

New Structure Model for the GaAs(001)- $c(4 \times 4)$ Surface

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(Received 17 June 2002; published 25 October 2002)

The surface structure of the As-stabilized GaAs(001)- $c(4 \times 4)$ surface has been studied. We show that the seemingly established three As-dimer model is incompatible with experimental data and propose here a new structure model which has three Ga-As dimers per $c(4 \times 4)$ unit cell. This mixed dimer model, confirmed by the rocking-curve analysis of reflection high-energy electron diffraction and first-principles calculations, resolves disagreements in the interpretation of several previous experiments. A good agreement between the observed scanning tunneling microscopy image and the simulated one further confirms the newly proposed model.

DOI: 10.1103/PhysRevLett.89.206102

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

The (001) surface of compound semiconductors, such as GaAs, InAs, and InSb, shows a variety of reconstructions depending on surface stoichiometries. The $c(4 \times 4)$ reconstruction has been commonly observed on these surfaces under most As (Sb)-rich molecular-beam epitaxy (MBE) conditions. It has been generally accepted that the $c(4 \times 4)$ structure consists of three As (Sb) dimers at the outermost layer [Fig. 1(a)] [1–12]. This model was supported by scanning tunneling microscopy (STM) observations [1–4] and was found to be stable by first-principles calculations [5,6].

Although the existence of As dimers in the GaAs(001)- $c(4 \times 4)$ reconstruction was confirmed by grazing-incidence x-ray diffraction (XRD) measurements [7], the data can be explained only when a mixture of the two [Fig. 1(b)] and three As-dimer models is considered [7]. Similar results were reported by Sasaoka, Kato, and Usui [8]: the $c(4 \times 4)$ surface consists of the single [Fig. 1(c)] and three As-dimer models. However, such a two-dimer or a single-dimer structure has not been observed by STM [1–4]. In addition, the two-dimer model is higher in energy with respect to the three dimer model [6]. On the other hand, recent low-energy electron diffraction (LEED) data for GaAs(001)- $c(4 \times 4)$ can be explained by the three As-dimer model without considering the possible coexistence with other structures [9], but the obtained structure parameters are incompatible with those from first-principles calculations [6]. Also, the angle-resolved photoemission spectra from the GaAs(001)- $c(4 \times 4)$ surface could not be well explained by the calculations based on the three As-dimer model [10]. Judging from these results, it appears that the structure identification of the $c(4 \times 4)$ surface is not fully convincing.

The GaAs(001)- $c(4 \times 4)$ surface is widely used as a substrate for crystal growth, especially for the fabrication of nanostructures (e.g., quantum dots) [13]. Thus, definitive structure analysis for the $c(4 \times 4)$ surface is particu-

larly important because of both fundamental and practical interests. This Letter reports a systematic study on the atomic structure of the GaAs(001)- $c(4 \times 4)$ surface. Rocking-curve analysis of reflection high-energy electron diffraction (RHEED), STM, and reflectance difference spectroscopy (RDS) were used for this purpose. Here, we show that the $c(4 \times 4)$ structure consists of three Ga-As dimers per unit cell [Fig. 1(d)], contrary to the common belief. Our first-principles calculations lend further credence to the newly proposed model.

The experiments were performed in a dual-chamber MBE system [14]. Cleaned GaAs(001)- $c(2 \times 4)$ surfaces were first obtained by growing an undoped homoepitaxial layer ($\sim 0.5 \mu\text{m}$) on a thermally cleaned GaAs(001) substrate. The sample was then transferred via ultrahigh vacuum (UHV) transfer modules to another UHV chamber, where surfaces of GaAs(001)- $c(4 \times 4)$ were obtained by cooling the (2×4) surfaces below 450°C under As fluxes.

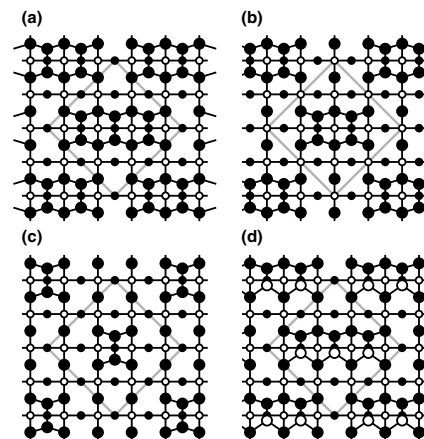


FIG. 1. Surface reconstruction models for GaAs(001)- $c(4 \times 4)$. Filled (open) circles denote As (Ga) atoms.

The STM experiments were performed using an STM chamber (Omicron GmbH, Germany) linked to a MBE growth chamber. The observations were performed at room temperature in the constant-current mode with a tunneling current of 0.3 nA and a negative sample voltage of -3.0 V. 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 ten spots, $(0\ 0)$, $(\pm\frac{1}{2}\ 0)$, $(\pm 1\ 0)$, $(\pm\frac{3}{2}\ 0)$, and $(\pm 2\ 0)$ for the $[110]$ direction, and $(0\ 0)$, $(0\ \pm\frac{1}{2})$, $(0\ \pm 1)$, $(0\ \pm\frac{3}{2})$, and $(0\ \pm 2)$ for the $[1\bar{1}0]$ direction, were used in a structure analysis. RHEED intensities were calculated by the multislice method [15], using eight fractional-order and nine integer-order reflections for both $[110]$ and $[1\bar{1}0]$ electron-incidence azimuths. Fourier coefficients of the elastic scattering potential were obtained from the atomic scattering factors for free atoms [16]. A correction due to condensation was made to fit the positions of bulk Bragg peaks at large glancing angles. For instance, the resulting mean inner potential of bulk GaAs was 13.6 eV. The imaginary part of the crystal potential for inelastic scattering was assumed to be 12% of its real part. The Debye-Waller parameters were taken to be 1.02 and 0.88 \AA^2 for Ga and As atoms, respectively [17]. In order to quantify the agreement between the calculated rocking curves and the experimental ones, the R factor defined in Ref. [18] was used. The RDS results are commonly displayed in terms of $\Delta\tilde{r}/\tilde{r} = (\tilde{r}_{1\bar{1}0} - \tilde{r}_{110})/\tilde{r}$, where $\tilde{r}_{1\bar{1}0}$ and \tilde{r}_{110} are the near-normal-incidence complex reflectances for light linearly polarized along $[1\bar{1}0]$ and $[110]$, respectively. We present only the data in the form $\Delta r/r = \text{Re}(\Delta\tilde{r}/\tilde{r})$.

Previous studies have shown that the As coverage of the $c(4\times 4)$ reconstruction varies considerably with temperature and As flux [2,3,8]. Thus, we first examined whether there exist more than one intrinsic $c(4\times 4)$ reconstruction using RHEED and RDS. The GaAs(001)- (2×4) surface was annealed at 550°C under an As_4 flux of 2.5×10^{-7} Torr for several hours. The substrate temperature was then decreased to 200°C in steps of $\sim 10^\circ\text{C}$ under As fluxes. Once the temperature reached a given value, the RDS and RHEED rocking-curve measurements were performed and the temperature was kept until the RD and RHEED intensities were saturated. The (2×4) reconstruction changes to $c(4\times 4)$ below $\sim 480^\circ\text{C}$. Figure 2(a) shows the RD spectrum obtained from the $c(4\times 4)$ surface at 250°C . The shape of the spectrum is in good agreement with that for the $c(4\times 4)$ surface reported by Kamiya *et al.* [19] and remains almost unchanged between 450 – 200°C . In this temperature range, the surface showed sharp $c(4\times 4)$ RHEED patterns. We also measured RHEED rocking curves and confirmed that the shape of the curves hardly depends on the substrate temperature between 450 – 200°C . These results enable us to conclude that there

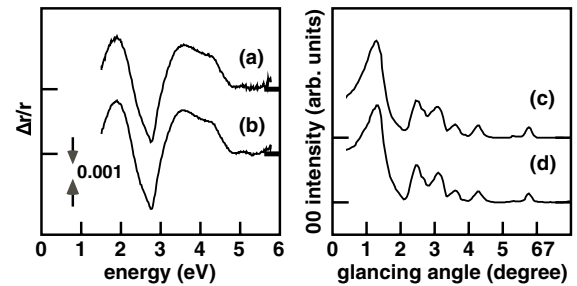


FIG. 2. (a),(b) RD spectra and (c),(d) RHEED rocking curves measured from the GaAs(001)- $c(4\times 4)$ surface at 250°C . (a) and (c) were measured under As fluxes.

exists only one intrinsic $c(4\times 4)$ reconstruction, at least under the present experimental condition.

After being annealed under As fluxes, the sample was kept at 250°C for several hours in a good UHV condition of $\sim 5\times 10^{-11}$ Torr (i.e., without As fluxes). The shapes of both RD spectrum [Fig. 2(b)] and RHEED rocking curve [Fig. 2(d)] measured after these procedures are almost all the same as those measured under As fluxes [Figs. 2(a) and 2(c)], indicating that the desorption of As from the $c(4\times 4)$ surface is negligible at this temperature. The surfaces prepared by these procedures have large terraces (~ 5000 \AA), as confirmed by STM observations at room temperature. Here, we note that our RDS and RHEED measurements evidenced that the $c(4\times 4)$ surface at room temperature stays essentially the same as that at 250°C .

Large-scale STM images from the $c(4\times 4)$ surface show a brickwork pattern of bright rectangular blocks, just as reported in Refs. [2,3]. However, observing carefully the magnified image shown in Fig. 3(a), we found

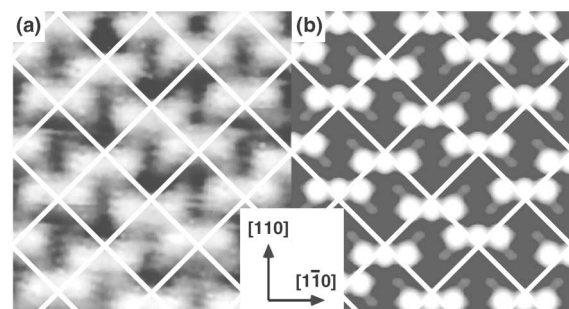


FIG. 3. (a) Filled-state STM image obtained from the GaAs(001)- $c(4\times 4)$ surface at a sample bias of -3 V. (b) Simulated STM image of the optimized model (Fig. 5) using a filled-state bias of 2.5 V below the valence band maximum, which corresponds to the range of bias used in the experiments. The solid lines show the $c(4\times 4)$ lattice mesh. Image dimensions are 48×52 \AA^2 . In the simulated image, two types of asymmetric $c(4\times 4)$ unit cells with opposite dimer orientations are distributed for comparison with the observed image.

that the position of a rectangular block is slightly shifted in the $[110]$ or the $[\bar{1}\bar{1}0]$ direction. This means that the $c(4 \times 4)$ structure has an asymmetric unit cell [21] and that symmetric $c(4 \times 4)$ RHEED patterns are ascribed to the coexistence of both types of unit blocks.

From the STM image shown in Fig. 3(a), we propose a new structure model shown in Fig. 1(d). This model, which consists of three Ga-As dimers per $c(4 \times 4)$ unit cell, is strongly supported by the following RHEED rocking-curve analysis. Figure 4 shows RHEED rocking curves measured from the $c(4 \times 4)$ surface, together with the calculated ones from the optimized model shown in Fig. 5.

The present RHEED analysis assumed the random distribution of the two types of asymmetric unit cells, on the basis of the STM image shown in Fig. 3(a). Atomic relaxations at the first, second, and third layers were permitted. The R factor for the optimized model is 0.052, showing an excellent agreement between the experiment and the calculation. On the other hand, other structures such as three As-dimer, two As-dimer, and single As-dimer models gave R factors larger than 0.15, even after the structure optimization including four surface layers. In addition to large R factors, these models resulted in unphysical atomic coordinates. We also tested the coexistence of two As-dimer and three As-dimer models, as has been suggested in Ref. [7], but could not reproduce the measured rocking curve.

The structure parameters of the optimized model (Fig. 5) are listed in Table I with errors evaluated from the half width of the range where the R factor is smaller than $1.1 \times R_{\min}$. The bond lengths between atoms in the

outermost two layers fall in the range of 2.32–2.53 Å which are close to the Ga-As bond length in bulk GaAs (2.45 Å). Ga1 and Ga2 atoms are displaced downward by a large amount of ~ 0.8 Å to form a planar sp^2 -type bonding configuration with their As nearest neighbors. On the other hand, As1, As2, As3, and As3' atoms produce p^3 -type bonds with their nearest neighbor atoms. Thus, this atomic arrangement can eliminate all of the Ga and As dangling bonds by transforming the As (Ga) dangling bonds into s -type fully occupied (p_z -type empty) states.

Further experimental supports for the mixed dimer model were obtained by comparing with the previous XRD [7] and LEED [9] results. The LEED analysis based on the mixed dimer model yielded the Pendry's R factor of 0.19, showing an excellent agreement with the experiment [22]. Also, the XRD intensities calculated from the mixed dimer model agree well with the measured ones in Ref. [7].

In order to support the present experimental results, we performed first-principles density-functional calculations [23–25] with the generalized gradient approximation [26]. A slab geometry was used for the simple calculation, which has the supercell consisting of eight atomic layers of GaAs with Ga-As dimers and of a vacuum region corresponding to six atomic layers in thickness. The atomic coordinates obtained by the present calculations are in good agreement with those from RHEED analysis, further proving the relevance of the mixed dimer model: deviations from the experiments in absolute coordinates are typically less than 0.1 Å. More details on the calculated results will be published elsewhere [27].

We extracted simulated STM images from the calculations using the Tersoff-Hamann formalism [28]. Figure 3(b) shows the simulated filled-state STM image. In this image, the surface As atoms manifest themselves as bright features, while the surface Ga atoms are hardly imaged, as expected. The $c(4 \times 4)$ unit cell has three protrusions in the simulated image, which are not resolved in Fig. 3(a). This is because the present simulation assumes an infinitely sharp STM tip, providing more resolution than in the image obtained experimentally.

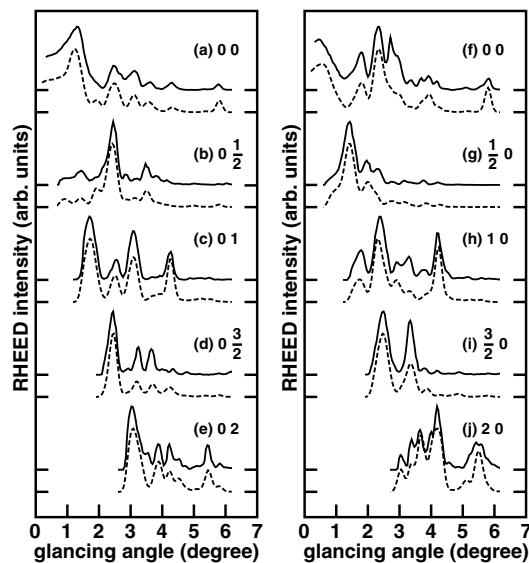


FIG. 4. RHEED rocking curves (solid curves) measured from the GaAs(001)- $c(4 \times 4)$ surface at 250 °C without As fluxes. The dashed curves are calculated from the optimized structure model shown in Fig. 5.

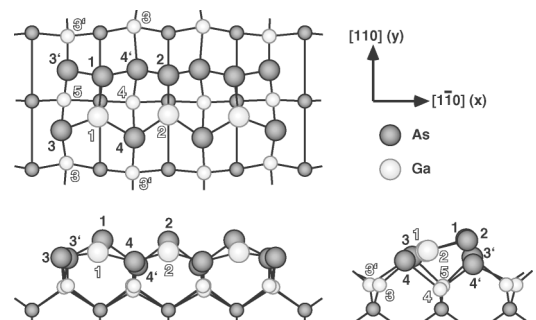


FIG. 5. Optimized structure model for the GaAs(001)- $c(4 \times 4)$ surface.

TABLE I. Atomic displacements from bulk positions in the optimized model in Å.

Atom	x	y	z
As1	0.28 ± 0.07	-0.55 ± 0.16	-0.15 ± 0.07
Ga1	-0.13 ± 0.13	1.09 ± 0.14	-0.85 ± 0.05
As2		-0.48 ± 0.27	-0.22 ± 0.13
Ga2		1.21 ± 0.28	-0.81 ± 0.11
As3	-0.28 ± 0.16	0.29 ± 0.14	0.25 ± 0.10
As3'	0.09 ± 0.16	-0.19 ± 0.15	0.21 ± 0.09
Ga3	0.01 ± 0.15	-0.14 ± 0.14	-0.01 ± 0.07
Ga3'	0.18 ± 0.10	-0.14 ± 0.09	-0.20 ± 0.05

Nevertheless, the relative shift of the bright features is well reproduced in the simulated image, providing further evidence for the Ga-As dimers.

The As coverage of the newly proposed model is 1.0, which is significantly smaller than the value for the three As-dimer model (1.75). On the other hand, high-resolution medium-energy ion scattering (MEIS) measurements showed that the $c(4 \times 4)$ surface is more Ga-rich than predicted from the three As-dimer model [12]: agreement between the MEIS data and Monte Carlo simulations can be achieved if the second-layer As atoms in the three As-dimer model are partially replaced by $\sim 1/2$ ML of Ga atoms. A similar atomic configuration was proposed on the basis of STM observations [1,3]. Thus, these MEIS and STM results are broadly consistent with the present analysis, although the existence of Ga at the outermost layer was not considered in Refs. [1,3,12].

Finally, a question should arise why the three As-dimer structure was identified by previous STM observations [1–3]. Our first-principles calculations showed that the three As-dimer structure should be the most stable under extreme As-rich conditions [27]. On the other hand, Kamiya *et al.* reported that the $c(4 \times 4)$ surface becomes less ordered under more As-rich conditions [21]. Such disordered $c(4 \times 4)$ surfaces show RD spectra different from those shown in Figs. 2(a) and 2(b) [21]. Thus, it seems reasonable to consider that the three As-dimer structure emerge only on less ordered $c(4 \times 4)$ surfaces prepared under more As-rich conditions.

In conclusion, we have proposed the new structure model for the GaAs(001)- $c(4 \times 4)$ surface. The proposed mixed dimer model explains well the present and previous experimental results in a consistent manner and is also supported by first-principles calculations. So far, atomistic growth processes on GaAs(001)- $c(4 \times 4)$ have been discussed on the assumption that the $c(4 \times 4)$ surface has the three As-dimer structure. The present results, however, clearly show that such an assumption is fatally inadequate and strongly suggest that a substantial reconsideration is required for a better understanding of the growth mechanisms on GaAs(001).

We are indebted to Dr. T. Hanada for use of the RHEED intensity calculation program and to Dr. J. Yamauchi for use of the first-principles calculation program. First-principles calculations were performed on Fujitsu VPP700/E at RIKEN. Helpful discussions with Dr. A. Nagashima and N. Naruse are gratefully acknowledged. This study was partly supported by NEDO.

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