GaP(111) reconstructed surface studied with STM and LEED

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Received 23 August 2002; accepted for publication 14 November 2002

Abstract

We have studied GaP(111) reconstructed clean surface with scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). We found that the surface consists of six equivalent mirror-symmetric domains and each domain has stripe structure. The stripe directions tilt from three (112) directions clockwise and counterclockwise at the same angle, resulting in six domains. The stripe period and the tilt angle are 1.30 nm and 6.8°, respectively. Magnified STM images revealed that all stripes in one domain have the same protrusion unit along the stripe direction, and that the origin of the protrusion unit is arranged by two vectors for the inter-stripe direction. The same unit-vector in the stripe direction and the two unit-vectors in the inter-stripe direction constitute two different surface-reconstruction units, namely units 1 and 2. We assigned the reconstruction matrices of units 1 and 2 in one domain to \( \begin{pmatrix} 3 & -1 \\ 2 & 5 \end{pmatrix} \) and \( \begin{pmatrix} 4 & 1 \\ 2 & 5 \end{pmatrix} \), respectively. A trial structure model assuming the same elements located at the protrusions well explains observed LEED patterns.

Keywords: Gallium phosphide; Surface relaxation and reconstruction; Surface structure, morphology, roughness, and topography; Scanning tunneling microscopy; Low energy electron diffraction (LEED)

1. Introduction

Gallium phosphide is one of the fundamental III–V compound semiconductors for optoelectronic devices. Various works on GaP crystals coupled with other materials have been performed to deduce valuable functions of these systems [1–3]. For instance, the heteroepitaxial growth of GaP on Si(001) substrate by virtue of small lattice mismatch and the following growth of GaAs or InP on the GaP buffer layers has been studied for optoelectronic integrated circuits [1]. The heteroepitaxial growth of GaAs on GaP(111) (i.e., (111)B, phosphorus face) substrate to provide the transparent substrate for GaAlAs diodes [2]. Recently, a single crystalline InN film with an excellent electronic transport property is successfully grown on GaP(111) substrate [3].

Well-defined GaP(110) cleaved surface have been investigated intensely so far not only for basic properties such as atomic structures and electronic
states but also photo-induced surface-atom reactions [4,5]. However, other GaP surfaces such as polar (111) surface, are not yet understood well though some early works reported them [6-11]. In addition to the application of the heteroepitaxial growth on GaP(111) substrates, we point out a possibility of selective growth of the (111) surface; anisotropic growth rate of various GaP surfaces has been reported [12,13]. In GaAs(111) the selective growth technique is used for the fabrication of one-dimensional quantum-well wires [14]. The fundamental research of (111) surface structure will stimulate the device applications using the epitaxial crystal growth and the other fabrication technique.

On GaP(111) reconstructed surface, even the reconstruction unit itself is unclear. So far, Bommel and Crombeen [6], and others [7,8] reported 17 × 17 super-structure of GaP(111) surface from low-energy electron diffraction (LEED) analysis. On the other hand, Wang et al. [9] suggested \(\sqrt{247} \times \sqrt{247} - R22.7^\circ\) super-structure from their LEED pattern. In the present paper we will show different reconstruction structure and morphological structure of GaP(111) clean surface from scanning tunneling microscopy (STM) and LEED observations.

The STM can reveal domain structure and atomic-scaled protrusion arrangement, which are sometimes hard to be determined by electron diffraction methods. On the other hand, the LEED can evaluate dimensions of reconstruction units and suggest atomic structure models, more precisely, referring the STM results. Therefore, the combination of STM and LEED can provide much more realistic model for unknown surfaces.

2. Experimental

The experiment was performed in an ultra-high vacuum (UHV) system equipped with an Ar-ion sputtering gun, a room-temperature STM (Omicron, micro-STM) and a LEED optics (OCI, BDL-600). The detailed setup is described elsewhere [15].

A GaP(111) mirror-polished wafer (0.3 mm in thickness, n-type, S doped at 2–10 × 10^{17} cm^{-3}) was cut in size of 4 × 15 mm², etched in HNO₃–HCl–H₂O (2:2:1) at 55–60 °C for 10 min, and rinsed in deionized water. Before the STM and LEED observations the specimen was sputtered (500 eV, 60° in incident angle, 1.5 μA/cm², 30 min) and annealed (500–600 °C, a few min) in UHV for several times repeatedly. We obtained stable reconstructed LEED patterns, which are similar to the previous reports [6-9]. The typical STM conditions were topographic image mode, sample bias-voltage \(V_s + 1.0\) V, and tunneling current \(I_t\) 0.1 nA. The STM tip was a 0.2 mmφ tungsten wire sharpened by electrolytic etching. An estimated scale-error in STM images due to the thermal drift is ±several % though we compensated it lately by calculation (Appendix A).

3. Results and discussion

Fig. 1(a) and (b) show typical LEED patterns at 30 and 40 eV, respectively. A schematic diagram of the patterns is illustrated in Fig. 1(c). In the LEED patterns we can recognize that 12 super-spots (one of them labeled as F) appear around the (00) spot (O) at the same distance \(|OF|\) and also other 12 super-spots (S) at the same \(|OS|\), and that the patterns are represented by the superposition of these super-spots around all fundamental spots. The intensity of the super-spots strongly changed with the primary electron energy. For instance, at 30 eV (Fig. 1(a)) super-spots corresponding to \(S, S'\) and \(S''\) have similar intensities, while super-spot \(S'\) becomes stronger than \(S\) and \(S''\) at 40 eV (Fig. 1(b)).

We could not observe other super-spots, in agreement with the previous works [6,9]. We note that Fig. 1(a) and (b) include modified background due to Morić pattern of the grid meshes. Weak streaks are also seen between the fundamental spots. The intensity of the streaks increased with increasing the dose and the kinetic energy of the Ar sputtering.

The obtained relations for the super-spots are \(|OF|/|OS|, |OS|/|OF| = 2.00 ± 0.05, \angle S-O-Q = 6.8° ± 0.5°, and |OP|/|OF| = 3.9 ± 0.1, here \(OQ\) is parallel to the [1 1 0] direction and \(P(R)\) is (1 0) spot ((0 1) spot). These values are the same for super-
spots from the other fundamental spots. The results lead to a commensurate reconstruction, \( 17OF = 5OP = 2OR \).

One might consider that the commensurate reconstruction suggests \( 17 \times 17 \) unit with many extinct super-spots (solid parallelograms in Fig. 1(c)), as suggested by the previous works [6–8]. However, the \( 17 \times 17 \) reconstruction and also the \( \sqrt{247} \times \sqrt{247} \) reconstruction are denied by our following STM results; this surface is not constituted by a single domain but six domains.

One might consider that \( OF \) and \( OF' \) form a new reconstructed reciprocal unit in one domain (a dotted parallelogram in Fig. 1(c)) with many extinct super-spots (one of them labeled as ‘\( \times \)’). However, we found that this is not true; either \( OF \) or \( OF' \) is a reciprocal unit-vector of the domain and the other is that of the other domain. In general, the reciprocal surface includes two independent unit-vectors when a domain consists of a single reconstruction unit. When the domain consists of mixture of multiple units, we can not define two unit-vectors in the domain simultaneously. Actually, one domain of the GaP(111) reconstruction surface includes two different units, and these will be displayed later. Therefore, when we try to study unclear surface of which diffraction patterns can be interpreted into many reconstruction models due to the lack of the information for local structures, such as domain and atomic-scale structures, we should combine other surface analysis techniques to observe the local structures.

Fig. 2 shows a wide area STM image of \( 390 \times 390 \) nm\(^2\). The stacks of wide terraces (\( \geq \) several tens nm in size) are seen. The shape of terrace tends to be a hexagon: the step-edge direction is nearly parallel to \( \langle \overline{1} \overline{1} 0 \rangle \) (i.e., \( \overline{1} \overline{1} 0 \), \( \overline{1} 0 1 \) and

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Fig. 1. LEED patterns of GaP(111) reconstructed surface at (a) 30 eV and (b) 40 eV. A schematic diagram of the pattern is also shown in (c). Symbols \( O \), \( P \) and \( R \) present \((00),(10)\) and \((01)\) fundamental spots, respectively. Vector \( OQ \) is parallel to the \([1\overline{1} 0]\) direction. Some super-spots are labeled as \( F, F', S, S', S'' \) and \( S' \). A smallest solid parallelogram presents a \( 17 \times 17 \) unit. A dotted parallelogram with ‘\( x \)’ presents one of reconstruction units in wrong models.

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Fig. 2. A wide image of GaP(111) surface \((390 \times 390 \) nm\(^2\), \( V_s = +1.0 \) V, and \( I_\text{t} = 0.1 \) nA). Flat terraces and small clusters are seen. The measured step height corresponds to the \((111)\) bilayer height.
[01\bar{1}]) directions. The measured step height was 0.32 nm being consistent with an ideal value 0.315 nm of the (111) bilayer height. Small clusters (\leq 10 nm) are also seen on the terraces. We could not remove the clusters in our preparation method except the heavy (1 keV) sputtering. However, the heavy sputtering destroyed the substrate before removing all the clusters. After annealing the heavily sputtered surface, STM images showed a number of small islands with the hexagonal structure resulting in the streaks in the LEED patterns.

A magnified STM image on a terrace is shown in Fig. 3 with 70 \times 70 \text{ nm}^2 in scanning size. The figure shows that the surface consists of stripes. The measured stripe period \( d \) was 1.3 nm. The stripe-domain boundary is also seen on the terrace. The density of domains larger than 100 nm in size (e.g., Fig. 3) was small. Typical size of domain was a few 10 nm. Fig. 4(a) shows a current image of multiple domains with small clusters. We found six domains with different directions of stripes on GaP(111) reconstructed surface. The figure displays five of them. The white lines indicate the stripe directions and solid curves domain boundaries or steps for the eye guide. The domains are classified by symbols \( A, B, C, D, E, \) and \( F \). The relation of the stripe directions to the crystal axis is illustrated in Fig. 4(b). We realize that the stripe directions tilt from three \{112\} (i.e., \{1\overline{1}2\}, \{121\} and \{2\overline{1}1\}) directions by +7° and -7°. The common absolute tilt-angles for domains \( A \) and \( B \) from the \{112\} axis suggests that domains \( A \) and \( B \) are mirror symmetric to the \{110\} plane, in other words, they are twins. Therefore, the reconstructed surface consists of six equivalent mirror-symmetric domains (three pairs of twin domains, \( A \) and \( B \), \( C \) and \( D \), and \( E \) and \( F \)).

The coherent length of our LEED optics is 10–20 nm at 100 eV, while the typical domain size was a few 10 nm. Since the domain size is wider than the coherent length, the LEED patterns corre-

![Fig. 3. A terrace image of GaP(111) surface (70 \times 70 \text{ nm}^2, V_s = +1.0 \text{ V}, and I_T = 0.1 \text{ nA}). Stripe domains and domain boundary are seen. Symbol \( d \) is the distance of stripe period.](image)

![Fig. 4. A multiple-domain image of GaP(111) surface (150 \times 90 \text{ nm}^2, V_s = +1.0 \text{ V}, and I_T = 0.1 \text{ nA}). The eye guide indicates stripe directions of different domains and domain boundaries (or steps). Domain symbols \( A-F \) are defined in (b) with stripe directions. The ladder patterns in (b) imply reconstruction units explained in Figs. 5 and 6.](image)
Fig. 5. A magnified stripe image of GaP(111) surface (5.4 × 6.3 nm², V₀ = +0.8 V, and I₀ = 0.2 nA). Black and gray open circles are marked at the protrusions. The black circles present the origins of surface reconstruction units. Each unit includes approximately ten protrusions. Some protrusions are paired by solid lines. We can recognize unit 1 (a₁ and b₁) and unit 2 (a₂ and b₂), taking account of the distance of the paired protrusion from the origin. The stripes of units 1 and 2 are randomly distributed.

Fig. 6. A trial model of surface reconstruction units on the ideal 1 × 1 (a₀ and b₀) mesh. Closed and open circles present P and Ga atoms, respectively. Large gray circles present the protrusions in Fig. 5, assuming the origin of the reconstruction units on top of a P atom. Reconstruction matrices of units 1 and 2 are \( \begin{pmatrix} 3/2 & -1/2 \\ 1 & 0 \end{pmatrix} \) and \( \begin{pmatrix} 4/2 & 1/2 \\ 1 & 0 \end{pmatrix} \), respectively.

LEED results are more accurate than those from the STM. In this simple stripe structure we expect that the third-order and over super-spots indicate similar intensities to the first- or the second-order super-spots in the LEED patterns, however, we could not observe the higher-order spots. Moreover, if the stripe has periodic structure inside along the stripe direction, we also expect other super-spots in this direction. However, they were not observed. Their disappearance can be explained by a complicated atomic structure of the stripe, as discussed later.

Fig. 5 displays a magnified STM image of the stripes in domain A. The scanning size is 5.4 × 6.3
nm$^2$, $V_S = +0.8$ V and $I_T = 0.2$ nA. Black and gray open circles are marked at the protrusions for the eye guide. We note the same protrusion units in all stripes. We observed at least over ten protrusion-units periodically repeated within a stripe without any phase change. The black circles present the origins of the protrusion units. We can distinguish the origin protrusion since the distance of the paired protrusions including the origin (solid lines) is longer than that of the other pairs (gray lines). Vector $b_S$ is the unit-vector of the protrusion arrangement repeated along the stripe direction. However, for the inter-stripe direction, we notice two unit-vectors $\vec{a}_{S1}$ and $\vec{a}_{S2}$ connecting the origins of the protrusion units. Thus, the single domain has two phases of the stripes. The stripe in each phase consists of either reconstruction unit 1 ($\vec{a}_{S1}$ and $b_S$) or unit 2 ($\vec{a}_{S2}$ and $b_S$). We observed only two types of the reconstruction units and the random mixture of the stripes of units 1 and 2, in a few different regions including several stripes. The density of units 1 and 2 stripes were almost the same.

As shown in Fig. 5 each unit includes approximately ten protrusions. Since this is an empty state image ($V_S = +0.8$ V) the protrusions would reflect Ga-induced electronic surface states as those on (110) surfaces [4]. Actually the electron-energy loss spectroscopy work [10] suggested the existence of empty surface states at 1.4 eV on Ga-rich GaP(111) surface and filled surface states at 0.8 eV on P-rich surface from the valence band maximum in the band gap (of which energy is 2.27 eV), though these surfaces showed a diffuse $1 \times 1$ LEED patterns. We expect that the surface Fermi level is pinned between these surface states and tunneling electrons can flow the conduction band through the Ga-induced surface states.

For filled states we could not obtain atomic protrusion images on the bright part in the stripe since the corrugation of the stripes themselves was very weak. However, we observed stripe images at both empty and filled states $V_S = +1.6$ and $-0.8$ V, respectively. This bias independence of the stripe images suggests that the groove part in the stripe is caused by geometric atomic structure but not electronic structure.

We propose commensurate reconstruction units on the basis of STM and LEED results as shown in Fig. 6. Here, vectors $a_0$ and $b_0$ indicate a $1 \times 1$ unit of the ideal surface. Closed and open circles correspond to P and Ga atoms, respectively. Large gray circles present the protrusions in Fig. 5 when we assume that the origin protrusion locates on top of a P atom. The matrix notation of unit 1 is

$$
\begin{pmatrix}
3 & -1 \\
2 & 5
\end{pmatrix}
$$

and that of unit 2 is

$$
\begin{pmatrix}
4 & 1 \\
2 & 5
\end{pmatrix}
$$

In the proposed reconstruction the widths of stripes are 1.300 nm for unit 1 and 1.377 nm for unit 2, and the tilt angle is 6.6°. This tilt angle is in good agreement with the LEED results. In the STM images it was hard to distinguish the small difference of the stripe widths owing to the drift. The similar occupation probability of units 1 and 2 in the obtained STM images suggests 1.34 nm in the average stripe period from this model. The averaged period is also within the error bar of the period obtained by the LEED patterns (1.30 ± 0.04 nm).

Fig. 5 shows the same protrusion arrangement on the bright part of the stripe. We recognized that the inter-stripe relation indicates two phases corresponding to units 1 and 2. These results imply that the atomic structure on the bright part is very stable and that the interaction between two adjacent stripes leads to the two phases. We consider that the stable quasi one-dimensional structure lies on the underneath substrate in either phase with the same energy minimum, that is, a simple double-well potential for the stable atomic structure.

Instead of the interpretation of units 1 and 2, one might consider that only a unit, either unit 1 or unit 2, including the stable atomic structure, determines the reconstructed surface assuming the above phase change which can occur stripe by stripe. Such an interpretation would be possible if the underneath substrate is completely the same for units 1 and 2. However, the structure of the underneath substrate, especially the dark part of the stripe, is unclear yet. Thus in this paper, we consider the two different units which include the above interpretation in a wide sense.

In Fig. 5 the protrusion arrangement in a bright stripe seems to be slightly asymmetric for the 180°
rotation around the surface normal direction (C\textsubscript{1} symmetry). Thus we placed the gray circles in the asymmetric arrangement. However, we empirically know that STM images on the same area are varied with the condition, such as the shape of the tip apex, the scanning angle, the feed-back condition, and so on. Hence, we can not deny the possibility of the C\textsubscript{2}-symmetric atomic structure; the protrusion arrangement is symmetric for the 180° rotation. Actually, some of other STM images could be interpreted as the C\textsubscript{2}-symmetric arrangement. Therefore, it is not yet obvious whether the atomic structure is C\textsubscript{1}-symmetric or C\textsubscript{2}-symmetric. In the case of the C\textsubscript{1} symmetry the anisotropy of the stable atomic structure would arise from the underneath Ga atoms in the second layer (Fig. 6) having geometric asymmetry for the 180° rotation, while in the C\textsubscript{2} symmetry only the P atoms in the first layer affect the atomic structure symmetry.

The reciprocal lattice of the reconstructed model surface is calculated for a single domain (Fig. 7(a)) and six domains (Fig. 7(b)). We assume the same atomic scattering factor located at the protrusions (Figs. 5 and 6) on the flat plane and randomly distributed stripes of units 1 and 2 in \( \approx 10 \times 10 \) nm\(^2\). The gray and solid parallelograms present the reciprocal lattice of units 1 and 2, respectively. We note that no peaks at the reciprocal lattice points of units 1 and 2 in the (01) direction originate from the extinction rule of the protrusion arrangement in the units, but not from the random distribution of the units. A simple calculation shows that the random distribution without the inside structures of the units results in streak patterns, for instance, a streak passing the above reciprocal lattice points, however, the streaks are disappeared owing to the inside structure in Fig. 7. The random distribution implies that we can not determine a reciprocal unit-vector in this direction.

Although the extinction rule and the random distribution dilute reciprocal peaks, we can still recognize strong reciprocal peaks in the other direction, being the inter-stripe direction. Peak 1 corresponds to the mixture of (\(5 \frac{7}{12} - \frac{1}{2}\)) spot for unit 1 and (\(5 \frac{7}{18} - \frac{1}{2}\)) spot for unit 2. These spots are very close to each other and peak 1 does not split because of the random distribution. Hence we understand that peak 1 corresponds to the reciprocal unit-vector in the inter-stripe direction.

The intensities of the third-order and over super-spots are much weaker than those of the first- and the second-order ones in agreement with the LEED results. However, the higher-order super-spots are faintly visible in Fig. 7(a). This is in disagreement with the LEED results where the

![Fig. 7. Calculated reciprocal lattice for (a) a single domain and (b) six domains. The gray and solid parallelograms indicate the reciprocal lattice units 1 and 2, respectively. Peaks 1–3 present the first-, the second- and the third-order super-spots, respectively. In the right half of (b) the third-order and over super-spots are removed for the eye guide. The LEED patterns (Fig. 1) are well represented by (b).](image-url)
higher-order super-spots are extremely weak or extinct. The difference would be attributed to our simple model. More suitable models with certain atomic structures will extinct the higher-order super-spots. To understand spot arrangement easily we removed the higher-order super-spots in the right half of Fig. 7(b). This pattern is quite similar to the LEED patterns of Fig. 1. Therefore, for the first approximation, the trial model in Fig. 6 can explain the LEED results well. As shown in Fig. 1(a) and (b) spot intensity I is a function of incident electron energy $V$. Thus, the detailed LEED $I-V$ analysis (or other diffraction analyses) will reveal the atomic structure more precisely on the basis of the above STM results.

4. Conclusion

Clean GaP(1 1 1) reconstructed surface has been studied with STM and LEED. The STM images display that the surface consists of six domains with stripes of which directions tilt from $\langle 1 1 2 \rangle$ clockwise and counterclockwise. The result suggests that two domains are twin with respected to $\{ 1 1 0 \}$ planes and three twins exist on the surface. The LEED results indicate the stripe periodic of $1.30 \pm 0.04$ nm and the tilt angle of $6.8^\circ \pm 0.5^\circ$. The magnified STM images show the same protrusion unit in all stripes. The protrusion unit is repeated along the stripe direction by unit-vector $b_s$. For the inter-stripe direction there are two unit-vectors $a_{s1}$ and $a_{s2}$. The surface reconstruction units are attributed to unit 1 ($a_{s1}$ and $b_s$) and unit 2 ($a_{s2}$ and $b_s$), and their reconstruction matrices are assigned to $\begin{pmatrix} 3 & -1 \\ 2 & 5 \end{pmatrix}$ and $\begin{pmatrix} 4 & 1 \\ 2 & 5 \end{pmatrix}$, respectively. A single domain consists of the random mixture of the stripes of units 1 and 2. The bias-voltage dependence of the stripes suggests that geometrical atomic positions form the stripes but not electronic states such as dangling-bond states. The trial model on the basis of the reconstruction matrices and protrusion structure observed in the STM images well explain the LEED patterns. The detailed diffraction analyses will reveal the atomic structure of each unit.

Acknowledgements

The authors thank T. Kawamura for discussions of the LEED results, and thank T. Nishida for X-ray diffraction. This work was performed using facilities of the Institute for Solid State Physics, the University of Tokyo. This work was partially supported by a grant-in-aid for University and Society Collaboration (11792001) from the Ministry of Education, Science, Sports and Culture in Japan.

Appendix A. Calculation of drift compensation for obtained STM images

We consider two $xyz$-right-hand coordinate systems ($z$ is the surface normal direction): the real surface system $xe_x + ye_y$ and the scanning image system $xe'_x + ye'_y$. The latter system is rotated at the scanning angle $\theta$ counterclockwise ($\theta \geq 0$) from the former. Here, $e_{x',y'}$ and $e_{x,y}$ are unit-vectors on each system. Prime indicates variables on the scanning image system. The rotation matrix is defined as $R = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix}$. The scanning speed [nm/s] $\vec{v}_s = \begin{pmatrix} v_{sx}' \\ v_{sy}' \end{pmatrix}$ ($v_{sx}' \gg v_{sy}'$), and the scanning time for frame-to-frame $T[s]$ are given parameters. We assume a fixed piezo-electrostriction constant [nm/V] for the $x$ and $y$ directions.

The simple way to estimate the drift speed $\vec{v}_{d}$ [nm/s] is measuring the same noticeable position such as a point defect on the series scanning images; $\vec{r}_1$ [nm] is on the first scan and $\vec{r}_2$ [nm] is on the second scan for the same surface position. In this case we obtain

$\vec{v}_{d} = \{ R(\vec{r}_2 - \vec{r}_1) \} / \{ T + (\vec{r}_2 - \vec{r}_1) \bullet \vec{p}_s' \}$

here

$\vec{p}_s' = \begin{pmatrix} 1 / v_{sx}' \\ 1 / v_{sy}' \end{pmatrix}$.

Then the drift correction matrix $D$ is given by

$D = R - \begin{pmatrix} v_{dx} / v_{sx}' & v_{dx} / v_{sy}' \\ v_{dy} / v_{sx}' & v_{dy} / v_{sy}' \end{pmatrix}$.
We obtain the real image with the drift compensation \( \left( \begin{array}{c} x \\ y \end{array} \right) \) from the observed image without the compensation \( \left( \begin{array}{c} x' \\ y' \end{array} \right) \) by the transformation \( \left( \begin{array}{c} x \\ y \end{array} \right) = D \left( \begin{array}{c} x' \\ y' \end{array} \right) \).

References