

Ga-Rich Limit of Surface Reconstructions on GaAs(001): Atomic Structure of the (4×6) PhaseAkihiro Ohtake,^{1,*} Pavel Kocán,^{1,2} Kaori Seino,³ Wolf G. Schmidt,³ and Nobuyuki Koguchi¹¹National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan²Charles University, Faculty of Mathematics and Physics, V Holešovičkách 2, Prague, Czech Republic³Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität, Max-Wien-Platz 1, 07743 Jena, Germany

(Received 10 September 2004; published 20 December 2004)

The Ga-rich reconstruction of the GaAs(001) surface has been studied. Using scanning tunneling microscopy (STM), we have found the existence of a well-ordered (4×6) reconstruction under extreme Ga-rich conditions. A structure model, consisting of subsurface Ga-Ga dimers and surface Ga-As dimers, is proposed for the (4×6) surface. This model is found to be energetically favorable at the Ga-rich limit and agrees well with our experimental data from STM and reflection high-energy electron diffraction.

DOI: 10.1103/PhysRevLett.93.266101

PACS numbers: 68.35.Bs, 61.14.Hg, 68.35.Rh, 68.37.Ef

Atomic structures on the (001) surface of GaAs have been a subject of continuing interest over the past two decades. It is well known that a variety of reconstructions are formed on the GaAs(001) surface depending on the surface stoichiometries, such as As-rich $c(4 \times 4)$, As-rich (2×4) , and Ga-rich $c(8 \times 2)$ phases. The atomic structures of these phases have been extensively studied, and a consensus appears to be finally reached on the atomic structure of As-rich phases of $c(4 \times 4)$ [1–3] and (2×4) [4,5]. On the other hand, reconstructions prepared under Ga-rich conditions are still far from being completely understood. Although recent ground breaking papers proposed a new type of structure model for the Ga-rich reconstruction of $c(8 \times 2)$ [6,7], even the simple question as to whether the $c(8 \times 2)$ structure is the most Ga-rich phase still remains unanswered.

While it has been generally accepted that the $c(8 \times 2)$ reconstruction emerges under the most Ga-rich conditions, Xue *et al.* proposed that the (4×6) reconstruction is the most Ga-rich phase [8]. Their scanning tunneling microscopy (STM) images showed an array of large oval features on the $c(8 \times 2)$ phase with local (4×6) periodicity. They ascribed these oval features to Ga clusters consisting of 6–8 Ga atoms [8]. The existence of the (4×6) phase, however, has been questioned in several papers [9–14]. On the basis of chemical titration experiments, Kruse *et al.* suggested that the bright oval spots seen in STM images represent localized excess charge rather than Ga clusters [9]. In addition, the structure model proposed by Xue *et al.* was found to be energetically unfavorable [10,11]. Other studies [12–14] assigned the (4×6) symmetry seen by low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED) to a coexistence of the $c(8 \times 2)$ and the less Ga-rich (6×6) phases, rather than to an intrinsic (4×6) surface periodicity.

This Letter reports a systematic study on the Ga-rich limit of the GaAs(001) surface. We demonstrate that indeed there exists a genuine (4×6) reconstruction that is more Ga rich than the $c(8 \times 2)$ phase. A structure model featuring surface Ga-As dimers and subsurface Ga-Ga

dimers is proposed for the (4×6) surface. This model accounts for our measured STM images and RHEED rocking curves and is energetically favored for extremely Ga-rich conditions, as determined in first-principles total-energy calculations.

The experiments were performed in a system of interconnecting ultrahigh vacuum chambers for molecular-beam epitaxy (MBE) growth and for online surface characterization by means of STM and x-ray photoelectron spectroscopy [1–3]. The MBE chamber is equipped with RHEED and reflectance difference spectroscopy (RDS)

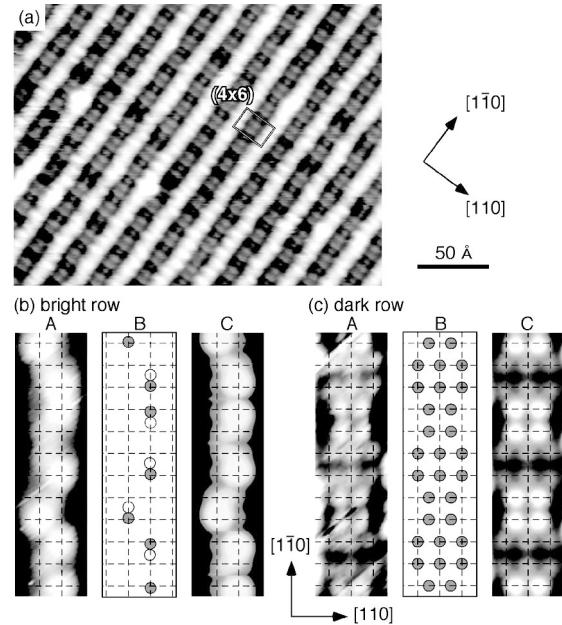


FIG. 1. (a) Typical filled-state STM image obtained from the GaAs(001)- (4×6) surface. (b) and (c), parts A are magnified images of bright and dark rows, respectively. The images were taken with a sample bias of -3.0 V. (b) and (c), parts B indicate the atomic positions of Ga (open circles) and As (solid circles). (b) and (c), parts C are simulated images of the optimized structure model shown in Fig. 2.

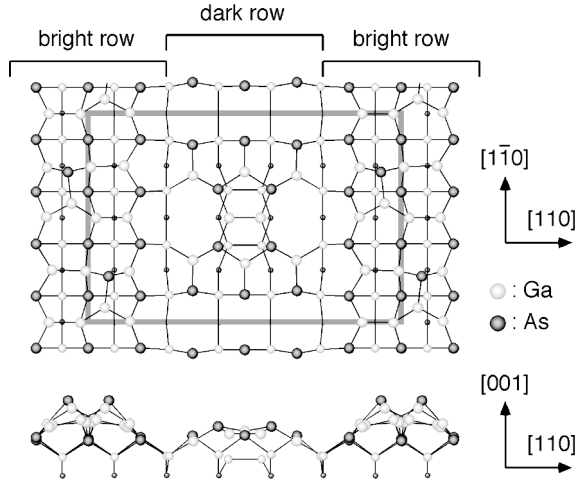


FIG. 2. The structure model for the GaAs(001)-(4 × 6) surface. The positions of bright and dark rows in STM images [Figs. 1(b) and 1(c)] are indicated.

apparatuses. The As-rich GaAs(001)-(2 × 4) surfaces were first obtained by MBE as described in our previous papers [1–3]. Then the (2 × 4) surface was heated and was kept at 500 °C for several hours in a good UHV condition of $\sim 5 \times 10^{-11}$ Torr (i.e., without As fluxes) to produce the more Ga-rich (6 × 6) reconstruction. The (4 × 6) reconstruction was obtained by depositing 0.2 ML of Ga on the (6 × 6) surface at 500 °C [15]. We carried out RDS measurements and RHEED observations during the Ga deposition and confirmed that the formation of the (4 × 6) reconstruction is completed at ~ 0.2 ML. Further Ga deposition does not change the (4 × 6) reconstruction, but rather results in the formation of large Ga droplets. The samples prepared in the MBE chamber were transferred via the UHV transfer modules to the STM chamber (Omicron, micro-STM), where the measurements were performed at room temperature in the constant current mode.

Figure 1(a) shows a typical STM image obtained from the GaAs(001)-(4 × 6) surface. Other phases, such as $c(8 \times 2)$, have not been observed even in larger scale images. The bright chains running along the $[1\bar{1}0]$ direction are separated by dark rows with a spacing of 24 Å (corresponding to the $\times 6$ periodicity). Such a structural feature is altogether different from that observed by Xue *et al.* [8], but is quite similar to that of the (6 × 6) reconstruction [14–18]. The difference between (4 × 6) and (6 × 6) is seen in the dark rows where the $4 \times$ periodicity in the $[1\bar{1}0]$ direction is clearly observed. Thus, the present results demonstrate the existence of a genuine (4 × 6) reconstruction. We note that earlier STM measurements could not resolve the $4 \times$ periodicity in the dark row, which might have prevented the (4 × 6) reconstruction from being identified in previous studies.

The detailed features of the (4 × 6) surface are clearly seen in Figs. 1(b) and 1(c), parts A. In the bright row [Fig. 1(b), part A], bright spots are aligned in two lines

separated by 4 Å, similar to the case for the (6 × 6) surface [12–17]. Bright spots observed on the (6 × 6) surface have been interpreted as As-As dimers [12–14,16,17], because As atoms usually manifest themselves as bright features in filled-state STM images. Carefully observing the image, however, we found that bright features are not equally spaced along the $[1\bar{1}0]$ direction. The random sequences can hardly be explained on the basis of As-As dimers. Instead, we propose Ga-As dimers to be the component of the bright row. As shown in Fig. 1(b), the coexistence of Ga-As and As-Ga dimers could reproduce separations of bright spots along the $[1\bar{1}0]$ direction. While the As-As dimers were occasionally observed in the bright rows, the density is less than 10%. Similar results were obtained for the (6 × 6) surface [15].

Figure 1(c), part A shows a magnified image of the dark row. It is clearly seen that the (2 × 2) and (2 × 3) subunits alternate along the $[1\bar{1}0]$ direction producing the $4 \times$ periodicity. The positions of bright spots in the (2 × 2) subunit are shifted by 2 Å along the $[110]$ direction relative to those in the (2 × 3) subunits. This means that the dark row contains surface As atoms at faulted sites relative to their bulk positions.

The existence of As atoms at faulted sites was found in the $c(8 \times 2)$ reconstruction: the recently proposed structure model contains 0.5 ML of surface As atoms at faulted positions, due to the presence of the Ga-Ga dimers in the second layer [6,7]. Thus, it is plausible to consider subsurface dimerization also for the (4 × 6) structure.

On the basis of the present STM observations, we propose a new structure model, shown in Fig. 2. This model is characterized by two Ga-As dimers, four surface As atoms at faulted positions, and two subsurface Ga-Ga dimers per (4 × 6) unit cell, and agrees with the electron counting heuristics [19]. Although the direct evidence of the subsur-

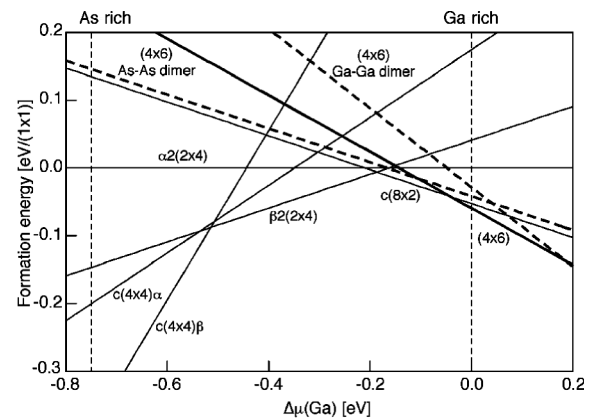


FIG. 3. Relative formation energy with respect to the $\alpha 2(2 \times 4)$ surface per (1 × 1) unit cell for GaAs(001) surface reconstructions as a function of the relative chemical potential of Ga with respect to the bulk Ga phase at 0 K. The thermodynamically allowed range is between −0.75 eV (As rich) and 0.00 eV (Ga rich).

face Ga-Ga dimers could not be obtained by STM, its existence was confirmed by our first-principles calculations and RHEED rocking-curve analysis, as we will show below.

The As coverage of the proposed structure model is $\frac{1}{12}$ ML, which is smaller than that for $c(8 \times 2)$ ($\frac{1}{4}$ ML): the proposed (4×6) model is more Ga rich than the $c(8 \times 2)$ model. In order to check the stability of this model, we performed first-principles total-energy calculations, based on the density functional theory (DFT) in generalized gradient approximation [20]. The Vienna ab initio simulation package (VASP) [21] implementation is used, with numerical details similar to the previous calculations [10,11].

Figure 3 shows the relative surface energies for GaAs(001) reconstructions as a function of the Ga chemical potential. The proposed (4×6) model (Fig. 2) is more stable than the $c(8 \times 2)$ structure at the Ga-rich limit. Also shown in Fig. 3 are the results for (4×6) models with As-As dimers and Ga-Ga dimers instead of Ga-As dimers (dashed lines). These models, however, were found to be unstable. Thus it is likely that the existence of a Ga-As dimer is a key to stabilize the (4×6) structure. The mixed anion-cation dimers were also found essential to explain cation-rich (001) surfaces of GaP and InP [10], and, interestingly, were recently detected at the anion-rich GaAs(001)- $c(4 \times 4)\alpha$ surface [1–3].

In order to prove the validity of the (4×6) structure, we simulated STM images following the scheme derived by Tersoff and Hamann [22]. Figures 1(b) and 1(c), parts C show the simulated filled-state STM images, where a bias voltage of -3.0 V was used to allow for a comparison with the experimental data. As can be seen, the agreement between the observed and simulated STM images is excellent.

Further experimental support for the proposed model was obtained by RHEED rocking-curve analysis based on dynamical diffraction theory. RHEED rocking curves were measured using the extended beam rocking facility (Staib, EK-35-R and k-Space, kSA400). The energy of the incident-electron beam was set at 15 keV. Integrated intensities of the 25 spots, $(0\ 0)$, $(0 \pm \frac{1}{6})$, $(0 \pm \frac{2}{6})$, ..., $(0 \pm \frac{11}{6})$, and (0 ± 2) for the $[1\bar{1}0]$ direction, and five spots, $(0\ 0)$, $(\pm 1\ 0)$, and $(\pm 2\ 0)$ for the $[110]$ direction, were used in a structure analysis. RHEED intensities were calculated by the multislice method proposed by Ichimiya [23]. Thirty fractional-order and nine integer-order reflections were used for the calculation along the $[1\bar{1}0]$ direction, while 24 fractional-order and nine integer-order reflections were used for the $[110]$ incidence azimuth. Parameters for the calculations, such as elastic potential, imaginary potential, and thermal vibrations, were fixed at the values used in the structure analysis for GaAs(001)- $c(8 \times 2)$ [18]. In order to quantify the agreement between the measured and calculated rocking curves, the R factor defined in Ref. [24] was used.

Figure 4 shows the RHEED rocking curves measured from the GaAs(001)- (4×6) surface at 500°C , together with the calculated ones using the atomic coordinates obtained by first-principles calculations. The majority of features in the measured rocking curves are well reproduced by the calculated ones (R factor = 0.179). While a smaller R factor of 0.110 was obtained after the structure optimization, deviations in the atomic coordinates from the initial values in absolute coordinates are typically less than $0.1\ \text{\AA}$, further corroborating the validity of the structure model proposed here. We confirmed that the analysis for the data obtained at room temperature yielded essentially the same results.

Finally, we briefly discuss the possible existence of Ga clusters [8] on the Ga-rich surfaces. Only when the $c(8 \times 2)$ surface was rapidly cooled from 600°C did we observe bright oval features on the $c(8 \times 2)$ surface coexisting with the (6×6) phase, as shown in Fig. 5(a). This surface showed fourfold and sixfold symmetries in the RHEED patterns obtained along the $[110]$ and $[1\bar{1}0]$ directions, respectively. However, the oval features, which slightly move from image to image on occasion, show only a local and weak (4×6) correlation. Thus, it is unlikely that these oval features give rise to the long-range ordered (4×6)

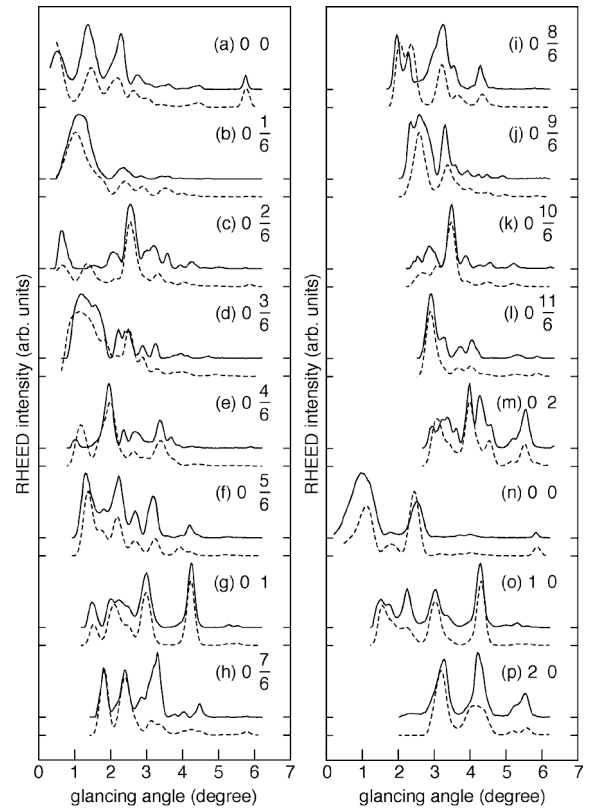


FIG. 4. RHEED rocking curve (solid curves) measured from the GaAs(001)- (4×6) surface at 500°C . The dashed curves are calculated from the atomic coordinates obtained by the first-principles calculations.

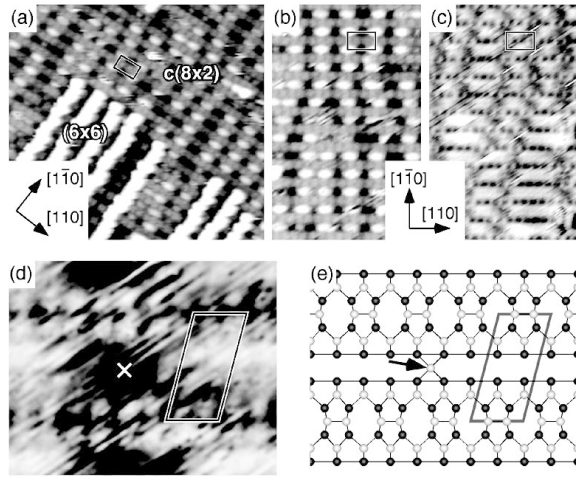


FIG. 5. (a) Filled-state STM image obtained from the $c(8 \times 2)$ surface coexisting with the (6×6) structure taken with a sample bias of -3.5 V. Image dimension is $240 \text{ \AA} \times 260 \text{ \AA}$. (b) and (c) are STM images of the $c(8 \times 2)$ phase taken with sample bias of -3.5 and -2.0 V, respectively. Solid rectangles in (a)–(c) indicate the (4×6) unit cell. (d) and (e) are the magnified image and the corresponding structure model, respectively, in which the $c(8 \times 2)$ unit cell is indicated. Bright and dark circles in (e) denote As and Ga atoms, respectively.

periodicity in LEED and RHEED patterns: the fourfold and sixfold symmetries observed by RHEED can be ascribed to the coexisting phases of $c(8 \times 2)$ and (6×6) . On the other hand, the bright features seen in the STM image seem to continue the bright rows of the (6×6) phase. This indicates that they may be related to the structure change from $c(8 \times 2)$ to (6×6) .

The oval features were observed only at relatively high bias voltages (-3.0 – -5.0 V), while we usually observed depressions at typical bias voltages of -1.8 – -3.0 V [Fig. 5(c)] instead of bright features [Fig. 5(b)] [25]. A comparison between the magnified image [Fig. 5(d)] and the $c(8 \times 2)$ structure model [Fig. 5(e)] shows that the X site corresponds to the position above the center of four unfaulted As atoms [arrow in Fig. 5(e)]. Recent x-ray diffraction analysis has shown that the X sites are partially occupied by additional Ga adatoms [7]. However, Ga adatoms on the X site on $c(8 \times 2)$ appear as bright features in the simulated STM images even at low bias voltages (not shown). Therefore, while no definitive answer is available at this stage, the Ga adatom model does not appear plausible.

In conclusion, we studied surface structures on GaAs(001) under Ga-rich conditions using STM, RHEED, and first-principles calculations. A (4×6) structure consisting of surface Ga-As dimers and subsurface Ga-Ga dimers is found to account for the experimental data

and to be energetically stable at the extremely Ga-rich condition. The present results will allow us to complete the puzzle of the surface reconstructions on GaAs(001).

This work was partially supported by the Ministry of Education, Science, Sports, and Culture, Grant-in-Aid for Young Scientists (B) (Grant No. 15710097). We are indebted to Dr. T. Hanada for use of the RHEED intensity calculation program. Grants for computer time from the Leibniz-Rechenzentrum München and the Höchstleistungs-Rechenzentrum Stuttgart are gratefully acknowledged.

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- [25] We point out that the contrast between faulted and unfaulted As atoms in the $c(8 \times 2)$ reconstruction reverses at different bias voltages [Figs. 5(b) and 5(c)], in qualitative agreement with the recent DFT calculation [6].