

Surface reconstructions for InAs(001) studied with density-functional theory and STM

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The stability of different surface reconstructions on InAs(001) is investigated theoretically and experimentally. Density-functional theory calculations predict four different surface reconstructions to be stable at different chemical potentials. The two dominant reconstructions are the $\beta 2$ (2×4) for high As, and the $\alpha 2$ (2×4) for low As overpressure. This trend is confirmed by scanning tunneling microscopy of carefully annealed InAs(001) surfaces. A similar behavior is predicted for GaAs(001).

Many high speed and optoelectronic devices are based on III-V compound semiconductor systems. The morphology of the interface between different heterolayers can significantly affect the performance of a quantum layer semiconductor device. It is therefore desirable to control the formation of these interfaces to a high degree of accuracy. In particular, experimental conditions such as deposition flux and temperature determine the reconstruction on the surface during epitaxial growth, which in turn influences the adatom dynamics on the surface.

In this article we focus on InAs(001) and GaAs(001). It has been observed experimentally that these systems exhibit an As terminated (2×4) reconstruction over a wide range of typical (As rich) growth conditions, and a (4×2) structure in the In/Ga rich regime. However, some of their dynamical behaviors are quite different. For example, Yamaguchi and Horikoshi¹ showed that the transition between the As rich (2×4) and the In/Ga rich (4×2) structures is a discontinuous, first-order phase transition with hysteresis for InAs(001), while it is continuous for GaAs(001). They attributed this to the fact that the (2×4) surface reconstructions for InAs(001) and GaAs(001) appear to be different. The results of Bell *et al.*² also suggest that the growth mechanisms of InAs(001) are different than those of GaAs(001).

It is therefore reasonable to assume that the different surface reconstructions play a crucial role in the different growth behavior for the two systems. Thus, in order to understand and ultimately control the morphology of a growing film, one needs to understand which surface reconstructions are stable under typical growth conditions. Scanning tunneling microscopy (STM) images suggest that GaAs(001) has a $\beta 2$ (2×4) reconstruction for a wide range of growth conditions. This reconstruction is characterized by two top and one trench dimer.³ The stability of this surface reconstruction has also been confirmed by thermo-dynamic arguments using density-functional theory (DFT) calculations.⁴ In contrast, the surface of InAs(001) often exhibits a reconstruction that has only one dimer per (2×4) cell.^{1,2} It has been suggested in Ref. 1 that this missing dimer structure might be the $\alpha 2$ (2×4) reconstruction.

In this article we present first-principles results that determine the thermodynamic stability of a large number of surface reconstructions on InAs(001). All reconstructions discussed in this article are schematically shown in Fig. 1. We find, in the experimentally relevant regime, that the $\alpha 2$ (2×4) and $\beta 2$ (2×4) reconstructions are stable in situations that correspond to As poor and As rich conditions, respectively. We therefore believe that these are indeed the structures that have been reported in Refs. 1 and 2. We also present STM results of systematic annealing experiments that confirm our theoretical predictions: the higher the As overpressure, the fewer missing dimer structures are observed on the surface: For As high (low) overpressure, the surface is dominated by the $\beta 2$ (2×4) [$\alpha 2$ (2×4)] reconstruction. The $\alpha 2$ (2×4) reconstruction has never been observed for the GaAs(001) surface. However, our calculations predict that it is also a stable surface reconstruction for GaAs(001).

The stable surface reconstruction is determined as the one with the lowest surface free energy density γ . For a system with two species, the stoichiometry of the surface is an additional degree of freedom. This is accounted for by introducing the chemical potential μ_i , which is the free energy per particle of species i in a reservoir. One can write

$$\gamma A = E_{\text{surf}} - \sum_i \mu_i N_i, \quad (1)$$

where N_i is the number of atoms of species i per surface area A . The chemical potentials are related to the experimental conditions; a high (low) value of the chemical potential μ_{As} corresponds to As rich (poor) conditions. Similarly, a high (low) value for μ_{In} implies Indium rich (poor) conditions. The values for μ_i are bounded by their respective bulk values

$$\mu_i < \mu_i^{(b)}. \quad (2)$$

This is a reasonable (but extreme) limit, because otherwise species i would form droplets on the surface. An additional equilibrium condition is that

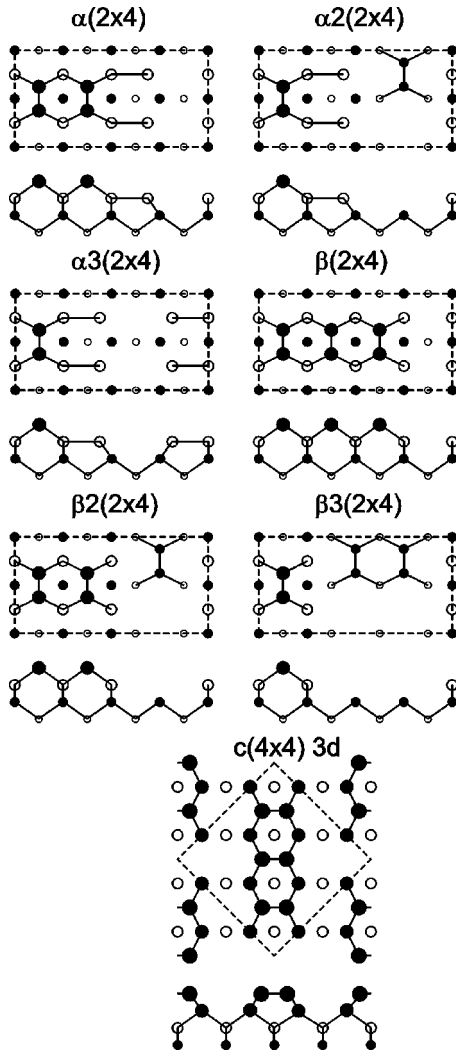


FIG. 1. Schematic representation of the relevant (2×4) structures and the $c(4 \times 4)$ with three top As dimers ($3d$). Closed (open) circles represent As (In) atoms, and the size reflects the height. The corresponding (4×2) structures are rotated by 90° , with In and As atoms exchanged.

$$\mu_{\text{In}} + \mu_{\text{As}} = \mu_{\text{InAs}}, \quad (3)$$

where μ_{InAs} is the energy per InAs pair in InAs bulk. This condition has to be satisfied because otherwise the system would adjust by forming more (or less) InAs bulk. From (2) and (3) the chemical potential of As is bound by

$$\Delta H = \mu_{\text{InAs}}^{(b)} - \mu_{\text{In}}^{(b)} - \mu_{\text{As}}^{(b)} < \mu_{\text{As}} - \mu_{\text{As}}^{(b)} < 0, \quad (4)$$

where ΔH is the formation enthalpy for InAs bulk.

DFT calculations in the local-density approximation (LDA) were employed to obtain the surface energy for all the surface reconstructions shown in Fig. 1. We used normconserving pseudopotentials^{5,6} and the computer code fhi98md.⁷ The electronic wave functions were expanded in a plane-wave basis that was truncated at a cutoff energy of $E_{\text{cut}} = 12$ Ry. For the \mathbf{k} summation we used the equivalent of 8×8 points in a (1×1) cell that were generated according to the scheme proposed by Monkhorst and Pack.⁸ Convergence of our results with respect to the value for E_{cut} and the number of \mathbf{k} points has been tested. DFT calculations are valid

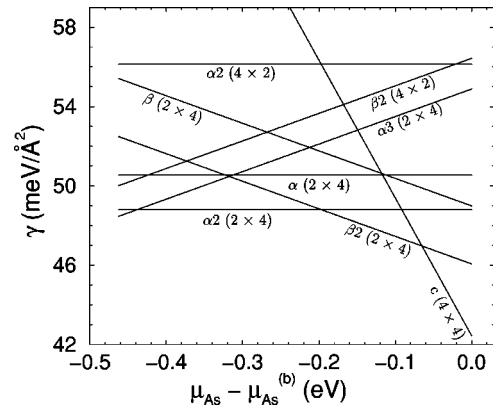


FIG. 2. Equilibrium phase diagram for InAs calculated with DFT.

for ground-state properties; thus, our results will represent the thermodynamic equilibrium for $T=0$.

All structures were calculated with a unit cell of size (2×4) [or (4×2)] and a slab thickness of 8 (or 7) atomic layers, so that the bottom layer was always a layer of group III atoms. This bottom layer was terminated with pseudohydrogen atoms of charge 1.25 to neutralize the dangling bonds. A vacuum separation equivalent to 8 or 10 atomic layers was chosen. We tested convergence of our results with respect to slab and vacuum thickness. All atoms were allowed to relax, except the lowest layer of In and As.

In Fig. 2 we present our resulting phase diagram for InAs(001) for all the surface reconstructions depicted in Fig. 1. For large μ_{As} , the $c(4 \times 4)$ with three dimers ($3d$) is stable. Other (4×4) structures or a (1×3) structure⁹ might also be relevant for μ_{As} close to μ_{As} (bulk) (but were not considered here). All structures discussed here satisfy the electron counting rule. Our results agree with those of Moll *et al.*¹⁰ However, those authors did not consider the $\alpha 2$ (2×4) or $\alpha 3$ (2×4) . We estimate the accuracy of all our calculations to be better than $1 \text{ meV}/\text{\AA}^2$.

For the experimentally most relevant regions in the phase diagram, we find that the $\beta 2$ (2×4) is stable at higher values of μ_{As} (As rich), while the $\alpha 2$ (2×4) is stable for lower values of μ_{As} (In rich). Only for extremely In rich conditions does our phase diagram predict that the $\alpha 3$ (2×4) reconstruction is stable. Thus, any model of growth of InAs(001) needs to consider (at least) two relevant (2×4) reconstructions, namely the $\alpha 2$ and $\beta 2$. The main difference between the two major stable reconstructions is that the $\beta 2$ has two top dimers, while the $\alpha 2$ has only one. This missing dimer will clearly affect diffusion of In atoms on the surface, and we therefore speculate that the growth on these two surface reconstructions will behave differently. This would also explain the change of the average island size for varying V/III ratio, as observed in Ref. 11.

The $\alpha 2$ ($\beta 2$) reconstruction has the same stoichiometry as the α (β). The difference in γ between the $\alpha 2$ and α is approximately 2 meV, while the one between $\beta 2$ and β is approximately 3 meV. This can be explained qualitatively as follows: Starting from the $\beta 2$ one has to remove an As-dimer and form bonds of the underlying In atoms to get to the $\alpha 2$. The same transformation leads from β to α . In both cases the changes in the neighbor configurations (bond types, length,

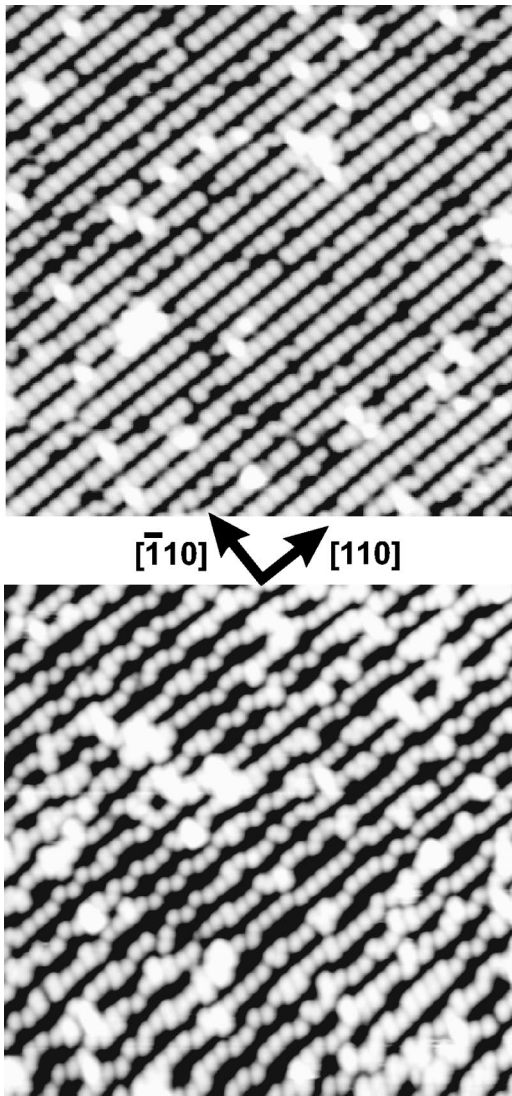


FIG. 3. STM images obtained under As rich (top) and As poor condition (bottom).

and angles) are almost identical. This suggests that the differences in surface energy densities $\gamma(\beta_2) - \gamma(\alpha_2)$ and $\gamma(\beta) - \gamma(\alpha)$ are approximately identical. Considering the electrostatic arguments of Northrup and Froyen,¹³ one can also explain the ordering of the reconstructions in the phase diagram (i.e., the observation that the β_2 (α_2) reconstruction is lower in energy than the β (α)).

As evident from Fig. 3, our predictions are confirmed by STM images under As rich (top) and As deficient (bottom) conditions. The InAs surfaces were prepared using a modified VG V80 MBE chamber and transferred in vacuo to a connected vacuum chamber containing a full wafer Omicron STM.¹¹ Prior to stabilizing the surfaces for reconstruction studies, 0.5 to 1 μm thick, doped InAs layers were grown on 0.05° oriented undoped *p*-type InAs(001) substrates at 450 °C. To ensure that the surfaces were well equilibrated, all surfaces were cooled at 1 °C/minute from the growth temperature to the stabilization temperature. The As poor and As rich surfaces were subsequently stabilized at 420 °C, using As₂ fluxes of 0.02 and 0.8 ML/s, respectively. After 10 minutes at 420° the surfaces were quenched by cutting the heater power, valving off the As source, and removing the samples

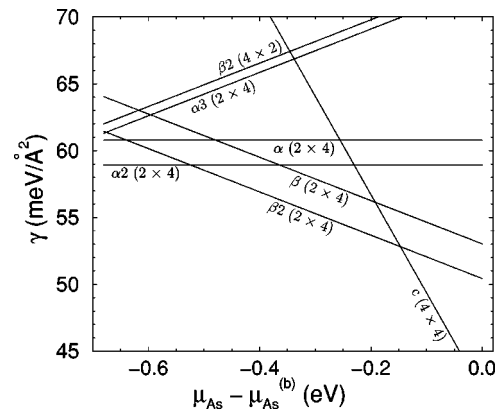


FIG. 4. Equilibrium phase diagram for GaAs calculated with DFT.

quickly from the growth chamber. All filled-states STM images were acquired in constant current mode using bias voltages between 1.1 and 3.0 V and tunneling currents between 0.03 and 0.2 nA.

For an As₂ flux of 0.8 ML/s, we find a nearly perfect β_2 (2×4) reconstruction. It is characterized by two dimers on the top, and one dimer in the trench. On the other hand, for an As₂ flux of 0.02 ML/s, we find many missing dimer structures. Our calculations strongly suggest that this is the α_2 (2×4) phase. We also see that there is a lot more disorder in the α_2 (2×4) reconstruction: While the trenches are aligned very well, we see large regions where the top dimers are shifted between neighboring cells. The reason is that the top dimer in the α_2 (2×4) cell can sit on two equivalent positions. We performed additional calculations (not shown here) that indicate that a surface with a (4×4) periodicity that consists of two parallel α_2 (2×4) cells, but the top dimers shifted, is energetically almost degenerate to the α_2 (2×4).

The α_2 (2×4) is the stable surface reconstruction for InAs(001) over a considerable range of experimental conditions. This is in contrast to experimental observations for GaAs(001), where the α_2 (2×4) has never been observed. We have therefore calculated the equivalent equilibrium phase diagram for GaAs(001) which is shown in Fig. 4. The results for the β_2 (4×2), α (2×4), and β_2 (2×4) are in agreement (within the accuracy of such calculations) with the DFT results of Moll *et al.*¹²

Our results show that the GaAs phase diagram is very similar to the one for InAs (the main difference is a shift of the boundaries values for the chemical potential). In particular, the α_2 (2×4) reconstruction is also stable for GaAs(001). However, the regime in which it is stable is much smaller for GaAs(001) relative to InAs(001). This small region of stability might be the reason why the α_2 (2×4) phase has never been conclusively observed experimentally on GaAs(001).¹⁴ Also, other structures such as the ($n \times 6$) structures as suggested by Biegelsen *et al.*¹⁵ might be stable in this regime preventing the formation of the α_2 phase. These structures have not been considered in the present study.

The similarity between the InAs and GaAs phase diagram can also be explained with an electrostatic model as introduced by Northrup and Froyen.¹³ Their model predicts quantitatively that the β_2 reconstruction should be approximately 3 meV lower in energy than the β reconstruction. With the

assumption that atomic relaxations for InAs and GaAs are similar, this model would then also predict that the phase diagram for InAs and GaAs are similar, just scaled by a factor that is related to the ratio of the respective dielectric constants and lattice constants. Comparison of Figs. 2 and 4 reveals that this is indeed the case.

We note that our results do not predict that any GaAs or InAs(001) (4×2) reconstruction is stable. For both systems the energetically lowest (4×2) reconstruction found is the $\beta 2$, but it is approximately $2 \text{ meV}/\text{\AA}^2$ higher in energy than the $\alpha 3$ (2×4) , which has the same stoichiometry [and is therefore parallel to the $\beta 2$ (2×4) , cf. Fig. 2]. On the other hand, RHEED experiments clearly show the appearance of a (4×2) pattern under In rich conditions. We speculate that this might be due to (any of) the following reasons: (i) our calculations are only valid at zero temperature; (ii) the formation of a (4×2) structure is kinetically limited (i.e., the observed (4×2) structure might not be an equilibrium structure); or (iii), we have simply missed a structure.

A simple argument that uses the formation enthalpy of a Ga vacancy¹⁶ and assumes a threefold coordination for all atoms at the surface estimates the temperature variation to be $\Delta T \sim 0.1 k_B T / \text{\AA}^2$ for GaAs.¹⁷ If this contribution was similar for all the structures under consideration, it would not reverse their order. On the other hand, it is possible that the magnitude of this contribution is different for structures that have different termination [i.e., the $\beta 2$ (4×2) and $\alpha 3$ (2×4)], so that we cannot rule out that (i) is the reason. A finite temperature might also affect the boundaries of the phase diagram. But since the slope of the $\beta 2$ (4×2) reconstruction is parallel to that of the $\alpha 3$ (2×4) , it will always be higher in

energy. We are currently in the process of building a kinetic model which could determine whether kinetic limitations play a role. There is also the possibility that we have missed a structure. In addition to all the structures discussed here, we have also studied a number of mixed dimer structures. So far, we have not found another surface reconstruction that is thermodynamically stable. We note that there are also indications in the literature that the surface might form a (6×2) reconstruction under In rich conditions.¹⁸ Other possibilities include structures with longer periodicity that still appear to have (4×2) symmetry in RHEED.

In conclusion, we have shown theoretically and experimentally that for InAs(001) the $\alpha 2$ (2×4) is an energetically preferred reconstruction for experimentally relevant conditions that are As deficient. For As rich conditions, the $\beta 2$ (2×4) is stable. Thus, we predict that a phase transition between the two phases will occur as a function of temperature and/or flux. For GaAs(001), our calculations predict that the $\alpha 2$ (2×4) is also stable in a small regime. Additional experiments for GaAs(001) under As deficient conditions (prior to the formation of the (4×2) phase) may determine whether the $\alpha 2$ (2×4) can be observed here as well.

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¹H. Yamaguchi and Y. Horikoshi, Phys. Rev. B **51**, 9836 (1995).

²G. R. Bell, M. Itoh, T. S. Jones, B. A. Joyce, and D. D. Vvedensky, Surf. Sci. **433-435**, 455 (1999).

³V. P. LaBella, H. Yang, D. W. Bullock, P. M. Thibado, P. Kratzer, and M. Scheffler, Phys. Rev. Lett. **83**, 2989 (1999).

⁴J. E. Northrup and S. Froyen, Phys. Rev. Lett. **71**, 2276 (1993).

⁵D. R. Hamann, Phys. Rev. B **40**, 2980 (1989).

⁶M. Fuchs and M. Scheffler, Comput. Phys. Commun. **119**, 67 (1999).

⁷M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, Comput. Phys. Commun. **107**, 187 (1997).

⁸H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

⁹G. R. Bell, J. G. Belk, C. F. McConville, and T. S. Jones, Phys. Rev. B **59**, 2947 (1999).

¹⁰E. Pehlke, N. Moll, A. Kley, and M. Scheffler, Appl. Phys. A: Mater. Sci. Process. **65**, 525–534 (1997).

¹¹J. H. G. Owen, W. Barvosa-Carter, and J. J. Zinck, Appl. Phys. Lett. **76**, 3070 (2000).

¹²N. Moll, A. Kley, E. Pehlke, and M. Scheffler, Phys. Rev. B **54**, 8844 (1996).

¹³J. E. Northrup and S. Froyen, Phys. Rev. B **50**, 2015 (1994).

¹⁴We speculate that the dimer vacancy rows in Fig. 13(b) of Ref. 1 could actually be an indication for the $\alpha 2$ (2×4) phase for GaAs(001).

¹⁵D. K. Biegelsen, R. D. Bringans, J. E. Northrup, and L. E. Swartz, Phys. Rev. B **41**, 5701 (1990).

¹⁶M. Bockstedte and M. Scheffler, Z. Phys. Chem. (Munich) **200**, 195 (1997).

¹⁷A. Kley, Ph.D. thesis, Technische Universität Berlin, Berlin (1997).

¹⁸Q. K. Xue and T. Sakurai, Phys. Rev. B **57**, 6862 (1998).

¹⁹L. G. Wang, P. Kratzer, and M. Scheffler (private communication).