figure 6. Surface energies in meV Å^{-2} of the GaAs(111) structures plotted versus $\mu_{\mathrm{Ga}} - \mu_{\mathrm{Ga(bulk)}}$.

3.3. The (111) surface

The ideal bulk truncated GaAs(111) surface is Ga terminated. Diffraction experiments, such as LEED [29] and synchrotron x-ray diffraction ones [30], have provided detailed studies of the surface reconstruction patterns of the (111) surface. A (2×2) reconstruction is observed, which is attributed to a Ga vacancy. Kaxiras *et al* [31] investigated various possible atomic arrangements for the experimentally observed (2×2) periodicity and found that under

Ga-rich growth conditions a Ga vacancy is energetically the most favourable model, thus confirming the LEED analysis of Tong *et al* [29]. Under As-rich growth conditions they determined a structure with As trimers—see figure 5—to be thermodynamically stable. Thornton *et al* [32] obtained STM images and concluded that, in addition to the Ga vacancy structure, there should indeed be an As trimer structure.

In our calculation, the energetic ordering—see figure 6—is very similar to that of the scf-LDA calculations of Moll *et al* [1]: over a large range of μ_{Ga}, the Ga vacancy structure is energetically favourable, whereas in the As-rich environment, the As trimer configuration has the lowest surface energy. Since the scf-LDA results for the absolute values for the (111) surface energies of Moll *et al* [1] are lower by 38 meV Å^{-2} than those given by Chetty and Martin [16], we are not surprised to find our energies to be 11 meV Å^{-2} higher than those of Moll *et al* [1] but 27 meV Å^{-2} lower than the results of Chetty and Martin [16]. The reason that the three groups find differing values for the absolute energy values, while finding the same energetic ordering, is obviously due to the partition of the (111) slab necessary to deduce absolute values for surface energies. In the diagram we also show the energies of some other surface models, the ideal surface, the As adatom and the buckled geometry—see figure 5—which, in agreement with Kaxiras *et al* [31], are found not to be equilibrium structures.

Comparing the geometry determined for the Ga vacancy surface with data derived from LEED analysis by Tong *et al* [29], we obtain reasonable agreement: the sp^2-bonded Ga atom has an average bond angle of 119.0° which compares very well with the value of 119.8° derived from the LEED analysis. For the p^3-bonded As atom we derive an average bond angle of 98.3°, whereas Tong *et al* [29] reported 92.9°. As we do not know of any experimental data concerning the geometry of the As trimer, we compare our data with the theoretical results of Moll *et al* [1] and Kaxiras *et al* [33]. In very good agreement with their data, we find that the As adatoms form an equilateral triangle and develop subsurface bonds at 105.8° (106.2°) [1] to the underlying Ga atom. This yields an average bond angle of 90.4° (90.8°) [1], (91.7°) [33]. The As–As bond length is 2.48 Å (2.44 Å [1]) and the threefold-coordinated Ga atom relaxes inward, developing a bond angle of 117.3° (118.4°) [1], (114.7°) [33].

4. Conclusion

We have presented a detailed investigation of the atomic structure and the relative energetic stabilities of GaAs(110), (100) and (111) surfaces. A large variety of possible surface reconstruction models were examined and compared with experiments and previous theoretical predictions. The results are in good agreement with scf-LDA calculations, thus demonstrating the efficiency of the DF-TB method and its suitability for the investigation of extended surface reconstructions, such as the $(\bar{1}\bar{1}\bar{1})$ $(\sqrt{19} \times \sqrt{19})$ surface obtained under Ga-rich growth conditions, as well as for the examination of interfaces and extended defects.

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