The α, β, and γ phases of the GaAs(001)-(2 × 4) surface have been studied using rocking-curve analysis of reflection high-energy electron diffraction (RHEED) and reflectance difference spectroscopy (RDS). We have measured RHEED rocking curves and RD spectra from GaAs(001) under an As flux of 2.5 × 10⁻⁷ Torr, and have identified the temperature ranges where each of the α, β, and γ phases is stable. The 2 × 4 reconstruction was observed in the range of 480–600 °C. The β phase, which is stable in the range of 510–550 °C, has a β 2(2 × 4) structure, in good agreement with previous experimental and theoretical results. The γ and α phases are stable below 510 °C and above 550 °C, respectively. While the data from the γ phase are well explained by a mixture of β 2(2 × 4) and c(4 × 4) phases, we propose that the α phase has a β 2(2 × 4) structure, the atomic coordinates of which are slightly different from those of the β phase.

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Fig. 1(c), the structure model proposed for the $\alpha$ phase [$\alpha$ (2×4) model] is similar to the $\beta$ 2(2×4) model, but with Ga atoms in the missing dimer trenches. In the model proposed for the more As-rich phase of $\gamma$ [$\gamma$ (2×4) model], an extra As dimer is formed on the $\beta$ (2×4) surface along the [110] direction [Fig. 1(d)]. Northrup and Froyen performed first-principles calculations for several GaAs(001) surfaces, and found that the $\alpha$ (2×4) structure is stable in a limited range of surface stoichiometry, while the $\gamma$ (2×4) structure is unstable with respect to dissociation into the $\beta$ 2(2×4) and c(4×4) structures. Schmidt, Mibt and Bechstedt recently predicted that the $\alpha$ 2(2×4) structure [Fig. 1(e)] is more stable than the $\alpha$ (2×4) structure.

In agreement with the theoretical predictions, recent STM observations clearly demonstrated that only two As dimers are present at the outermost layer for all three phases. In particular, Hashizume et al. reported that the $\gamma$ phase is a locally ordered $\beta$ 2(2×4) phase with fractions of the c(4×4) phase, so that the $\gamma$ (2×4) model shown in Fig. 1(d) can be ruled out. On the other hand, there has been no direct experimental evidence of the existence of the $\alpha$ 2(2×4) and/or $\alpha$ 2(2×4) structure. It was suggested that the $\beta$ 2(2×4) is the only structure formed, with the difference in RHEED intensities among three phases being due to surface disorder.

In this paper, the surface structures of GaAs(001)-(2×4) are studied using a rocking-curve analysis of RHEED and reflectance difference spectroscopy (RDS). A rocking-curve analysis of RHEED based on dynamical diffraction theory is used to determine atomic structures of crystal surfaces. While the structural information available from RHEED analysis is averaged over macroscopic areas of a surface and is associated with long-range orderings, RDS provides information about local electronic structures. Thus, simultaneous measurements of RDS with RHEED allow us to check whether differences in RHEED intensities for the $\alpha$, $\beta$, and $\gamma$ phases are ascribed to a periodic structural change in the 2×4 unit cell.

Since both RHEED and RDS are compatible with the molecular-beam geometry, allowing in situ characterization in actual MBE conditions, the GaAs(001) samples were characterized under As fluxes without being transferred from an MBE chamber to another ultra high-vacuum chamber for the analysis. This is of great advantage in evaluating the real surface structure of GaAs(001)-(2×4), because the experimental data can be analyzed without considering the effect of the adsorption and/or desorption of As, which might occur while transferring the sample from an MBE chamber. Information about the surface reconstructions of GaAs(001) under As fluxes is also important for a detailed understanding of initial growth processes of GaAs, because the MBE growth of GaAs is usually initiated by supplying Ga fluxes on GaAs substrates under excess As fluxes.

II. EXPERIMENT

The experiments were performed in a MBE system which is equipped with an x-ray photoelectron spectroscopy and a scanning tunneling microscope for on-line surface character-

![Image](https://example.com/image.png)
pected for a well-ordered surface. On the other hand, in the [110] direction [Fig. 2(b)], spots are observed for fractional-order reflections, but not for half-order ones, being consistent with the lack of diffraction spots on the half-order Laue zone in the [110] direction. Instead, extended streaks are observed in the half-order positions in Fig. 2(b), which are ascribed to the presence of one-dimensional disorder on the 2×4 surface. As shown in Figs. 2(c) and 2(d), if adjacent 2×4 unit cells along the [110] direction are out of phase, one-dimensional disorder boundaries could be formed in the [110] direction, which gives rise to streaks in the RHEED patterns (i.e., sheets in reciprocal space), as discussed in Refs. 23 and 24. Thus the fractional-order reflections in the [110] direction are excluded in the present RHEED analysis.

RHEED rocking curves of the GaAs(001) surfaces were measured along the [110] and [110] directions with an electron energy of 15 keV. The intensities of five spots—(0 0), (±1 0), and (±2 0) for the [110] direction—and 11 spots—(0 0), (0 ± 1 2), (0 ± 1 2), (0 ± 1 2), (0 ± 1), and (0 ± 2)—for the [110] direction—were measured using a charge-coupled-device camera with a microcomputer system. An averaging of the intensities of symmetry-equivalent spots led to three and six independent rocking curves for the [110] and [110] directions, respectively. The glancing angle of the incident electron beam was changed using the extended beam rocking facility (Staib, EK-35-R and k-Space, kSA400), with intervals of ~0.03°.

In RDS, the directly measured quantity is anisotropy in the complex reflectance \( \Delta r/r = (R_{110} - R_{110})/R = \Delta r/r + i\Delta \theta \), where \( R_{110} \) and \( R_{110} \) are the near-normal-incidence complex reflectances for light linearly polarized along the [110] and [110] directions, respectively. Here we present the data only in the form \( \Delta r/r = \text{Re}(\Delta r/r) \).

III. DYNAMICAL CALCULATION OF RHEED

Intensities of RHEED were calculated by the multislice method proposed by Ichimiya. \(^{25}\) Seven and 25 beams on the zeroth Laue zone were used in the calculation with the incident electron beam along the [110] and [110] directions, respectively: (0 0), (±1 0), (±2 0), and (±3 0) for the [110] direction, and (0 0), (1 ± 1 2), ..., (0 ± 1 2), and (0 ± 3) for the [110] direction. As mentioned in Sec. II, the 2×4 unit cells are positioned with different phases in the direction of two-fold periodicity (i.e., [110]) on the GaAs(001)-(2×4) surface [Fig. 2(c)]. This means that the structures of two domains having opposite phases are projected on the (110) plane. Thus the present RHEED calculations for the [110] incidence assumed that the 2×4 surface consists of these two domains with ratio of 1:1, as if the surface has a c(2×8) symmetry. We have confirmed that the calculations for the [110] incidence with and without fractional-order reflections yield the same results.

Fourier coefficients of the elastic scattering potential were obtained from the atomic scattering factors for free atoms calculated by Doyle and Turner. \(^{26}\) 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 is assumed to be 17% of its real part. \(^9\) The Debye-Waller parameters were taken to be 1.78 and 1.14 Å\(^2\) for the outermost bilayer and bulk layers, respectively. The thickness of a slice, in which the scattering potential was approximated to be constant toward the direction normal to the surface, was about 0.1 Å. In order to quantify the agreement between the calculated rocking curves and the experimental ones, the \( R \) factor defined in Ref. 19 was used. The calculated rocking curves were convoluted with a Gaussian which has a full width at half maximum of 0.1°, corresponding to the experimental resolution.

IV. RESULTS AND DISCUSSION

A. Identification of the \( \alpha, \beta, \) and \( \gamma \) phases

Figure 3 shows RD spectra measured from the GaAs(001) surfaces under an As\(_4\) flux of 2.5×10\(^{-7}\) Torr as a function of the substrate temperature. In the range of 430–480°C, where the surface showed c(4×4) RHEED patterns, the shape of the RD spectrum remains almost unchanged and is in good agreement with that for the c(4×4) surface reported by Kamiya et al. \(^{27}\) As the temperature is increased above ~480°C, the shape of the RD spectrum significantly changes, being accompanied by the changes in RHEED patterns from c(4×4) to (2×4). The dominant change in the RD spectrum is associated with the feature at ~2.6 eV, which changes its sign between 480 and 510°C. The shape of the spectrum stays essentially the same between 510 and 550°C. The 2.6 eV feature gradually shifts to lower energy above ~550°C, but principal features are preserved up to ~600°C. This energy shift is closely related with the structural change from the \( \beta \) phase to the \( \alpha \) phase, as we will show in Sec. IV D.
The 2\times4 RHEED pattern begins to give way to the diffuse 3\times1 pattern above \sim600 °C. On the other hand, quite different results have been obtained when the c(4\times4) surface is heated without As fluxes: while the 2\times4 reconstruction is observed in ranges of 400–490 °C, sharp RHEED patterns have never been observed.

The spectrum shape in the range of 510–550 °C is identical to that measured from the b phase. Although the b(2\times4) structure [Fig. 1(b)] was assumed for the b phase in Ref. 27, we note that the surface has the \beta2(2\times4) structure [Fig. 1(a)] in this temperature range, as we will show later. On the other hand, the RD spectra measured from the 2\times4 surface below \sim510 °C and above \sim550 °C are similar to the spectra for the \gamma and \alpha phases, respectively.

The evolution of dominant RD features with temperature is more clearly visualized in Fig. 4(a) (solid circles), where RD intensities at 1.74, 2.66, and 4.21 eV are plotted as a function of the substrate temperature. It is clearly seen that the RD intensities are almost constant in the ranges of 430–480 and 510–550 °C, where RD spectra characteristic of c(4\times4) and \beta2(2\times4) surfaces were obtained, respectively.

These RDS results are consistent with the RHEED results. Figures 5(a) and 5(b) show the RHEED rocking curves of 0 0 and 0 1 rods, respectively. RHEED intensities for the c(4\times4) surface are almost constant below \sim470 °C. While 2 \times4 RHEED patterns were observed in the range of 480–600 °C, the shape of RHEED rocking curve changes with temperatures below 510 °C and above 550 °C, similarly to the case for the RDS results. In particular, both 0 0 and 0 1 curves showed noticeable changes between 470 and 500 °C. This is explained by considering that the c(4\times4) (470 °C) and \beta2(2\times4) (500 °C) surfaces have quite different atomic structures. On the other hand, the change above 550 °C is gradual, suggesting the structural similarity between the \beta and \alpha phases.

Similar RDS and RHEED results were obtained when the temperature was decreased from 650 to 430 °C. Here we note that \sim100 min were required to obtain the equilibrium shapes of RD spectra in the range of 470–510 °C, as mentioned in Sec. II. When the temperature was kept only for 10 min at each step, the hysteresis with a width of \sim15 °C was clearly observed, as shown in Fig. 4(b). It is apparent that the structural change from 2\times4 to c(4\times4) more easily occurs than the opposite case. It was reported that a c(4\times4) surface is formed at a deeper level than a 2\times4 surface: while Ga atoms are detached from the 2\times4 surface to form the c(4\times4) reconstruction, the formation of the 2\times4 structure on the c(4\times4) terrace requires the Ga atoms to be supplied. Thus the result in Fig. 4(b) can be explained by considering that no Ga flux was supplied in the present experiment.

From these results, we can conclude that the GaAs(001) surfaces change their atomic structures and/or atomic coor-
dinates with substrate temperatures below \( \sim 510 \, ^\circ C \) (the \( \gamma \) phase) and above \( \sim 550 \, ^\circ C \) (the \( \alpha \) phase). On the other hand, the \( c(4 \times 4) \) and \( \beta 2(2 \times 4) \) phases are stable against a slight change in the temperature, and, therefore, can be regarded as equilibrium phases.

B. Structure analysis of the \( \beta 2(2 \times 4) \) surface

RHEED patterns obtained from the \( \alpha \) and \( \beta \) phases consist of sharp spots lying on a semicircle, while diffuse and streaky fractional-order reflections were observed for the \( \gamma \) phase. Since the quantitative RHEED analysis is not available for the surface showing the streaky RHEED patterns, we restricted our RHEED analysis to the \( \alpha \) and \( \beta \) phases. In the following, we first examine the atomic structure of the \( \beta \) phase.

Figure 6 shows RHEED rocking curves (solid curves) measured from the GaAs(001)-(2×4) surface at 530 \( ^\circ C \) under an As flux of \( 2.5 \times 10^{-7} \) Torr. These curves are in good agreement with those measured by Larsen et al.\(^{29}\) under an As flux. Also shown in Fig. 6 are the calculated rocking curves (dashed curves) from the optimized structure based on the \( \beta 2(2 \times 4) \) model [Fig. 1(a)], for which the atomic coordinates are listed in Table I. The atomic coordinates were optimized using a method reported previously.\(^{18}\) In the present analysis, we assume that the surface relaxation extends no further than the fourth atomic layer. In Fig. 6, most of the features in the measured rocking curves are well reproduced in the calculated ones. The \( R \) factor for the opti-

\( RHEED \) rocking curves of GaAs(001)-(2×4) surface under As flux.
TABLE I. Atomic displacements from bulk positions in the \(\beta 2(2 \times 4)\) structure for the \(\beta\) phase (in \(\text{Å}\)).

<table>
<thead>
<tr>
<th>RHEED analysis (this study)</th>
<th>First-principles calculations (Refs. 11 and 28)</th>
<th>X-ray diffraction (Ref. 7)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>(x) (y) (z)</td>
<td>(x) (y) (z)</td>
</tr>
<tr>
<td>AS(1)</td>
<td>+0.81 (\pm 0.06) +0.07 (\pm 0.07) +0.09 (\pm 0.05) +0.73 +0.06 +0.07 +0.74 (\pm 0.01) +0.06 (\pm 0.02) +0.07 (\pm 0.03)</td>
<td></td>
</tr>
<tr>
<td>Ga(1)</td>
<td>+0.42 (\pm 0.06) +0.61 (\pm 0.10) +0.37 (\pm 0.08) +0.11 +0.61 +0.31 +0.14 (\pm 0.01) +0.62 (\pm 0.02) +0.29 (\pm 0.06)</td>
<td></td>
</tr>
<tr>
<td>Ga(2)</td>
<td>+0.70 (\pm 0.15) fixed +0.03 (\pm 0.07) +0.21 +0.05 +0.03 +0.23 (\pm 0.01) fixed +0.03 (\pm 0.03)</td>
<td></td>
</tr>
<tr>
<td>As(2)</td>
<td>+0.84 (\pm 0.23) fixed +0.04 (\pm 0.11) +0.72 +0.01 +0.12 +0.75 (\pm 0.01) fixed +0.02 (\pm 0.03)</td>
<td></td>
</tr>
<tr>
<td>As(3)</td>
<td>fixed +0.14 (\pm 0.15) +0.08 (\pm 0.15) 0.00 0.00 +0.04 fixed fixed fixed +0.10 (\pm 0.03) +0.03 (\pm 0.03)</td>
<td></td>
</tr>
<tr>
<td>As(4)</td>
<td>fixed +0.18 (\pm 0.12) +0.39 (\pm 0.08) 0.02 -0.12 -0.24 fixed fixed fixed +0.14 (\pm 0.02) +0.13 (\pm 0.03)</td>
<td></td>
</tr>
<tr>
<td>As(5)</td>
<td>fixed +0.05 (\pm 0.17) fixed fixed fixed fixed fixed fixed fixed fixed</td>
<td></td>
</tr>
<tr>
<td>Ga(5)</td>
<td>fixed +0.15 (\pm 0.09) -0.02 +0.03 +0.26 fixed fixed fixed</td>
<td></td>
</tr>
<tr>
<td>Ga(6)</td>
<td>fixed -0.14 (\pm 0.19) +0.13 (\pm 0.15) 0.00 +0.05 +0.03 fixed fixed fixed</td>
<td></td>
</tr>
<tr>
<td>Ga(4)</td>
<td>fixed +0.24 (\pm 0.26) -0.08 (\pm 0.24) -0.01 -0.02 -0.17 fixed fixed fixed</td>
<td></td>
</tr>
<tr>
<td>Ga(5)</td>
<td>+0.06 (\pm 0.13) +0.32 (\pm 0.15) -0.01 (\pm 0.13) +0.10 +0.16 +0.04 +0.14 (\pm 0.02) +0.20 (\pm 0.02) +0.02 (\pm 0.02)</td>
<td></td>
</tr>
<tr>
<td>Ga(6)</td>
<td>-0.04 (\pm 0.13) +0.14 (\pm 0.15) -0.03 (\pm 0.13) -0.13 +0.24 -0.10 -0.14 (\pm 0.02) +0.20 (\pm 0.02) +0.02 (\pm 0.03)</td>
<td></td>
</tr>
</tbody>
</table>

The atomic coordinates obtained by the present RHEED analysis results are in good agreement with the results from first-principles calculations.\(^{11,30}\) On the other hand, the rocking curves calculated from the x-ray-diffraction (XRD) data (Ref. 7) give a large \(R\) factor of 0.172. The XRD measurements were carried out after transferring the sample from a MBE chamber to another ultrahigh-vacuum chamber where As was not supplied. Thus it is possible that As atoms are desorbed from the surface prior to the analysis, so that the surface structure in Ref. 7 is different from the real \(\beta 2(2 \times 4)\) surface. Another possible reason for the worse fit is that the XRD analysis in Ref. 7 fixes the atomic positions of As(5), As(6), Ga(3), and Ga(4) at the bulk positions.

In the optimized structure model shown in Fig. 7, the As-As bond length for the outermost As dimers is 2.38 Å, and that for the third-layer As dimers is 2.32 Å. These values are slightly smaller than those obtained by first-principles calculations (2.50–2.52 Å),\(^{11}\) and that of bulk As in a threefold-coordinated system (2.51 Å).\(^{31}\) Instead, halves of the obtained values (1.19 and 1.16 Å) are close to the covalent radius of As (1.18 Å).\(^{32}\) Also, atomic displacements of Ga(1) and Ga(2) atoms in the [110] direction are quite a bit larger than those reported in Ref. 11. However, the bond lengths between As(1)-Ga(1) (2.40 Å) and As(1)-Ga(2) (2.43 Å) are close to the Ga-As bond length in bulk GaAs (2.45 Å). We note that the strain induced by the relatively large displacements of Ga(1) and Ga(2) is relaxed by the downward (upward) displacements of As(4) and As(6) [As(3) and As(5)] atoms at the third layer.

The outermost As(1) atoms are displaced upward (0.09 Å), the bond angles of Ga(1)-As(1)-Ga(2), As(1)-As(1)-Ga(1), and As(1)-As(1)-Ga(2) being 90.0°, 92.6°, and 99.2°, respectively. These values are significantly smaller than the 109.47° expected for an ideal \(sp^3\) arrangement, indicating that the As(1) atom is in a \(p^3\)-type bonding configuration. On the other hand, Ga(1) atoms are laterally displaced toward the first-layer As dimers, producing \(sp^2\)-type bonds with As(3) and As(4) atoms instead of \(sp^3\) type, as clearly seen in Fig. 7. Thus this atomic arrangement indicates that all Ga and As dangling bonds are eliminated by transferring charge from Ga atoms to As atoms.

The As(2) atoms at the third layer are slightly displaced toward the bulk (0.04 Å), in contrast to the case for the first-layer As(1) atoms. In addition, the As(2)-Ga(6) bond length (2.31 Å) is smaller than that in bulk GaAs, and the bond angles of As(2) atoms with their nearest neighbors are 93.3°–108.6°, which are somewhat larger than those for
first-layer As(1) atoms (90.0°–99.2°). These results suggest that the electronic rehybridization is less complete at the third layer than the first layer, and can be explained by considering that threefold-coordinated Ga(1) atoms at the second layer can be displaced more easily than fourfold-coordinated Ga(5) and Ga(6) atoms at the fourth layer.

Here we note that the atomic coordinates in the [110] direction in Table I are slightly different from those we reported previously, although the shape of measured rocking curves in Ref. 9 are quite similar to that in Fig. 6. The structural analysis in Ref. 9 were performed on the basis of the ideal $2\beta(2\times4)$ structure ($R_{\text{min}}=0.091$). On the other hand, since, as mentioned earlier in this paper, the 2×4 unit cells are positioned with different phases in the [1 1 0] direction on the real GaAs(001)-(2×4) surface, the present RHEED calculations for the [110] incidence assumed that the 2×4 surface consists of these two domains with opposite phases. Thus the atomic coordinates determined in this study are more reliable than those in Ref. 9.

**C. $\gamma$ phase**

As shown in Figs. 3 and 4, RD spectra measured from the $\alpha$ and $\gamma$ phases are different from that for the $\beta$ phase. On the other hand, previous studies showed that the $\alpha$ and $\gamma$ phases are merely two variants of the less ordered $\beta$ phase. Hashizume et al. reported that the $\gamma$ phase is a locally ordered $\beta2(2\times4)$ phase with fractions of the $c(4\times4)$ phase. However, the question as to whether the $\alpha$ phase is preserved in the STM chamber still remain unresolved. In other words, the $\gamma(2\times4)$ structure, which is unstable with respect to dissociation into the $\beta2(2\times4)$ and $c(4\times4)$ structures, might exist under actual growth conditions. If the $\gamma$ phase under As fluxes is indeed a mixture of $\beta2(2\times4)$ and $c(4\times4)$ phases, the RD spectra for the $\gamma$ phase should be representable as linear combinations of the RD spectra for the $\beta2(2\times4)$ and $c(4\times4)$ surfaces, because RDS is sensitive to local electronic structures rather than long-range ordering. Thus we have tried to reproduce the RD spectra obtained from the $\gamma$ phase by linear combinations of the $\beta2(2\times4)$ and $c(4\times4)$ spectra. The results are shown in Fig. 8. The RD spectra measured from the $\gamma$ phase are well reproduced, confirming the results of STM observations and first-principles calculations. In addition, it is clearly seen that the ratio of $\beta2(2\times4)$ to $c(4\times4)$ reasonably increases with the substrate temperature. From these results, we conclude that the $\gamma$ phase is a mixture of $c(4\times4)$ and $\beta2(2\times4)$ phases. Similar results were recently reported by Be garney et al.

**D. $\alpha$ phase**

As mentioned in Sec. III A, the $\alpha$ phase emerged in the range of 550–600°C. At first, we tried to reproduce the RD spectra measured from the $\alpha$ phase by linear combinations of the spectra measured from the $\beta2(2\times4)$ surface and those for high-temperature phases, such as $3\times1$, $4\times6$, and $4\times2$, similarly to the case for the $\gamma$ phase described in Sec. III C. However, the measured RD spectra could not be reproduced by any of the linear combinations, suggesting that the $\alpha$ phase is not a mixture of the $\beta$ and high-temperature phases. In addition, as mentioned at the beginning of Sec. IV B, RHEED patterns consisting of sharp spots were observed for the $\alpha$ phase. If the $\alpha$ phase consists of more than one structure, the RHEED pattern from the $\alpha$ phase should be diffuse and streaky, similar to the case for the $\gamma$ phase. Thus we can rule out the possible coexistence of high-temperature phases in the $\alpha$ phase.

Here we note that the surface might include both 2×4 and 3×1 phases above ~590°C, because the surface showed a diffuse and streaky 2×4 RHEED phase. Thus we have performed a RHEED rocking-curve analysis for the data obtained at 584°C. Figure 9 shows RHEED rocking curves (solid curves) measured from the GaAs(001)-(2×4) surface at 584°C under an As$_4$ flux. Also shown by dashed, dotted, and dashed-dotted curves are the rocking curves calculated from the optimized structure models of $\alpha(2\times4)$, $\beta2(2\times4)$, and $a2(2\times4)$ [Figs. 10(a)–10(c)], respectively. In this analysis, the Debye-Waller parameters of the surface atoms were also optimized. The obtained value is ~1.8 Å$^2$, which is close to the value used in the calculations for the $\beta$ phase (Fig. 6). In addition, the atomic coordinates optimized for the $\beta$ phase (Table I) gives a worse fit ($R_{\text{min}}=0.131$) with the experimental data at 584°C, even after the optimization of the Debye-Waller parameter. Thus it is likely that the difference in the rocking curves between 530 and
584 °C is not ascribed to the enhancement of the thermal vibrations of surface atoms at a higher temperature of 584 °C.

*R* factors for the \( a(2 \times 4) \), \( b(2 \times 4) \), and \( a(2 \times 4) \) models are 0.075, 0.077, and 0.113, respectively. In view of a large \( R \) factor \( (R_{\text{min}}=0.113) \), the \( a(2 \times 4) \) model can be discarded. In addition, atomic coordinates optimized for the \( a(2 \times 4) \) model (Table II) are unphysical on the following points. (i) The bond length between Ga(2) and Ga(1') is extremely large (3.36 Å), while the As(1)-Ga(1) bond is extremely small (1.97 Å). (ii) The outermost As atoms hardly dimerize (the As-As bond length is 3.08 Å). On the other hand, both rocking curves calculated for the \( a(2 \times 4) \) \( (R_{\text{min}}=0.075) \) and \( b(2 \times 4) \) \( (R_{\text{min}}=0.077) \) models show good agreement with the experiment. The optimized atomic coordinates for both models appear to be physically reasonable, as seen in Table II. Thus it is difficult to conclude which is the more favored structure model for the \( \alpha \) phase from the present RHEED analysis.

Recently, Lee, Moritz, and Scheffler performed first-principles calculations for various GaAs(001) surfaces, and plotted surface energies as a function of the chemical potential of As.\(^{34}\) The \( a(2 \times 4) \) model, which is lower in energy with respect to the \( a(2 \times 4) \) model, is the most stable only at the boundary between the ranges of the As chemical potential where the Ga-rich \( \zeta(4 \times 2) \) and As-rich \( b(2 \times 4) \) models are most stable.\(^{34}\) Thus, if we assume that the surface structures not included in Ref. 34 are even lower in energy between the \( b(2 \times 4) \) and \( \zeta(4 \times 2) \) phases, both \( a(2 \times 4) \) and \( \alpha(2 \times 4) \) models can be ruled out. However, no definitive answer is available without further studies.

Finally, although not conclusive, one comment can be made about the atomic coordinates of the \( \alpha \) phase. As shown in Fig. 3, the position of the peak at \( \sim 2.6 \) eV is shifted by \( \sim 0.1 \) eV to lower energy as the substrate temperature is in-

![FIG. 9. Same as in Fig. 6, but at 584 °C.](image)

![FIG. 10. Relaxed geometry of the \( \alpha(2 \times 4) \) (a), \( \beta(2 \times 4) \) (b), and \( \alpha(2 \times 4) \) (c) structures for the \( \alpha \) phase of GaAs(001).](image)
TABLE II. Structural parameters of the $\alpha$($2\times4$), $\beta$($2\times4$), and $\alpha$($2\times4$) models for the GaAs(001)-(2$\times4$) surface (in Å).

<table>
<thead>
<tr>
<th>Model</th>
<th>$\beta$ phase</th>
<th>$\alpha$ phase</th>
</tr>
</thead>
<tbody>
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<td>$\alpha$($2\times4$)</td>
<td>$\beta$($2\times4$)</td>
<td>$\alpha$($2\times4$)</td>
</tr>
<tr>
<td>As(1)-As(1)</td>
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<td>2.22</td>
</tr>
<tr>
<td>As(1)’-As(1’)</td>
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<td>2.15</td>
</tr>
<tr>
<td>As(2)-As(2)</td>
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<td>2.23</td>
</tr>
<tr>
<td>As(1)-Ga(1)</td>
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<td>2.25</td>
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<tr>
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</tbody>
</table>

increased from 540 to 584 °C. The observed peak shift is too large to be explained by the temperature dependence of the optical-transition energies in GaAs.\textsuperscript{35} Tight-binding calculations by Murayama and Nakayama\textsuperscript{36} predicted that an increase of the As-dimer bond length should induce a red shift of the 2.6-eV peak in the RDS spectrum. Thus, when compared to the $\beta$ phase, the As-As bond length of the As dimers might be expanded in the $\alpha$ phase. Such a trend is indeed observed for the $\beta$($2\times4$) model, as seen in Table II.

V. CONCLUSIONS

We have studied the surface structures of the $\alpha$, $\beta$, and $\gamma$ phases of GaAs(001)-(2$\times4$) under an As flux of 2.5 $\times$ $10^{-7}$ Torr. The RDS and RHEED results clearly show that the $\beta$ phase is stable against a change in the temperature between 510 and 550 °C. The present RHEED rocking-curve analysis confirms that the $\beta$($2\times4$) model is most favorable for the structure of the $\beta$ phase. The $2\times4$ surfaces change their atomic structures with substrate temperature below ~510 °C (the $\gamma$ phase) and above ~550 °C (the $\alpha$ phase). The low temperature phase of $\gamma$ is a mixture of c($4\times4$) and $\beta$($2\times4$) phases, the fraction of the $\beta$($2\times4$) phase being increased with temperature. For the high-temperature $\alpha$ phase, the slightly distorted $\beta$($2\times4$) model has been proposed as one of the possible structure models.

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30W. G. Schmidt (private communication).