Structures of As-Rich GaAs(001)-(2 × 4) Reconstructions

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Scanning tunneling microscope (STM) images together with reflection high-energy electron diffraction (RHEED) showed for the first time convincingly that the molecular-beam epitaxially grown GaAs(001)-(2 × 4) α, β, and γ phases all have the same outermost surface layer of the unit cell, which consists of two As dimers and two dimer vacancies. Based on the STM and RHEED observations and dynamical RHEED calculation, a structure model consistent with various observations is proposed.

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The GaAs(001) surface grown by molecular-beam epitaxy (MBE) exhibits various phases ranging from the most As-rich $c(4 \times 4)$ to the Ga-rich (4 × 2) phase [1–19]. The As-rich (2 × 4) phases are the most important structures commonly used in the technological applications of MBE.

It is generally accepted that the top layer of the As-rich (2 × 4) phase is made of As dimers along the [$\bar{1}$10] direction [3]. There are two distinctly different models of the (2 × 4) phase unit cell: one with three As dimers and one dimer vacancy and the other with two As dimers and two dimer vacancies at the outermost surface layer. Chadi performed tight-binding-based total-energy calculations and suggested that there are two stable phases possible with three As dimers [Fig. 1(a)] and with two As dimers [Fig. 1(b)] [17]. Scanning tunneling microscopy (STM) has been utilized for the study of the unit-cell structure. Pashley *et al.* obtained the first STM images of the (2 × 4) phase with an *ex situ* MBE and the As-capping technique [12], and concluded that Chadi's three As-dimer model [Fig. 1(a)] is most appropriate. Biegelsen *et al.* also supported the three As-dimer model based on their STM observation of the *in situ* MBE grown (2 × 4) phase, although they observed the (2 × 4) phase with the two As-dimer unit grown under less As-rich conditions [13].

Farrell and Palmstrom (FP) analyzed the experimental results for the (2 × 4) phase and classified them into three (α, β, and γ) phases depending on the RHEED (reflection high-energy electron diffraction) spot intensities [4]. According to their analysis the $\frac{2}{4}$ spot intensity is weak in the α phase, is strong and equal to $\frac{1}{4}$ and $\frac{3}{4}$ in the β phase, and is almost absent in the γ phase. Based on the kinematical RHEED calculation, they concluded that the outermost surface layer of the unit cell is made of two As dimers for the α phase [Fig. 1(c)], three As dimers for the β phase [Fig. 1(a)], and extra As dimers sitting on the β phase for the γ phase [Fig. 1(d)] [4]. The two As-dimer model was later examined by Northrup and Froyen (NF) [19], and the relaxation of the second layer Ga atoms was introduced for the stability of the model [Fig. 1(c)]. FP's scheme has been used widely for experimental [10,11,14,16] and theoretical [18,19] study. However, Heller *et al.* recently reported, based on their *in situ* STM observation, that the two As-dimer unit is dominant in various (2 × 4) phases [15]. The stability of the γ phase model [Fig. 1(d)] was also questioned by the first-principles calculation [19].

In this Letter, we report, based on the first comprehensive study of the GaAs(001) surface, using STM images, simultaneous RHEED observations, and dynamical RHEED calculations, that the outermost surface layer of the unit cell of the (2 × 4) α, β, and γ phases all consist of two As dimers and that the α and β phases are different in the atomic arrangements of the second and third layers exposed by the dimer vacancy rows. It is also concluded that the γ phase is the less ordered β phase with "open areas" exposing the underneath disordered $c(4 \times 4)$ phase.

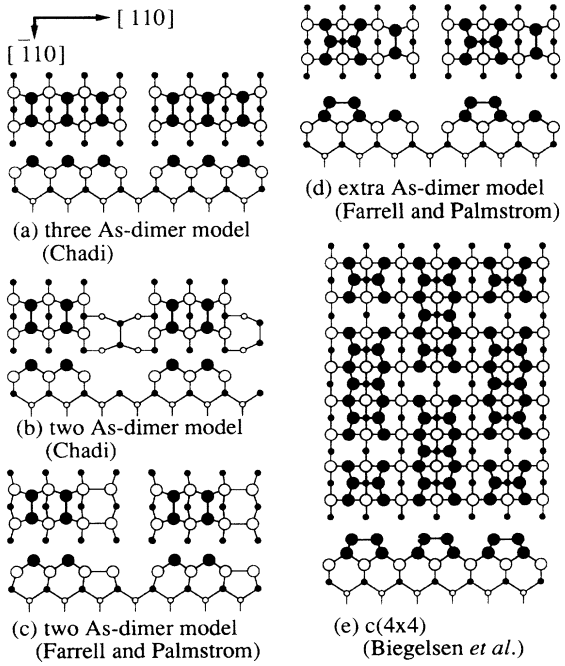

FIG. 1. Structure models (a), (b), (c), and (d) for the As-rich GaAs(001)-(2 × 4) phases and (e) for the $c(4 \times 4)$ phase. Filled (open) circles denote As (Ga) atoms. The As surface coverages are (a) 0.75, (b) 0.75, (c) 0.5, (d)1, and (e) 1.75 ML.

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The experiments were carried out by an FI-STM (field-ion scanning tunneling microscope) [20] combined with the MBE. The surface oxide layer was evaporated at 600 °C, and the buffer layers were grown on the GaAs(001) specimen (dopant Si, 1×10^{18} cm^{-3}) at the growth temperature in the range of 540–630 °C, at the As_4/Ga flux ratio of ~30 and at a growth rate of 0.15 μm/h. The Si doping level was calibrated by secondary-ion mass spectroscopy and kept below 1.5×10^{18} cm^{-3} to minimize dopant-induced surface defects [14]. The RHEED intensity profiles were monitored during the sample preparation and after the STM observation, using the beam energy of 10.0 KeV and the incident angle of 1.6° ± 0.2°. The STM images were taken at the sample bias of $V_s = -3.5$ to −2.0 V, and the current $I_t = 20$ pA. The β phase was prepared by annealing the substrate at 540–630 °C, maintaining the As_4 flux fluence until the $\frac{2}{4}$ intensity grew to the comparable intensity with the $\frac{1}{4}$ and $\frac{3}{4}$ following FP [4]. The α, γ, and $c(4 \times 4)$ phases were obtained by annealing at 640, 510, and 490 °C, respectively, while maintaining the As_4 flux fluence. The γ, β, and α phases were also obtained from the $c(4 \times 4)$ phase by gradually increasing the substrate temperature from 300 up to 460 °C without the As_4 flux [13].

Typical STM images of the α, β, and γ phases are shown in Figs. 2(a), 2(b), and 2(c), respectively, together with the enlarged images and the corresponding RHEED patterns taken at room temperature. We confirm the characteristic features in the RHEED spot intensities reported by FP. The $\frac{2}{4}$ feature of RHEED is weak for the α phase, relatively strong and comparable to $\frac{1}{4}$ and $\frac{3}{4}$ for the β phase, and absent for the γ phase. The RHEED patterns were basically the same during the growth (at elevated temperature) and after the STM observation (at room temperature), assuring the sufficiently high quenching rate. The zoom-in STM images show that there are two humps along the [110] direction in each unit cell [21]. Therefore, we conclude that the (2×4) outermost surface layer of the unit cell consists of two As dimers and two dimer vacancies for all the α, β, and γ phases.

The stable β phase [Fig. 2(b)] has a high degree of ordering and individual domains are large, extending over 300 Å along the [$\bar{1}$10] direction and 3000 Å along the [110] direction [22]. The α phase is less ordered and each domain is typically 60 and 500 Å in the [$\bar{1}$10] and [110] directions, respectively. The γ phase [Fig. 2(c)] is the least ordered and there are open areas randomly distributed, resulting in small domains of ~60 and 100 Å. We have found that the majority (60%) of open areas has the width of $d = 7a_0$ or larger [$a_0 = 4.0$ Å: the unit of the GaAs(001) 1×1 surface. Fig. 2(c) and Fig. 3(a) for the definition of d]. The narrow open region of $d = 5a_0$ is no more than a few percent. One can observe faint lines in the open area running in the [$\bar{1}$10] direction [shown by arrows in Fig. 2(c)]. These faint lines in the open area

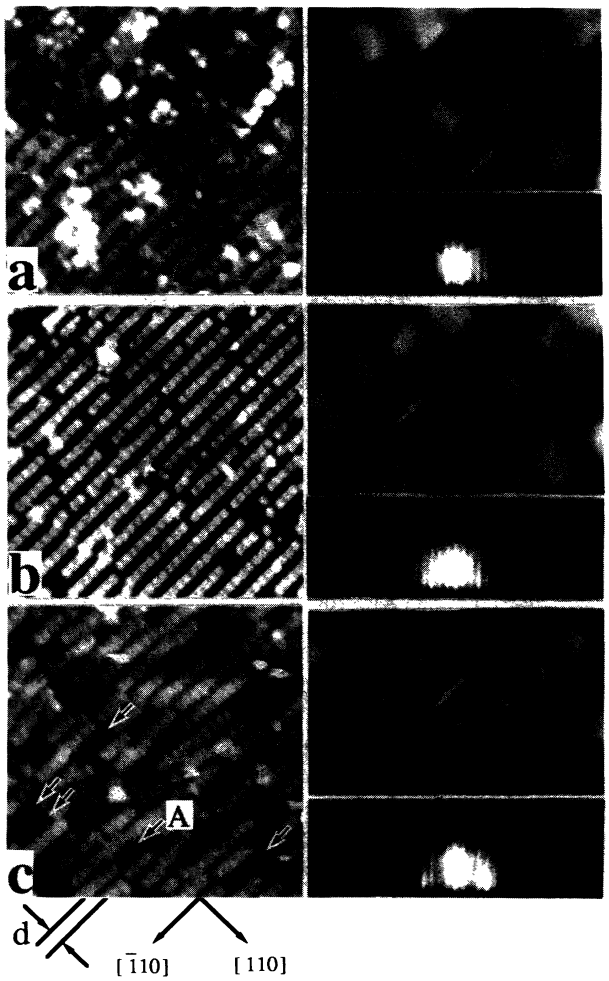

FIG. 2. Typical STM images (260 Å × 260 Å) of the (a) α, (b) β, and (c) γ phases together with the zoom-in images (44 Å × 28 Å) and their corresponding RHEED patterns.

lie 1.4 Å (one-half of the bilayer step height $h = 2.8$ Å) below the top As dimers. The depth profile of the STM images of the α, β, and γ phases reveals that the trough with $d \geq 5a_0$ is as deep as h for the α phase, while it is only $\frac{1}{2}h$ for the $\beta(\gamma)$ phase, suggesting the structural differences in the second and/or third layers.

In order to investigate the detailed nature of the γ phase, we followed the transition of the $c(4 \times 4)$ phase to the γ phase which takes place with decreasing As_4/Ga flux ratio, by utilizing the MEE (migration-enhanced epitaxy) technique [23,24]. The STM image in Fig. 4(a) is typical for the $c(4 \times 4)$ phase during the MEE growth

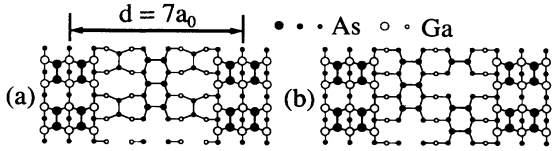

FIG. 3. Possible structure models of the open area with a separation $d = 7a_0$.

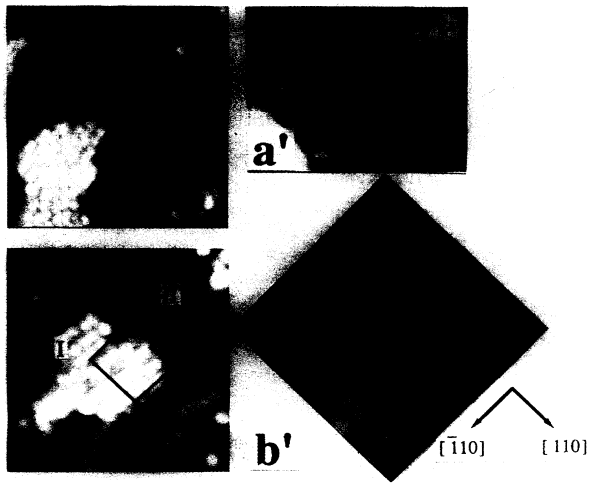

FIG. 4. Typical STM images (160 Å × 160 Å) of (a) the $c(4 \times 4)$ phase and (b) the mixed $c(4 \times 4)$ phase and (2×4) phases. (a′) and (b′) are their structure models. (Color code: green for Ga, blue for As on Ga, red for As on As, magenta for the second layer As. Open green circles elucidate the shape difference between the As dimers on Ga and the As dimers on As.)

at 500 °C with the As_4/Ga flux ratio of 20:1. The ordering is not perfect in the STM image, but a good quality $c(4 \times 4)$ RHEED pattern was observed as reported previously [4]. The STM image is consistent with the $c(4 \times 4)$ model shown in Fig. 1(e) and accepted by many groups [10,13,18,19]. We note that the model shows only the ideal case and that the number of the top layer As dimers may vary in the real surface [19].

Figure 4(b) shows a mixture of the $c(4 \times 4)$ and (2×4) phases, grown by MEE at 500 °C using the As_4/Ga flux ratio of 17:1. In Figs. 4(a) and 4(b), there are three types of bright protrusions: (I) brightest, (II) medium intensity, and (III) least bright. The measured height difference is $\frac{1}{2}h$ between both type I and type II, and type II and type III, and h between type I and type III. Type I and type III are imaged round, while type II is imaged elongated toward the [$\bar{1}$10] direction as illustrated (open green circle) in Fig. 4(b′) and is the same as an As dimer in the zoomed-in image in Fig. 2(c), suggesting different chemical environments between them.

We reconstructed the structure model of Fig. 4 as follows: (1) Based on the discussion above on Fig. 4(a), type III protrusions of $c(4 \times 4)$ are assigned to be As dimers sitting on top of the As layer. (2) Type II protrusions are assigned to be two As dimers on the Ga atoms, similar to the As dimers in the (2×4) phase, based on the height difference. (3) The brightest spots, type I, are assigned to be As dimers sitting on top of the As layer, similar to type III: the As dimers in the $c(4 \times 4)$ phase, based on the height and image shape similarity between Type I and III and also the As-rich environments during the growth. (4) Then, As atoms under these As dimers can be positioned uniquely. Similarly the positions of Ga atoms are plotted. In this procedure, every step is unique, except that some of the type II As dimers cannot be resolved clearly because of their marginal contrast. Importantly, this ambiguity does not impose any adverse effect on our main arguments and conclusions.

To fully understand the structures of the α, β, and γ phases, we have calculated the RHEED spot intensities for the possible (2×4) models using the dynamical theory [25]. Since the details of the calculation will be published elsewhere a brief description is given here. For the calculation, 19 beams in the zeroth Laue zone of the [$\bar{1}$10] incidence were taken into account. As the RHEED intensities in the zeroth Laue zone are insensitive to the displacement lateral to the incident direction, relaxations along the [$\bar{1}$10] direction have not been taken into account. The atom positions being used are (1) the As dimers contracted by 0.2 Å perpendicular to the surface and have no displacement along the [110] direction and (2) other atoms occupying the bulk positions. We have also examined the influence of the small changes in the atom positions to the spot intensities. In the case of the two As-dimer model of Fig. 1(c), we studied the effect of the dimerization and relaxation of the second layer Ga atoms. The rocking curves for the five zeroth order Laue zone reflections (0 0), (0 $\frac{1}{4}$), (0 $\frac{1}{2}$), (0 $\frac{3}{4}$), and (0 1) were calculated, and the spot intensities were obtained by averaging over the incident angle of $\pm 0.2°$. The results are summarized in Figs. 5(a), 5(b), 5(c), and 5(d) for models (a), (b), (c), and (d) of Fig. 1, respectively.

In order to qualitatively compare the theory and experiment, we used a photomultiplier with pin point fiber optics to measure the RHEED spot intensities. Those results are plotted in Figs. 5(e), 5(f), and 5(g) after deconvolution. Calculated spot intensities (a) and (d) do not agree with any experimental results. We note that the spot intensities

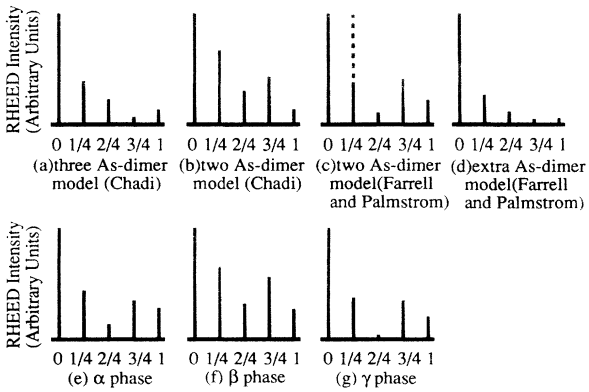

FIG. 5. Dynamical theory RHEED spot intensities for the (2×4)-phase models in Figs. 1(a), 1(b), 1(c), and 1(d) and spot intensities measured experimentally for the (e) α, (f) β, and (g) γ phases. The dotted line in (c) indicates possible intensity variation depending on the degree of the second layer Ga relaxation and the first layer As dimer contraction.

reported by McCoy *et al.* for model (a) of Fig. 1 are very similar to Fig. 5(a) [26]. Furthermore, these models are not consistent with the detailed analysis of the STM images (Fig. 2). Therefore, models (a) and (d) in Fig. 1 are completely ruled out. Spot intensities (c) for the two As-dimer model proposed by FP [4] with the relaxation of the second layer Ga atoms introduced by NF [19] agree with those of the α phase [Fig. 5(e)]. While the $\frac{2}{4}$ spot intensity is always weak, the $\frac{1}{4}$ spot intensity for this model is sensitive to (1) the formation of the Ga dimers in the second layer proposed by FP [4] and (2) the contraction of the As dimers [broken line of the $\frac{1}{4}$ feature of Fig. 5(d)]. Spot intensities (b) for the two As-dimer model proposed by Chadi [Fig. 1(b)] agree well with spot intensities (f) of the β phase. While the kinematical calculation for this model yields a very weak $\frac{2}{4}$ intensity [8% of the (0 0) spot intensity], the dynamical effect enhances the $\frac{2}{4}$ spot intensity, resulting in a relatively strong $\frac{2}{4}$ spot intensity, comparable to the $\frac{1}{4}$ and $\frac{3}{4}$ intensities. We have also found that the spot intensities for this model are not sensitive to the relaxation of the second layer Ga atoms along the [110] direction or the contraction of the As dimers. In the case of the γ phase which consists of randomly distributed small domains of the β phase, the dynamical effect diminishes. Thus, the kinematical calculation yields the characteristic absence of the $\frac{2}{4}$ fractional order feature and agrees well with spot intensities (g).

We can now reconstruct the open area with $d = 7a_0$ of the γ phase [Fig. 2(c)]. The faint line running at the middle of the open area is 1.4 Å lower than the top As layer. The fact that both the top layer and lower layer are imaged brightly in the filled state and that the height difference is 1.4 Å ($\frac{1}{2}h$) imply that both of them are the image of As dimers. Since the top layer rows consist of two As dimers [Fig. 2(b)] and there are five atomic spacings ($5a_0$) in the open area, there are only two reasonable structures, as shown in Fig. 3(a) and 3(b). A single faint line in the middle prefers model (a) over (b). This model can be further supported by the fact that Fig. 3(a) is simply an addition of a building block of the $c(4 \times 4)$ phase (As double layer) at the middle of the β phase. We therefore conclude that the features we observe in the open area of the γ phase [Fig. 2(c)] consist of the unit of the $c(4 \times 4)$ phase, namely As dimers sitting on top of the As layer.

Our proposed model implies that the surface As coverages of the (2×4) α, β, γ, and $c(4 \times 4)$ phases are 0.5, 0.75 (0.25 ML in the third layer), ~1, and 1.75 monolayer, respectively, which are consistent with the previous results [10,19]. We expect that our model for the (2×4) α, β, and γ phases can explain the recent results by Falta *et al.* [11]. The successive increase of the Ga intensity in their results from $c(4 \times 4)$ to γ, β, and to α is consistent with our model. The disagreement Falta *et al.* pointed out regarding the As top layer models [11] concerns the absolute value in the As/Ga intensity ratio for the (2×4) α phase. However, in the detailed NF model of the α phase [Fig. 1(c)] [19], all the first layer As dimers and the second layer Ga atoms are shifted from the original position and should therefore reduce the blocking of the scattering intensity from the sixth layer Ga atoms, which may increase the Ga intensity and resolve the intriguing discrepancy.

In conclusion, we have performed a systematic study of the MEE/MBE grown As-rich GaAs(001)-$c(4 \times 4)$ and (2×4) α, β, and γ phases by using STM, RHEED and dynamical RHEED calculation, and proposed a model: the two As-dimer model by Chadi for the most stable β phase, and the FP two As-dimer model incorporated with the relaxation proposed by NF for the α phase, while the γ phase is the locally ordered β phase with the disordered $c(4 \times 4)$ unit in the open area.

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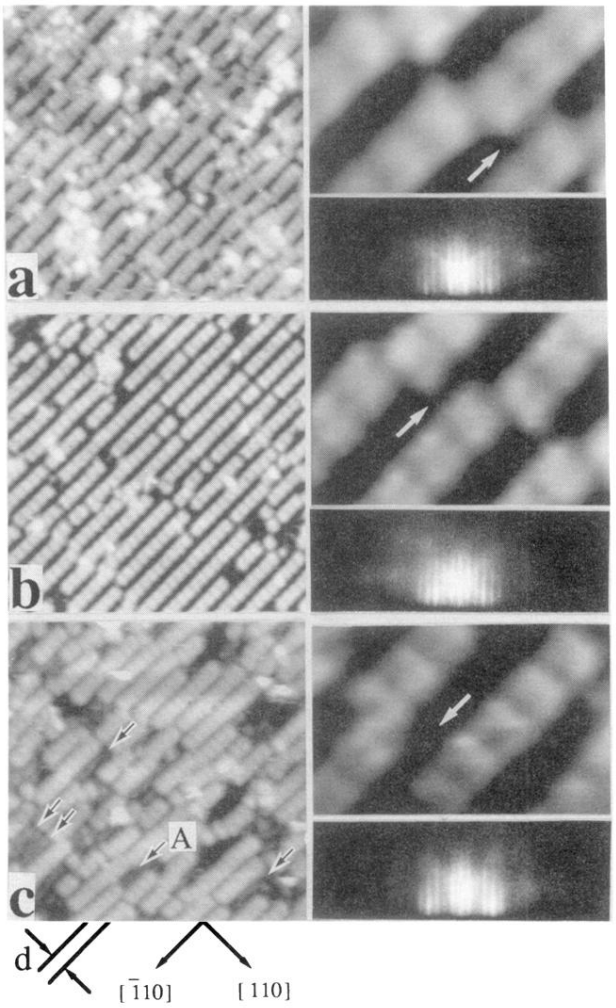

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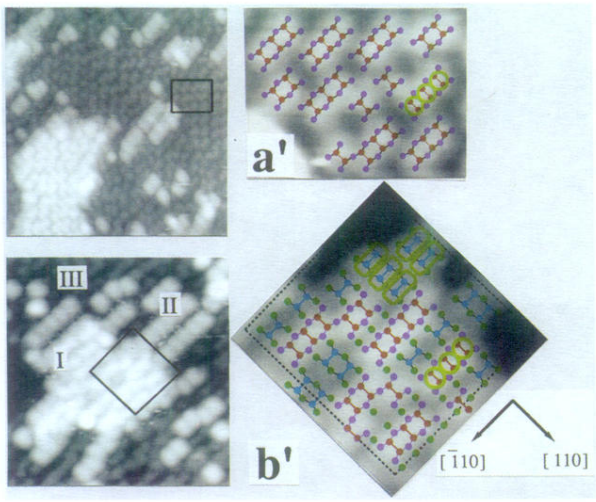

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