

Ga-rich GaAs(001) surface from *ab initio* calculations: Atomic structure of the (4×6) and (6×6) reconstructions

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Total-energy calculations for a series of GaAs(001) (4×6) and (6×6) surfaces are presented. For the Ga-rich limit, we confirm the GaAs(001) (4×6) surface model proposed by Ohtake *et al.* [Phys. Rev. Lett. **93**, 266101 (2004)]. The calculations indicate that the bright chains along the $[1\bar{1}0]$ direction observed experimentally for (4×6) and (6×6) surfaces are derived from surface Ga-As heterodimers. The near energetic degeneracy of different arrangements of these mixed dimers explains naturally the disorder of bright chains. A long-range correlation between (6×6) surface units proposed by Kocán *et al.* [Phys. Rev. B **70**, 201303(R) (2004)] allows for fulfilling the electron counting rule and renders a surface based on (6×6) units more favorable.

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I. INTRODUCTION

Much scientific interest in the structure and stability of the GaAs(001) surface has been caused by its large variety of surface reconstructions. In addition, it is a technologically important substrate for electronic, photonic, and magnetic devices. In the past, Ga-rich GaAs(001) surfaces were studied less extensively than As-rich (2×4) and $c(4 \times 4)$ reconstructions. More recently, however, substantial progress has been made in understanding the Ga-rich reconstructions. Total-energy calculations prompted Lee *et al.*¹ to suggest a rather complex, so-called ζ structure for the Ga-rich (4×2) reconstructed GaAs(001) surface [Fig. 1(a)]. This reconstruction is also supported by x-ray diffraction (XRD) analysis^{2,3} and rocking-curve analysis of reflection high-energy electron diffraction (RHEED) data,^{4,5} and is now generally accepted.

However, the Ga-rich (4×2) reconstruction is not the only Ga-rich GaAs surface phase. Xue *et al.*⁶ pointed out that a (4×6) reconstruction is the most Ga-rich surface phase. On the other hand, a (6×6) reconstruction, also described variously as $(n \times 6)$, (1×6) , (2×6) , or $(2 \times 6)/(3 \times 6)$, is observed at the lower end of the temperature region of the (4×2) phase, i.e., between the As-rich (2×4) and the Ga-rich (4×2) phase.^{7–14}

These large reconstructions are not really understood on an atomic scale. Xue *et al.*⁶ proposed a (4×6) model featuring an array of Ga clusters on top of the (4×2) reconstructed surface. However, there are experimental and computational findings that contradict the cluster model for the (4×6) surface.^{15–17} Scanning tunneling microscopy (STM) images in a previous work by the present authors¹⁸ show the existence of a well-ordered (4×6) reconstruction under extreme Ga-rich conditions that is interpreted in terms of the structure

model shown in Fig. 1(b). This model has structure elements in common with the $\zeta(4 \times 2)$ surface shown in Fig. 1(a) as well as heterodimers formed by surface Ga and As atoms.

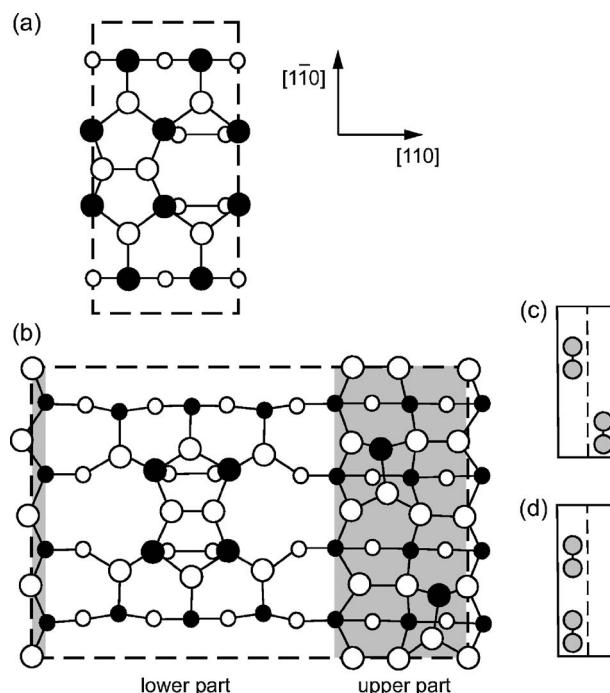


FIG. 1. (a) Top view of the $\zeta(4 \times 2)$ surface structure. (b) Top view of the structure model for the (4×6) reconstruction proposed in Ref. 18. Empty (filled) circles represent Ga (As) atoms. Positions in the uppermost two atomic layers are indicated by large symbols. (c) Zigzag dimer model and (d) straight dimer model for the the upper part. The gray circles present Ga or As atoms in two dimers at the upper part.

The formation of heterodimers has been observed for several III-V(001) surfaces^{16,19} and GaAs(001)- $c(4\times 4)$ reconstructions.²⁰ In the present case, the heterodimers are assumed to form chains running along the $[1\bar{1}0]$ direction. However, the precise nature of these chains is not clear from the STM data.¹⁸

Various models have been proposed for the (6×6) surface during the past two decades.^{9,11,13,14} Recently, Kocán *et al.*²¹ observed well-ordered (6×6) surfaces using STM. They noted some similarity with the structural features of the (4×6) phase and proposed a (6×6) model for this reconstruction that is quite different from previous suggestions. The model contains structural motifs from both the $\zeta(4\times 2)$ and the (4×6) models shown in Fig. 1.

Theoretical work on GaAs(001) surfaces has previously focused on the (4×2) , (2×4) , $c(4\times 4)$, or (2×6) phases, see, e.g., Refs. 1, 16, 17, and 22–24. Due to the large size of the surface unit cell, no *ab initio* calculations have been performed to explore the energetics of the different (6×6) models proposed by now or the structural details of the (4×6) phase. This paper aims at filling that gap. It reports a comprehensive study of the GaAs(001)- (4×6) and (6×6) surface energetics based on *first-principles* total-energy calculations within density functional theory (DFT).

II. COMPUTATIONAL METHOD

The total-energy and electronic-structure calculations are performed using the Vienna *ab initio* simulation package (VASP) implementation²⁵ of the gradient-corrected²⁶ density functional theory [DFT generalized-gradient approximation (DFT-GGA)]. The electron-ion interaction is described by non-norm-conserving ultrasoft pseudopotentials.²⁷ The Ga 3*d* electrons are frozen into the core. The electronic wave functions are expanded into plane waves up to an energy cutoff of 13 Ry.

The GaAs surface is modeled with a periodically repeated slab. The supercell consists of eight or nine atomic GaAs layers and a vacuum region equivalent in thickness to about ten atomic layers. The cation terminated bottom layer of the slab is saturated with fractionally charged ($Z_H=1.25$) pseudo *H* atoms. All calculations are performed using the calculated GaAs equilibrium lattice constant of 5.725 Å. The topmost five or six layers of the slab are allowed to relax.

Our calculations employ the residual minimization scheme—direct inversion in the iterative subspace (RMM-DIIS) algorithm^{28,29} to minimize the total energy of the system. The surface structure is considered to be in equilibrium when the Hellmann-Feynman forces are smaller than 2 meV/Å. The Brillouin zone integrations are performed using sets corresponding to 64 **k** points in the full (1×1) surface Brillouin zone.

In order to compare energetically the surface structures with different stoichiometry, we consider the thermodynamic grand canonical potential Ω in dependence on the chemical potentials μ of the surface constituents. Here it is written as a function of the chemical potential of Ga with respect its bulk Ga phase, $\Delta\mu(\text{Ga})$. It may assume values between

$-\Delta H_f \leq \Delta\mu(\text{Ga}) \leq 0$, where ΔH_f is the heat of formation of GaAs. We calculate a heat of formation of 0.75 eV. The surface formation energies are given relative to the $\alpha 2$ structure of the GaAs(001) surface.³⁰ We apply the method of Chetty and Martin³¹ for determining the surface stoichiometry.

III. RESULTS AND DISCUSSION

A. (4×6) structure

The (4×6) reconstruction model proposed in Ref. 18 is energetically favorable at the Ga-rich limit and agrees well with the STM and RHEED data. As shown in Fig. 1(b), the model contains two surface Ga-As dimers in the upper part and one Ga-Ga dimer as well as two subsurface Ga-Ga dimers in the lower part, similar to the $\zeta(4\times 2)$ model shown in Fig. 1(a). However, the Ga dimers formed in the second layer in the (4×6) model are displaced by one lattice constant along the $[110]$ direction. The dimer length for the topmost Ga dimer amounts to 2.48 Å. The subsurface Ga-Ga dimers have a length of 2.58 Å, i.e., they are slightly longer than the topmost Ga dimer. These dimer lengths agree with the values we calculate for the $\zeta(4\times 2)$ structure.

Bright chains of seemingly randomly arranged building blocks along the $[1\bar{1}0]$ direction appear on STM images of the (4×6) surface.¹⁸ If As-As or Ga-Ga dimers are assumed to form the base structures of these features, it is difficult to explain the STM images. Thus, Ga-As dimers were proposed instead. We calculate a length of 2.50 Å for the mixed dimers, close to the calculated bond length in bulk GaAs (2.48 Å).

To examine the composition and arrangement of the top dimers computationally, we study five possible combinations: (i) Ga-Ga and Ga-Ga dimers, (ii) As-As and As-As dimers, (iii) As-As and Ga-Ga dimers, (iv) Ga-Ga and Ga-As dimers, and (v) As-As and As-Ga dimers in addition to the model with two mixed dimers. In the STM images of the (4×6) surface the bright chains are aligned in two lines separated by 4 Å. Thus, two possible arrangements, a zigzag chain and a straight chain as shown in Figs. 1(c) and 1(d), respectively, are probed for the dimer combinations discussed above. All these models comply with the so-called electron-counting rule (ECR), which was found to govern the reconstruction of many semiconductor surfaces.³²

The relative formation energies calculated for these (4×6) models are plotted in Fig. 2. The panels (a) and (b) in Fig. 2 show the calculated results using the zigzag [Fig. 1(c)] and straight [Fig. 1(d)] chains, respectively. All dimer combinations (i)–(v) are unfavorable with respect to the formation of rows formed completely by heterodimers. The model (iii) has the same stoichiometry as the model with the Ga-As dimers in the chains, but the total energy is 26 meV per 1×1 unit cell higher. Figure 2(c) shows that straight and zigzag chains of mixed Ga-As dimers are energetically nearly degenerate. This reasonably explains the random arrangement seen in the STM images.¹⁸ Moreover, different orientations of the mixed dimers with respect to each other lead to only small energy differences, i.e., values that are

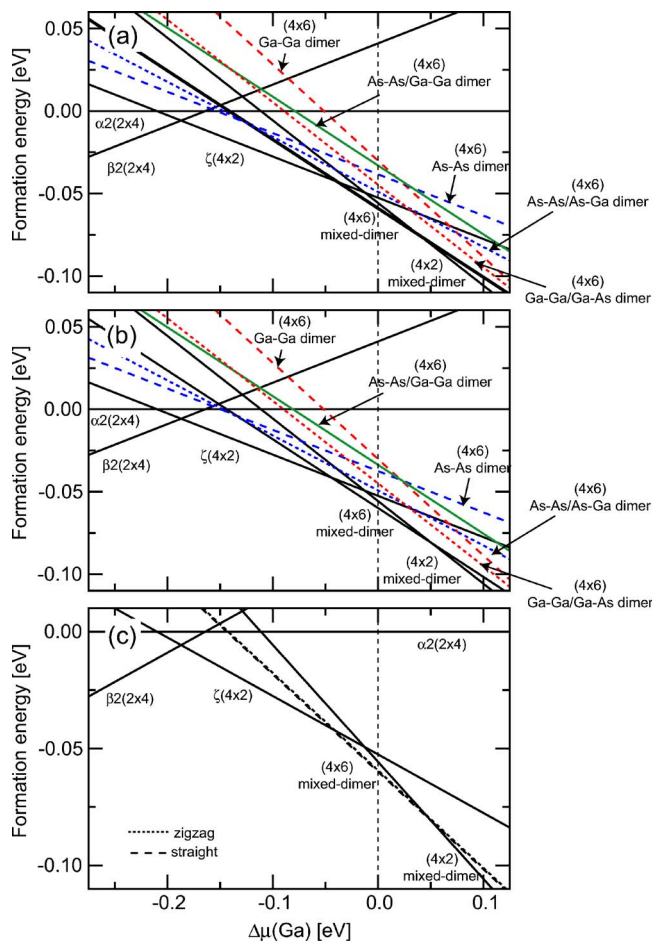


FIG. 2. (Color online) Relative formation energies per (1×1) unit cell for GaAs(001) surface reconstructions as a function of the Ga chemical potential. In (a) and (b), zigzag and straight dimer chains, respectively, form in the upper part of the (4×6) model. In (c), a comparison of zigzag and straight dimer chains is shown for the case of Ga-As dimers.

below 10 meV per 1×1 unit cell. In fact, disorder in the positioning of the atoms in the bright chains, previously interpreted as As-As dimers, was observed already earlier.^{13,14,33}

STM images for the (4×6) model with mixed Ga-As dimers simulated according to the scheme of Tersoff and Hamann³⁴ and using bias voltages $V_b = \pm 3.0$ V are shown in Figs. 3(a) and 3(b), respectively. The agreement between the measured and simulated filled-states images is excellent, as discussed previously.¹⁸ The bright protrusions in the dark rows are mainly related to the four second-layer As atoms. The simulated empty-state image shows large bright protrusions in the dark rows due to the surface Ga dimer atoms and small bright protrusions due to empty p_z states of sp^2 bonded Ga atoms in the second layer.

Finally, we briefly discuss the possibility of Ga adatoms or clusters on the Ga-rich surface for the (4×6) surface. Xue *et al.*⁶ observed a (4×6) surface characterized by an array of oval features using the STM. They assigned the oval features to Ga clusters, each containing six to eight atoms. However, the existence of these Ga clusters has been questioned in

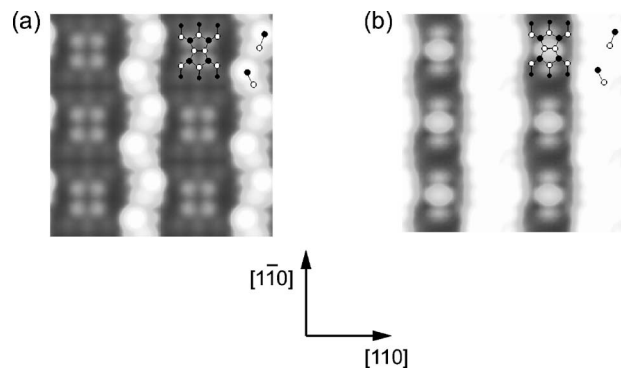


FIG. 3. STM images for the GaAs(001) (4×6) surface simulated for sample biases of 3.0 V below (a) and above (b) the valence band maximum.

several studies.^{15–17} On the other hand, similar features were observed also in more recent STM works.^{2,18} In Ref. 2 these features were proposed to be single Ga adatoms on a $\zeta(4 \times 2)$ reconstructed surface.

To model these structures computationally, the surface unit cell of the $\zeta(4 \times 2)$ structure is triplicated along the $[110]$ direction and decorated with single Ga adatoms (C1) or Ga addimers (C2) as shown in Figs. 4(a) and 4(b), respectively. From earlier calculations,¹⁷ the preferred bonding position of C1 adatoms is known to be located in the trenches, fourfold coordinated between the doubly occupied dangling bond of the first-layer As atoms. This agrees with the experimental findings by Kumpf *et al.*² We assume the C2 addimer to reside at the same position. The STM images simulated for the C1 and C2 models are shown in Figs. 4(a) and 4(b), respectively. The filled-state image features of the $\zeta(4 \times 2)$ reconstruction reproduce previous *first-principles* results.¹ The bright spots between the bright rows are due to the adatoms. The spots are oval for the case of the Ga-Ga dimers [cf. Fig. 4(b)]. The simulated images are indeed similar to the STM images for the $c(8 \times 2)$ surface from Kumpf *et al.*² and Ohtake *et al.*¹⁸ and also to the earlier findings by Xue *et al.*⁶ According to this, the Ga clusters would be much smaller than the 6–8 atoms suggested in Ref. 6.

However, there remain questions. (i) The calculated surface phase diagram in Fig. 4(c) shows that the C1 and C2 structures are unstable compared to the $\zeta(4 \times 2)$ and (4×6) surfaces. (ii) The STM images for the low bias voltage do not reproduce the experimental images.¹⁸ (iii) Noncontact atomic force microscopy indicates the oval features to be of electronic and not structural origin.³⁵ Further studies are therefore needed to clarify the origin of the (4×6) array of oval features superimposed on the GaAs(001) (4×2) phase.

B. (6×6) structure

Figure 5 shows structure models proposed to explain the (6×6) reconstruction. An early explanation for $\times 6$ periodicities is the structural model for a (2×6) surface proposed by Biegelsen *et al.*⁹ In a later study by Kuball *et al.*,¹¹ this model was modified to explain the (6×6) surface, see Fig. 5(a). In recent years, further models were derived from STM

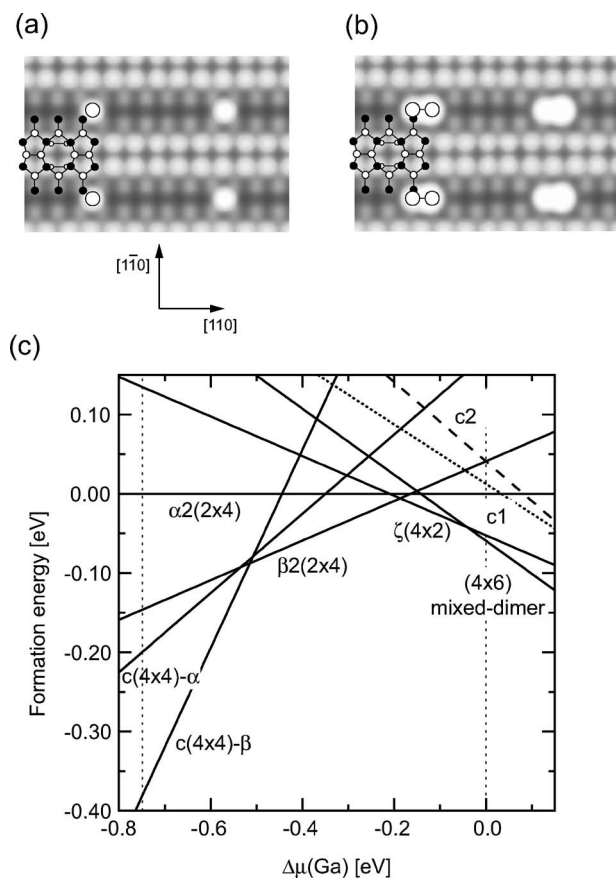


FIG. 4. Simulated STM images for the $\zeta(4 \times 2)$ reconstruction with Ga clusters in the (4×6) unit cell (see text); (a) one Ga adatom (C1) and (b) a Ga-Ga dimer (C2) on the $\zeta(4 \times 2)$. (c) Relative formation energies per (1×1) unit cell for GaAs(001) surface reconstructions with C1 and C2 models as a function of the Ga chemical potential.

data.^{13,14} The model in Fig. 5(b) shows chains of As dimers along the $[1\bar{1}0]$ direction between troughs of two adjacent Ga dimers. The surface As coverage of this model is lower than that of the model shown in Fig. 5(a). A modified, more As-rich version of this model was proposed by Xu *et al.*¹⁴ Here, as shown in Fig. 5(c), the surface unit cell contains a zigzag As dimer structure and alternating double Ga dimers between the As dimer rows.

The (6×6) reconstruction has also been investigated using reflectance anisotropy spectroscopy²⁴ (RAS). The measured RAS spectra were compared with results from *first-principles* calculations for simplified versions of previously suggested structures.^{9,11} From this comparison, the replacement of the top As dimers by mixed Ga-As dimers for a modified version of the model in Fig. 5(a) was suggested.

Recently, Kocán *et al.*²¹ showed that well-ordered (6×6) surfaces can be obtained by slowly cooling the Ga-rich $c(8 \times 2)$ surface or by heating the As-rich (2×4) surface. The structural model suggested in Ref. 21 [Fig. 5(d)] shows geometrical motifs different from those of the previous models. Kocán *et al.*²¹ suggested a model with structural elements similar to the (4×6) surface, discussed in Sec. III A.

Figure 6 shows the surface phase diagram calculated for the structures in Fig. 5. All models are unstable with respect

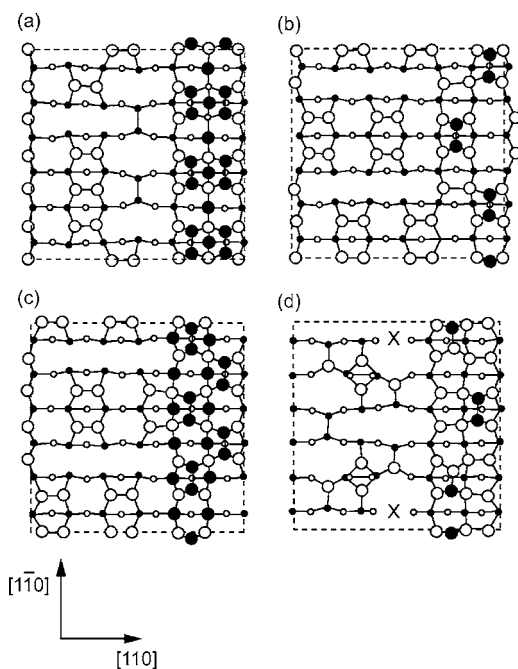


FIG. 5. Reconstruction models proposed for the GaAs(001)- (6×6) surface: (a) model of Kuball *et al.* (Ref. 11), (b) model of McLean *et al.* (Ref. 13), (c) model of Xu *et al.* (Ref. 14), (d) model of Kocán *et al.* (Ref. 21). Empty (filled) circles represent Ga (As) atoms. Positions in the uppermost two atomic layers are indicated large symbols.

to smaller surface reconstructions. Kocán's model²¹ is more stable than the previously proposed models, but still less stable than the $\zeta(4 \times 2)$ and (4×6) reconstructions.

The simulated filled-state image for the model proposed by Kocán *et al.* (see Fig. 7), however, agrees nicely with the measured STM image (cf. Fig. 2(c) in Ref. 21). In both the measured and simulated STM images, the topmost As atoms in the troughs are pronounced and two brighter rows repeat along the $[1\bar{1}0]$ direction. Therefore, it appears promising to consider modifications of the Kocán model. The model as originally proposed does not satisfy the ECR. The STM images in Ref. 21 show no perfect (6×6) symmetry: Missing spots in the pattern of the (6×6) dark troughs [marked by crosses in Fig. 5(d)] were randomly observed at the position

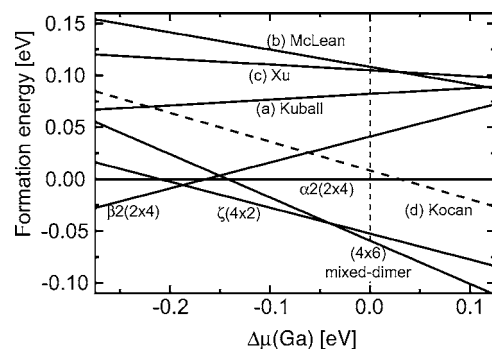


FIG. 6. Relative formation energies per (1×1) unit cell for the (6×6) models shown in Fig. 5 as a function of the Ga chemical potential.

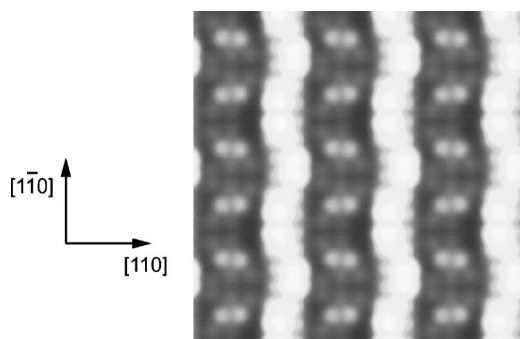


FIG. 7. Simulated STM image of the (6×6) model proposed by Koán *et al.* (Ref. 21) using bias voltage of -3.0 V below the valence band maximum.

of the As-As dimer. The missing spots may be ascribed to missing As-As dimers. If 25% of the As-As dimers in the (6×6) unit cell are missing, the structure satisfies the ECR. The minimum unit cell size satisfying this condition corresponds to a (12×6) reconstruction.

Three models based on Kocán *et al.* are studied: (i) a model with two As-As dimers, (ii) a model with one As-As dimer [and one missing As-As dimer, i.e., the model shown in Fig. 5(d)], and (iii) a model with two missing As-As dimers. In addition, the (12×6) periodicity shown in Fig. 8 is investigated. This model features three As-As dimers (“AD” in Fig. 8) and one missing As-As dimer (“X” in Fig. 8) and complies with the ECR. In the (12×6) surface unit cell, 778 atoms are included. The coexistence of Ga-As, As-Ga, and As-As dimers in the upper part for the dimer chain of the (6×6) phase was concluded from the STM experiment.²¹ The ratio of heterodimers has been estimated from the STM images to be 75%, while the value for the (4×6) symmetry is more than 90%.^{18,21} For the calculation of these three models, we therefore assume a combination of Ga-As, As-As, and As-Ga dimers in the upper part of the (6×6) model. The surface As coverages θ_{As} on a scale ranging from 0 to 1 for hypothetical bulk termination with either Ga or As, respectively, are 0.278 [model (i)], 0.222 [model (ii)], 0.167 [model (iii)], and 0.250 for the (12×6)

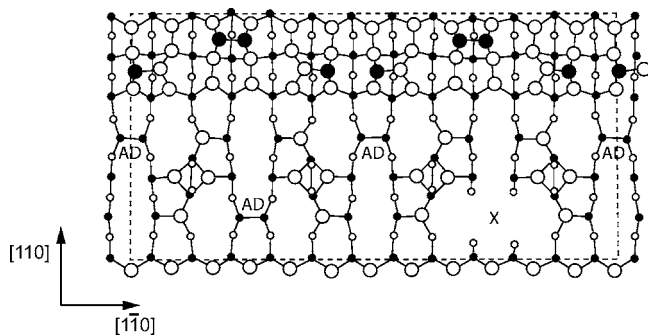


FIG. 8. Structure model of the GaAs(001) surface with (12×6) symmetry.

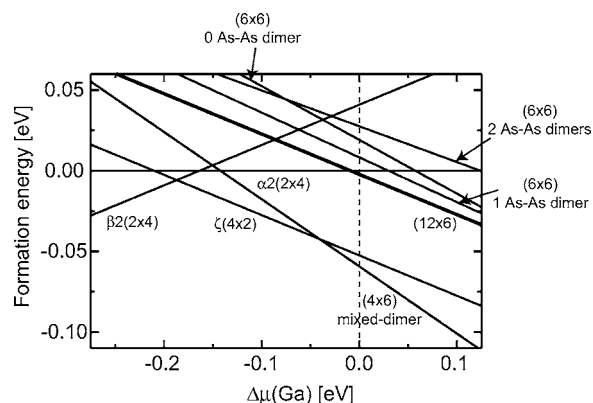


FIG. 9. Relative formation energies per (1×1) unit cell for several modifications of the (6×6) model proposed by Kocán *et al.* (Ref. 21) as a function of the Ga chemical potential.

surface. A (6×6) reconstruction is generally considered to be less Ga-rich than the Ga-rich (4×2) phase ($\theta_{\text{As}}=0.250$).^{9,10,12,21}

In Fig. 9, the surface phase diagram calculated for the three different (6×6) models and the (12×6) surface is shown. Among the (6×6) structures derived from Kocán’s model,²¹ the formation energy of the model including one As-As dimer is lowest. However, the model with the (12×6) unit cell that complies with the ECR is even more favored. It is expected that the difference of the surface As coverage between the Ga-rich (4×2) and (6×6) phases would be small. Still, none of the (6×6) and (12×6) structures investigated here is a low-energy structure at the Ga-rich limit. However, because of the agreement between the STM images simulated based on Kocán’s model with experiment, we believe that either the observed (6×6) structures are indeed energetically metastable or are structurally closely related to the geometry suggested in Ref. 21.

IV. SUMMARY

The (4×6) and (6×6) reconstructed GaAs(001) surface structures were studied using *first-principles* calculations. Recently proposed (4×6) and (6×6) models containing surface Ga-As mixed dimers and subsurface Ga-Ga dimers are favored compared to structures suggested earlier. The (4×6) model is energetically stable at the Ga-rich limit. The energetic degeneracy of different arrangements of Ga-As mixed dimers explains the random sequence within the bright chains observed by STM. The (6×6) model may be stabilized by forming larger reconstructions that allow for complying with electron counting heuristics. However, it remains unstable with respect to the (4×2) and (4×6) structure for Ga-rich conditions.

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- ¹S.-H. Lee, W. Moritz, and M. Scheffler, Phys. Rev. Lett. **85**, 3890 (2000).
- ²C. Kumpf, L. D. Marks, D. Ellis, D. Smilgies, E. Landemark, M. Nielsen, R. Feidenhans'l, J. Zegenhagen, O. Bunk, J. H. Zeysing, Y. Su, and R. L. Johnson, Phys. Rev. Lett. **86**, 3586 (2001).
- ³D. Paget, Y. Garreau, M. Sauvage, P. Chiaradia, R. Pinchaux, and W. G. Schmidt, Phys. Rev. B **64**, 161305(R) (2001).
- ⁴A. Ohtake, S. Tsukamoto, M. Pristovsek, N. Koguchi, and M. Ozeki, Phys. Rev. B **65**, 233311 (2002).
- ⁵A. Ohtake, S. Tsukamoto, M. Pristovsek, and N. Koguchi, Appl. Surf. Sci. **212-213**, 146 (2003).
- ⁶Q. Xue, T. Hashizume, J. M. Zhou, T. Sakata, T. Ohno, and T. Sakurai, Phys. Rev. Lett. **74**, 3177 (1995).
- ⁷P. Drathen, W. Ranke, and K. Jacobi, Surf. Sci. **77**, L162 (1978).
- ⁸T.-C. Chiang, R. Ludeke, M. Aono, G. Landgren, F. J. Himpsel, and D. E. Eastman, Phys. Rev. B **27**, 4770 (1983).
- ⁹D. K. Biegelsen, R. D. Bringans, J. E. Northrup, and L.-E. Swartz, Phys. Rev. B **41**, 5701 (1990).
- ¹⁰C. W. Snyder, J. Sudijono, C.-H. Lam, M. D. Johnson, and B. G. Orr, Phys. Rev. B **50**, 18194 (1994).
- ¹¹M. Kuball, D. T. Wang, N. Esser, M. Cardona, J. Zegenhagen, and B. O. Fimland, Phys. Rev. B **51**, R13880 (1995).
- ¹²I. Chizhov, G. Lee, R. F. Willis, D. Lubyshev, and D. L. Miller, Surf. Sci. **419**, 1 (1998).
- ¹³J. G. McLean, P. Kruse, and A. C. Kummel, Surf. Sci. **424**, 206 (1999).
- ¹⁴H. Xu, Y. G. Li, A. T. S. Wee, C. H. A. Huan, and E. S. Tok, Surf. Sci. **513**, 249 (2002).
- ¹⁵P. Kruse, J. G. McLean, and A. C. Kummel, J. Chem. Phys. **113**, 2060 (2000).
- ¹⁶W. G. Schmidt, Appl. Phys. A **75**, 89 (2002).
- ¹⁷K. Seino, W. G. Schmidt, F. Bechstedt, and J. Bernholc, Surf. Sci. **507-510**, 406 (2002).
- ¹⁸A. Ohtake, P. Kocán, K. Seino, W. G. Schmidt, and N. Koguchi, Phys. Rev. Lett. **93**, 266101 (2004).
- ¹⁹W. G. Schmidt, F. Bechstedt, N. Esser, M. Pristovsek, C. Schultz, and W. Richter, Phys. Rev. B **57**, 14596 (1998).
- ²⁰A. Ohtake, J. Nakamura, S. Tsukamoto, N. Koguchi, and A. Natori, Phys. Rev. Lett. **89**, 206102 (2002).
- ²¹P. Kocán, A. Ohtake, and N. Koguchi, Phys. Rev. B **70**, 201303(R) (2004).
- ²²T. Ohno, Phys. Rev. Lett. **70**, 631 (1993).
- ²³J. E. Northrup and S. Froyen, Phys. Rev. Lett. **71**, 2276 (1993).
- ²⁴M. Pristovsek, S. Tsukamoto, A. Ohtake, N. Koguchi, B. G. Orr, W. G. Schmidt, and J. Bernholc, Phys. Status Solidi B **240**, 91 (2003).
- ²⁵G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
- ²⁶J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
- ²⁷J. Furthmüller, P. Käckell, F. Bechstedt, and G. Kresse, Phys. Rev. B **61**, 4576 (2000).
- ²⁸P. Pulay, Chem. Phys. Lett. **73**, 393 (1980).
- ²⁹D. M. Wood and A. Zunger, J. Phys. A **18**, 1343 (1985).
- ³⁰W. G. Schmidt, S. Mirbt, and F. Bechstedt, Phys. Rev. B **62**, 8087 (2000).
- ³¹N. Chetty and R. M. Martin, Phys. Rev. B **44**, 5568 (1991).
- ³²M. D. Pashley, Phys. Rev. B **40**, 10481 (1989).
- ³³Q. Xue, T. Ogino, Y. Hasegawa, H. Shinohara, and T. Sakurai, Phys. Rev. B **53**, 1985 (1996).
- ³⁴J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).
- ³⁵J. J. Kolodziej, B. Such, and M. Szymonski, Phys. Rev. B **71**, 165419 (2005).