GaAs $c(4 \times 4)$ surface structure in organometallic vapor-phase epitaxy

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While GaAs(001) surface reconstructions have been studied extensively in the ultrahigh-vacuum environment associated with molecular-beam epitaxy (MBE), comparatively little is known of these structures in the chemically rich environment associated with organometallic vapor-phase epitaxy (OMVPE). This work presents a structural study of the $c(4\times4)$ surface reconstruction stabilized in an arsenic-rich OMVPE environment. Measurements of the in-plane structure were performed *in situ* using grazing-incidence x-ray scattering with synchrotron radiation. Structural refinement confirms the presence of arsenic-arsenic dimers arranged with the $c(4\times4)$ symmetry. In concurrence with similar studies performed in the MBE environment, it is found that the surface is a mixture of structural domains composed of two- and three-dimer variants of the $c(4\times4)$ reconstruction. Atomic positions associated with these structures are presented. The size, aspect ratio, and orientation of the reconstructed regions are shown to be closely related to the atomic step geometry on the crystal surface.

I. INTRODUCTION

Surface reconstructions on the GaAs(001) surface have been the object of significant scientific interest, stemming not only from the widespread use of epitaxially grown GaAs, but also from the rich variety of behavior exhibited by this surface. Through numerous electrondiffraction and photoemission studies,¹⁻⁵ it has been determined that the GaAs surface assumes a variety of surface structures depending on the ratio of As to Ga surface concentrations. Generally, the structures are composed of a characteristic arrangement of arsenic or gallium dimers on the crystal surface. Recent applications of scanning tunneling microscopy (STM) to the GaAs(001) surface have provided graphic confirmation of this dimerization and many of the diverse surface structures based on these dimers.^{6,7}

Most investigations of GaAs(001) surface structures have been conducted in the ultrahigh vacuum (UHV) environment associated with molecular-beam epitaxy (MBE). Despite the widespread use of chemical vaporphase growth techniques such as organometallic vaporphase epitaxy (OMVPE), comparatively little is known of surface reconstructions in the high-pressure environment (~100 Torr) associated with these methods. Given the fundamentally different chemistry involved in such processes, it is not evident *a priori* whether similar surface structures should be expected or whether stable reconstructed surfaces should occur at all. This question provided the motivation for the present study.

Before discussing the experiment, it is worthwhile clarifying an aspect of semantics. Throughout this work we will refer to the $c(4 \times 4)$ reconstruction "in the OMVPE environment" or "in the MBE environment." These phases are intended only to contrast the two environments; they should not be interpreted as describing the structure *during* the actual growth process, since the measurements in this study (and in most of the MBE experiments) were not performed concurrently with crystal growth. In cases where we have explicitly monitored the behavior of surface reconstructions during growth, we find that long range ordering is generally *suppressed*.⁸

One important difference between this experiment and previous MBE studies should be emphasized. Because of the relatively high vapor pressure of arsenic, this species will gradually evaporate from the heated crystal surface unless otherwise treated. In this experiment, the sample was maintained in steady flow of dilute tertiarybutylarsine (TBAs) to counter the effect. In this way, the surface is maintained in a *dynamic equilibrium* with its vapor throughout the experiment. MBE studies are typically performed after growth with the crystal surface exposed to hard vacuum, thereby constituting an inherently nonequilibrium system. One would thus expect OMVPE surface structures to more closely approximate equilibrium configurations as opposed to transient or metastable structures.

The relative dearth of information on chemical vaporphase growth stems in large part from the limitations associated with the gaseous environment, which precludes the use of electron-based analytical techniques. Because photons can penetrate the growth environment, photonbased techniques such as synchrotron x-ray scattering are being exploited as an avenue for studying OMVPE

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growth in situ.^{9,10} In structural investigations, x-ray scattering offers the additional advantage of a straightforward kinematic interpretation,¹¹ and provides high-resolution information on the atomic structure. In recent experiments, grazing incidence x-ray scattering (GIXS) was used to study the $p(2 \times 1)$ dimerization in GaAs(001) in the OMVPE environment.¹² Earlier investigations suggested that under slightly different conditions a $c(4 \times 4)$ reconstruction also occurs.⁸ In the present work, a more detailed examination of this reconstruction is presented.

At typical growth temperatures (~500 °C), the $c(4 \times 4)$ reconstruction is an arsenic-rich surface struc-



FIG. 1. Three possible arrangements of As-As surface dimers consistent with the $c(4\times4)$ structure in GaAs(001). Arsenic atoms in the chemisorbed surface layer are represented by black circles, while arsenic atoms in the bulk termination layer underneath are denoted by grey circles. (a) One-dimer clusters, (b) two-dimer clusters, and (c) three-dimer clusters. The unit cell for each structure is designated by the dashed lines. The xycoordinate frame follows the [110] and [110] symmetry axes of the $c(4\times4)$ structure. Dimerized atoms in the chemisorbed surface layer are labeled with upper-case letters (A,B), while those in the bulk termination layer are labeled with lower-case letters (a,b,c).

ture which persists over a range of arsenic concentrations.¹³ This has generally been attributed to a variation in the population of chemisorbed As-As dimers on the bulk termination layer of arsenic. In Fig. 1, the dimerized arsenic atoms in the chemisorbed surface layer are denoted by black circles, while the arsenic atoms in the bulk termination layer underneath are represented by the grey circles. Figures 1(a)-1(c) illustrate three possible $c4 \times 4$ reconstructions based on one-, two-, and threedimer clusters, respectively. While the $c4 \times 4$ symmetry is maintained in each case, the population of arsenic atoms in the chemisorbed surface layer varies from 25% to 50% to 75%. The square area bounded by the dashed lines denotes the unit cell for each structure. The xycoordinate system, with axes along the $[1\overline{10}]$ and [110]directions, is used to represent the atomic positions within each cell. Dimerized arsenic atoms in the chemisorbed surface layer are represented by upper-case letters (A,B), while those in the bulk termination layer are designated by lower-case letters (a, b, c) The XY coordinate system follows the bulk crystallographic [100] and [010] directions.

From the results of electron diffraction and photoemission studies of GaAs surfaces in the MBE environment, Larsen *et al.* suggested the one- and two-dimer structures for the $c(4\times4)$ reconstruction.³ Later x-ray studies by Sauvage-Simkin *et al.* found a mixture of two- and three-dimer $c(4\times4)$ structures.^{14,15} STM images in the work of Biegelson *et al.* illustrate a $c(4\times4)$ surface structure composed of three-dimer clusters.⁷ In the present study, we investigate the possibility of one-, two-, and three-dimer variants of the $c(4\times4)$ reconstruction. We find, however, that in the OMVPE environment the surface structure is best represented by a mixture of twoand three-dimer clusters, similar to the findings of Sauvage-Simkin *et al.* in the MBE environment.

II. APPARATUS, SAMPLE AND MEASUREMENTS

The apparatus used in this experiment consists of an OMVPE reactor integrated with a four-circle diffractometer, enabling high-resolution x-ray diffraction to be performed concurrently with crystal growth. The apparatus is described in detail elsewhere¹⁷ and will be described only briefly here. The vertical OMVPE growth reactor is equipped with the appropriate x-ray windows and goniometric motions required for a synchrotron xray scattering experiment. Triethylgallium (TEG) and tertiarybutylarsine (TBAs) are introduced into a hydrogen carrier gas flowing through the reactor. When the organometallic molecules contact the heated substrate, they decompose, releasing atomic gallium and arsenic species which are subsequently incorporated in the growing crystal.

The diffractometer employs a z-axis scattering geometry^{17,18} in which the sample surface and scattering plane are nearly horizontal, and the incident synchrotron beam forms a grazing angle with the sample surface. The experiment was performed on beamline 10-2 of the Stanford Synchrotron Radiation Laboratory. This beamline

is equipped with a 31-pole wiggler magnet, focusing mirror, and double-crystal monochromator. A photon energy of 10000 eV (λ =1.24 Å) was used in all measurements, and the grazing angle was held at 0.2°, which is slightly below the critical angle for total external reflection.

A GaAs(001) wafer (25 mm in diameter $\times 1$ mm thick), offcut by approximately 0.25° toward [111] A, was used in the experiment. The epi-ready substrate¹⁶ was removed from its packaging, indium mounted on a molybdenum substrate platen, and installed in the reactor. Radial scans along the [110] and [110] azimuths in reciprocal space were performed in order to assess the surface quality as represented by the crystal truncation rod (CTR) intensity. Initial radial scans prior to substrate heating revealed only the bulk [220]-type Bragg reflections. However, after heating to 520 °C in the TBAs-enriched hydrogen atmosphere (70-Torr H_2 +0.35-Torr TBAs), the [110] and $[1\overline{1}0]$ CTR intensities increased to roughly 5×10^3 cps, and additional peaks at $\left[\frac{3}{2},\frac{3}{2},0\right]$ and $\left[\frac{3}{2},\frac{3}{2},0\right]$ were observed, signalling the presence of a two-dimensionally ordered surface structure.

To further investigate the surface reconstruction, the intensity of the $[\frac{3}{2}, \frac{3}{2}, 0]$ reconstruction peak was optimized by stabilizing the sample at 460 °C at a TBAs partial pressure of 0.23 Torr. A total of 34 in-plane reflections were then measured. The locations for the measurements were selected to reveal information relevant to the surface reconstruction rather than the



FIG. 2. Reciprocal space map of measured (open semicircles) and calculated (filled semicircles) structure factor amplitudes (square root of the integrated intensity) of the GaAs $c(4\times4)$ surface reconstruction. All intensities have been corrected for area of illumination, Lorentz, and polarization factors. The symmetry of the measured reflections across the [110] azimuth is indicative of the mm2 symmetry of the $c(4\times4)$ structure, in which the mirror planes correspond to the [110] and [110] directions.

bulk structure. Thus reciprocal space locations corresponding to bulk Bragg reflections (asterisks in Fig. 2) and crystal truncation rods (diamonds) were excluded from the data set. The in-plane resolution functions¹⁹ in our scattering geometry is asymmetric, being several times longer along a radial azimuth than along a transverse (circumferential) azimuth. To first order, the radial resolution is limited by the acceptance of the 2θ detector slits (~0.5°), while the transverse is limited by the angular divergence of the synchrotron beam (~0.1°). Given the higher transverse resolution, the intensity of each reconstruction peak was measured using a transverse scan (rocking curve).

III. ANALYSIS AND RESULTS

A. Patterson analysis

If one assumes that the intensity distribution of each reflection is isotropic in surface reciprocal space, the line shape measured in a rocking curve can be used to estimate the corresponding integrated peak intensity, I(h,k)and the associated structure factor amplitude S(h,k), where $S(h,k) = \sqrt{I(h,k)}$. To this end, each reflection was fit to a pseudo-Voigt function (linear combination of Gaussian and Lorentzian line shapes), from which the integrated peak intensities and associated structure factor amplitudes were calculated. These amplitudes, corrected for area of illumination, Lorentz, and polarization factors, are represented by the open semicircles in Fig. 2. The diameter of each semicircle represents the structure factor amplitude S(h,k) while the area is a measure of the integrated intensity I(h,k). The mirror symmetry across the [110] azimuth is evident in the figure, as expected for the mm2 symmetry of the $c4 \times 4$ structure in which the mirror planes correspond to the [110] and [110] directions, as illustrated in Fig. 1.

To assess the dominant interatomic correlations, a Patterson map¹¹ was constructed from the integrated intensities in Fig. 2. The Patterson function P(X, Y) was calculated using the expression

$$P(X,Y) = \sum_{n} I_n(h,k) \cos\left[2\pi \left[h_n \frac{X}{a_0} + k_n \frac{Y}{a_0}\right]\right], \qquad (1)$$

in which the sum extends over all 34 integrated intensities, $I_n(h,k)$. The quantity a_0 in this expression is the GaAs lattice parameter, which is 5.657 Å at the temperature of this experiment. The quantities X and Y in Eq. (1) correspond to distances along the [100] and [010] crystallographic directions, as indicated in Fig. 1.

Figure 3(a) illustrates the resulting Patterson map. For clarity, only the positive values of the Patterson function are shown, and the map has been oriented such that the $[1\overline{10}]$ azimuth is horizontal for consistency with Fig. 1. The $c(4\times4)$ structure is clearly revealed by the 16-Å faced-centered array of high-correlation positions. These correspond to translation vectors among the neighboring dimer clusters illustrated in Fig. 1. All shorter-range correlations correspond to distinct interatomic vectors between arsenic atoms within a *single* dimer cluster. These correlations are indicated inside the dashed region of the Patterson map, and are labeled in correspondence with the interatomic vectors shown in Fig. 3(b). All other correlations appearing in the Patterson map are nonunique; they are generated from the reflection and translation symmetry operations associated with the $c(4 \times 4)$ structure.

Comparison of the Patterson map [Fig. 3(a)] and the dimer cluster [Fig. 3(b)] indicates that some correlations (i.e., 02 and 03) necessarily result from the three-dimer cluster depicted. Other correlations (i.e., 01 and 04), however, might also be attributed to the two- or three-dimer clusters, while correlation 05, representing the fundamental arsenic dimerization along [110], is common to all three of structures illustrated in Fig. 1. It should be emphasized that the Patterson provides direct evidence of the three-dimer $c(4 \times 4)$ structure. The possible presence of the one- and two-dimer structures in addition to the three-dimer structure will be addressed through the structural refinement described in Sec. III B.





FIG. 3. (a) Patterson map of interatomic correlations. The $c(4\times4)$ structure of the surface is clearly reflected in the 16-Å face-centered array of high correlation positions (i.e., correlation 00). These correspond to translation vectors among the neighboring dimer clusters illustrated in Fig. 1. Weaker unique correlations (01-05, inside dashed rectangle) correspond to atomic displacements within a single dimer cluster. These are labeled in correspondence with the interatomic vectors shown in (b). All other features in the Patterson map result from reflection and translation and symmetry operations. For clarity, only the positive values of the Patterson are illustrated. (b) Interatomic displacements corresponding to labeled peaks in the Patterson map. While some of the correlations result explicitly from the three-dimer cluster illustrated, others are common to the two- and one-dimer $c(4\times4)$ variants as well.

B. Structural refinement

To gain a more exact description of the $c(4 \times 4)$ reconstruction, crystallographic refinement of the x-ray data was performed using each of the structures illustrated in Fig. 1 as initial models. Under the kinematic approximation for surface reciprocal space, the structure factor amplitude S(h,k) is given by

$$S(h,k) = \left| \sum_{m} f_{m} \exp\left[-i(hX_{m} + kY_{m})\right] \right|, \qquad (2)$$

in which the sum extends over all m arsenic atoms in two-layer surface cells illustrated in Fig. 1. At the critical grazing angle for total external reflection, x-ray scattering is sensitive only to the in-plane projection of the electron density, and hence the Z_m atomic coordinate does not appear in Eq. (2). The scattering factors f_m for both arsenic layers were held equal in all cases.

Structural refinement was carried out numerically using a standard Levenberg-Marquardt χ^2 reduction routine²⁰ which minimizes the residual between the observed structure factor amplitudes (S_n^0) and those calculated from the model (S_n^c) :

$$\chi^2 = \sum_n \frac{1}{\sigma_n^2} (S_n^c - S_n^0)^2 .$$
(3)

In this expression, we have replaced $S_n(h,k)$ by S_n for brevity. The sum is carried out over all n = 34 measured intensities. A $1/\sigma_n^2$ prefactor weights each observation using $\sigma_n = 1/2 + 0.10S_n$. The first term accounts for statistical fluctuations while the 10% scaling of the latter term accounts for the experimental error associated with each peak measurement (this was estimated from the average fractional difference between symmetry-related peaks). As an indication of the absolute accuracy of the refinement, the crystallographic R factor (residual) is used,²¹ which is simply proportional to χ^2 according to

$$R = \left[\chi^2 / \sum_{i} \frac{1}{\sigma_i^2} (S_i^0)^2 \right]^{1/2} .$$
 (4)

Although a total of 34 crystalline reflections were measured in the experiment, only 18 are crystallographically independent. Caution must be exercised in performing structural refinement with models in which the number of adjustable parameters (p) approaches the number of independent experimental observations (n). To this end, we estimate the relative confidence of each refinement according to the significance tests outlined by Hamilton.²² These tests are best clarified by example. Suppose we have two models (model 1 and model 2) with different numbers of adjustable parameters p_1 and p_2 , where $p_2 > p_1$. The additional parameters associated with model 2 generally lead to a better fit to the observations: $R_2 < R_1$. To assess whether this decrease in R factor is significant, however, confidence tests must compare the R-factor decrement against (i) the change in the number of free parameters, $p_2 - p_1$, and (ii) the remaining degrees of freedom involved in the refinement, $n - p_2$. Using such tests, one can establish (on a strictly mathematical basis) to what degree of confidence model 1 can be rejected in favor of model 2. These methods were applied to establishing the confidence of each resulting structural refinement.

Refinements were carried out on each of the dimer structures individually, as well as on linear combinations among them. In each case, atomic displacements were limited to the uppermost two arsenic layers illustrated in Fig. 1 (i.e., the chemisorbed surface As layer and the underlying bulk termination As layer). Although other atomic configurations are conceivable, only atomic displacements strictly consistent with mm2 symmetry were allowed (e.g., symmetric atomic displacements parallel to the x and y axes in Fig. 1). Through the assumption of mirror plane symmetry, the one-, two-, and three-dimer structures can be uniquely described by a maximum of four atomic positions. The only other independent fitting parameters employed in the refinements were an overall constant scaling factor, and an isotropic rms atomic displacement $\sqrt{\langle \Delta r^2 \rangle}$, representing both thermal and static disorder through a Debye-Waller prefactor.¹¹

Figure 4 is a ternary diagram summarizing the results of the refinement using a variety of $c4 \times 4$ dimer structures. The pure one-, two-, and three-dimer clusters are located at the vertices of the equilateral triangle, while linear combinations between structures are denoted by points along the sides of the triangle. The diagram lists (i) the number of adjustable parameters p associated with each model, (ii) the R factors resulting from the best fit, and (iii) the relative confidence C between selected models, indicated by dashed arrows and percent confidence



FIG. 4. Ternary diagram illustrating the best fits to various atomic models of the GaAs $c(4\times 4)$ surface reconstruction. One-, two-, and three-dimer models are pictorially located at the vertices of the triangle while linear combinations among models are located along the sides according to the relative fraction of each. The number of adjustable parameters (p) and the resulting R factors (residuals) are listed for each model. Dashed arrows between models indicate the relative confidence (C) by which one model can be rejected in favor of the other. Of all models considered, the two-/three-dimer hybrid model provides the best fit to the data.

levels. As indicated, the R factors for the individual one-, two-, and three-dimer structures are 0.420, 0.341, and 0.284, respectively. This indicates that of all the pure structures, the three-dimer $c4 \times 4$ model illustrated in Figs. 1(c) and 3(b) provides the closest agreement to the experimental data. Confidence tests indicate that the pure one- and two-dimer models can be rejected in favor of the three-dimer model with a confidence of over 95% (i.e., the dashed arrow at the bottom of the triangle in Fig. 4).

Although the R factor of 0.284 for the pure threedimer cluster is not unreasonably high, significantly improved fits resulted from *linear combinations* among the dimer models. Physically, these hybrid models correspond to a surface comprising distinct patches two or more of the candidate $c4 \times 4$ structures. Such mixed surface structures have been reported for GaAs surfaces in the MBE environment.^{14,15} As indicated in Fig. 4, the hybrid models do indeed lead to lower R factors. Because these models incorporate a greater number of adjustable parameters, however, one must critically examine the significance of the resulting fits. For this reason, we explain the hybrid models in enhanced detail and justify their results in terms of the confidence tests discussed earlier.

The most straightforward means of combining two $c4\times4$ models is simply to weight each model by an adjustable fraction while retaining all the free position parameters of each original model (a single scaling factor and rms vibration amplitude are then reassigned for the entire combination). For example, if we combine the two- and three-dimer clusters in this way, we obtain a model with p = 1+6+7+2=16 adjustable parameters. Because the number of parameter is approaching the number of independent observations (n = 18), a very large decrease in the R factor is required to impart reasonable confidence to the resulting fit. Clearly it is advantageous to reduce the number of adjustable parameters associated with the hybrid models.

We elected to reduce the number of parameters by holding certain interatomic separations in the bulk termination arsenic layer equal for both models comprising the hybrid. Figures 3(a) and 3(b) illustrate that the dominant features in the Patterson function are attributed to correlations between the surface arsenic dimer atoms (black) and, conversely, that the underlying bulk termination As atoms (grey) are less important. Thus, to capture the dominant features of the scattering without introducing excessive parameters, we maintained the original degrees of freedom in the surface dimer As atoms while partially constraining the underlying As atoms in the bulk termination layer. Specifically (see Fig. 1), the vertical and horizontal separation between arsenic atoms surrounding the end dimer of each cluster were held equal for each model in the hybrid. For example, in the two-/three-dimer model, we impose $[x_b]_2 = [x_b - x_a]_3$ and $[y_b]_2 = [y_b]_3$, where the subscripts refer to the twoand three-dimer cluster models respectively. This approach eliminates two adjustable parameters in each hybrid model. In addition to being physically reasonable, these constraints were supported by the fact that unconstrained least-squares fitting to the individual cluster models resulted in similar values for these interatomic separations.

Returning to Fig. 4, it is evident that the hybrid models produce a better fit than the individual dimer cluster models in all cases. By applying the confidence tests, it was found that the individual one-, two-, or three-dimer models could be rejected in favor of the appropriate hybrid with confidence levels ranging from between 88-98%. The best fit (R = 0.108) was achieved with 30:70% mixture of the two- and three-dimer models, in this case with a confidence of 95% and 92% over the individual two- and three-dimer models, respectively, as indicated by the dashed arrows on the right side of the triangle in Fig. 4. It is also worthwhile examining the relative confidence in the two-/three-dimer fit over that from the other hybrid models. In this case the confidence tests show that the one-/three-dimer and one-/two-dimer models can be rejected in favor of the two-/three-dimer model with a confidence of 82% and 95%, respectively. We note that a linear combination of all three dimer structures is not represented in Fig. 4 since no local minima in R was found within this regime.

Thus, of the models considered, the two-/three-dimer structure for the $c(4 \times 4)$ reconstruction most closely fits the scattering observations. The solid semicircles in Fig. 2 illustrate the structure factor amplitudes calculated for this hybrid structure. The illustrated fit employs a Debye-Waller factor with isotropic rms atomic displacement $\sqrt{\langle \Delta r^2 \rangle} = 0.28$ Å. With reference to the coordinate system and labels in Fig. 1, the (x, y) coordinates of arsenic atoms associated with this fit are listed in Table I, along with the standard deviations (σ) of each parameter. The As-As dimer spacing for the two-dimer structure is 2.44 Å, while the spacing between adjacent dimers (horizontal separation in Fig. 1) is 3.81 Å. For the threedimer $c(4 \times 4)$ structure, the As-As spacing for the central dimer is 2.50 Å, while that for the end dimers exhibits a significantly smaller value of 2.26 Å. The horizontal separation between adjacent dimers in this case is 3.69 Å. Each of these dimensions is within $\sim 10\%$ of corresponding dimensions observed for the $c(4 \times 4)$ structure in UHV.¹⁴ The largest deviation from the ideal 4.00-Å interatomic spacing in the bulk termination arsenic layer is the ~ 3 Å separation between atoms a and c in the twodimer structure illustrated in Fig. 1(b).

TABLE I. Atomic positions corresponding to the best-fit $c4 \times 4$ structure consisting of a 30%:70% mixture of two- and three-dimer clusters depicted in Figs. 1(b) and 1(c). The x and y coordinates of the various atoms correspond to the coordinate axes and labels in Fig. 1. The standard deviation (σ) associated with each parameter is listed. All quantities in Å.

Two-dimer					Three-dimer				
Atom	x	σ_x	у	σ_y	Atom	x	σ_x	у	σ_y
A	1.89	0.07	1.23	0.08	A	0.00		1.26	0.06
а	0.00		2.21	0.09	B	3.69	0.07	1.13	0.05
b	3.71	0.07	1.91	0.04	а	2.11	0.07	1.71	0.06
с	0.00		5.20	0.18	b	5.86	0.08	1.91	0.04

C. Lateral coherence

In addition to revealing information about the structure of the $c(4\times4)$ reconstruction, the rocking curve measurements described earlier also shed light on the size and shape of the reconstructed domains. The width of the rocking curve through a particular reflection $\Delta q(h,k)$ is inversely related to the crystalline coherence length of the structure along the rocking direction, $L[\bar{k}h0]$:

$$\Delta q(h,k) = \frac{2\pi}{L} \left[\overline{k}h0 \right] . \tag{5}$$

Using the above formula, the 34 measured peak widths were used to construct the plot shown in Fig. 5. Each rocking curve measurement yields a pair of data points at $\pm L/2$ along the $[\bar{k}h0]$ direction. As shown in the figure, the ensemble produces an image of the reconstructed domain, which in this case is approximately elliptical. The solid line is a least-squares fit to the data using an ellipse, indicating principle axes of 1420 ± 7 and 630 ± 3 Å, respectively (aspect ratio greater than 2:1). The major axis is canted approximately 21° away from the [100] direction.

As mentioned earlier, the substrate in this experiment was nominally offcut by 0.25° toward the [111]A direction. A perfectly offcut crystal would exhibit atomic height steps and terraces running along the $[1\overline{10}]$ direction. This manifests itself in the x-ray scattering by a bifurcation of all CTR peaks along the [110] direction.



FIG. 5. Plot illustrating the mean size, shape, and orientation of $c4\times4$ reconstructed domain in relation to atomic steps and terraces in the GaAs surface. Each diametrically opposed pair of data points was obtained from a rocking-curve measurement. The ellipse drawn through the data points is a least-squares fit through the data. Atomic steps and terraces resulting from substrate offcut are indicated by successive light and dark regions. The step direction and terrace width were measured from CTR bifurcation. Note that the $c(4\times4)$ domain is aligned parallel to the step edges and extends nearly completely across the terrace. Similarly, the orientation and separation between steps on an arbitrarily offcut crystal can be determined by measuring the bifurcation of several crystal truncation rods at different azimuthal angles θ in reciprocal space²³ $(\theta = \tan^{-1}[k/h]$ in Fig. 2). To determine the step spacing W and azimuthal step orientation α , the CTR splitting $\Delta q(\theta)$ was measured at the (110), (310), and (310) positions in Fig. 2. These values were then least-squares fit to the function

$$\Delta q(\theta) = (2\pi/W)\cos(\alpha - \theta) , \qquad (6)$$

in which α and W are unknowns. The results of this fit are also illustrated in Fig. 5. Dark and light areas designate different terraces separated by atomic height steps. The step orientation is given by $\alpha = -22\pm 5^{\circ}$ as indicated in the figure. The mean terrace width determined from the above analysis is $W = 720\pm 60$ Å.

Figure 5 illustrates several interesting behaviors. First, the domain is asymmetric, being longer along the step edge than perpendicular to it. Second, the major axis of the reconstructed domain is oriented parallel to the step edges, within experimental accuracy. Third, the reconstructed domain extends almost completely across the terrace along the direction of offcut. These behaviors are all related by nature of the interruption of crystalline coherence which evidently occurs at a step edge. Crystalline coherence can naturally be maintained over greater lengths *along* the terraces rather than in the perpendicular direction, since atomic steps break the coherence of the reconstruction.

It is useful to consider two hypothetical scenarios. First imagine a $c(4 \times 4)$ reconstruction stabilized on a singular surface (no offcut). Imagine the reconstructed domain has an isotropic coherence length L so that the domain is circular. Now consider an offcut surface with terrace width W such that W < L. If the $c(4 \times 4)$ reconstruction were stabilized on this surface, the coherence would be reduced to the terrace width in the offcut direction. To first order, one would thus expect elliptical domains (major axis L and minor axis W) oriented parallel to the step edges. This is exactly the observed behavior illustrated in Fig. 5.

One might justifiably wonder why crystalline anisotro-

py plays no apparent role in determining the equilibrium shape and orientation of the reconstructed domains. For example, if the [110] dimer axis were a particularly stable direction for dimer attachment, one would expect the equilibrium domain to be elongated along the [110] direction. Figure 5 indicates that this is not the case, however. If anisotropy effects do exist, they are clearly of lesser importance than terrace geometry, and may be observable only on singular crystalline surfaces in which the terrace width is larger than the equilibrium domain size.

IV. CONCLUSIONS

Through a series of in situ x-ray measurements on a GaAs(001) surface, we have presented a structural characterization of the $c(4 \times 4)$ surface reconstruction in the OMVPE environment. By a Patterson analysis we confirmed that the As-As dimerization and three-dimer clusters participate in the $c(4 \times 4)$ reconstruction. A more detailed structural refinement indicated the surface to contain a mixture of two- and three-dimer variants of the $c(4 \times 4)$ reconstruction. The interatomic dimensions associated with these refined structures agree closely with those reported previously for the $c(4 \times 4)$ in MBE. Analysis of the in-plane crystalline coherence length revealed that the size, aspect ratio, and orientation of the reconstructed domain are strongly influenced by the geometry of atomic terraces on the crystal surface. A general result of the study is that despite the striking physical and chemical differences between the OMVPE and MBE, under appropriate conditions, similar surface reconstructions are observed in both cases. Although surface reconstructions are generally sensitive functions of physical and chemical parameters, this study illustrates that driving forces stimulating surface reconstruction persist in diverse environments.

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- ¹J. H. Neave and B. A. Joyce, J. Cryst. Growth **44**, 387 (1978).
- ²P. K. Larsen, J. F. van der Veen, A. Mazur, J. Pollman, J. H. Neave, and B. A. Joyce, Phys. Rev. B 26, 3222 (1982).
- ³P. K. Larsen, J. H. Neave, J. F. van der Veen, P. J. Dobson, and B. A. Joyce, Phys. Rev. B 27, 4966 (1983).
- ⁴G. Qian, R. Martin, and D. Chad, Phys. Rev. B **38**, 7649 (1988).
- ⁵P. K. Larsen and D. Chadi, Phys. Rev. B 37, 8282 (1988).
- ⁶M. D. Pashley, K. W. Haberern, W. Friday, J. M. Woodall, and P. D. Kirchner, Phys. Rev. Lett. **60**, 2176 (1988).
- ⁷D. K. Biegelsen, R. D. Bringans, J. E. Northrup, and L.-E. Swartz, Phys. Rev. B **41**, 5701 (1988).
- ⁸F. J. Lamelas, P. H. Fuoss, P. Imperatori, D. W. Kisker, G. B. Stephenson, and S. Brennan, Appl. Phys. Lett. **60**, 2610 (1992).

- ⁹P. H. Fuoss, D. W. Kisker, G. Renaud, K. L. Tokuda, S. Brennan, and J. L. Kahn, Phys. Rev. Lett. **63**, 2389 (1989).
- ¹⁰P. H. Fuoss, D. W. Kisker, F. J. Lamelas, G. B. Stephenson, P. Imperatori, and S. Brennan, Phys. Rev. Lett. **69**, 2791 (1992).
- ¹¹B. E. Warren, X-Ray Diffraction (Addison-Wesley, Reading, MA, 1969).
- ¹²F. J. Lamelas, P. H. Fuoss, D. W. Kisker, G. B. Stephenson, and S. Brennan (unpublished).
- ¹³L. Daeweritz and R. Hey, Surf. Sci. 236, 15 (1990).
- ¹⁴M. Sauvage-Simkin, R. Pinchaux, J. Massies, P. Calverie, N. Jedrecy, J. Bonnet, and I. K. Robinson, Phys. Rev. Lett. 62, 563 (1989).
- ¹⁵M. Sauvage-Simkin, R. Pinchaux, J. Massies, P. Calverie, N. Jedrecy, J. Bonnet, and I. K. Robinson, Surf. Sci. 211/212, 39

(1989).

- ¹⁶American Xtal Technology, Dublin, CA.
- ¹⁷S. Brennan, P. H. Fuoss, J. L. Kahn, and D. W. Kisker, Nucl. Instrum. Methods A 291, 86 (1990).
- ¹⁸J. M. Bloch, J. Appl. Cryst. 18, 33 (1985).
- ¹⁹I. K. Robinson, in *Handbook of Synchrotron Radiation* (Elsevier, Amsterdam, 1991), Vol. 3.
- ²⁰W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T.

Vetterling, Numerical Recipes, the Art of Scientific Computing (Cambridge University Press, Cambridge, 1989).

- ²¹John M. Cowley, *Diffraction Physics* (North-Holland, Amsterdam, 1984).
- ²²W. C. Hamilton, Acta Crystallogr. 18, 502 (1965).
- ²³G. Renaud, P. H. Fuoss, J. Bevk, and B. S. Freer, Phys. Rev. B 45, 9192 (1992).



FIG. 1. Three possible arrangements of As-As surface dimers consistent with the $c(4\times4)$ structure in GaAs(001). Arsenic atoms in the chemisorbed surface layer are represented by black circles, while arsenic atoms in the bulk termination layer underneath are denoted by grey circles. (a) One-dimer clusters, (b) two-dimer clusters, and (c) three-dimer clusters. The unit cell for each structure is designated by the dashed lines. The xycoordinate frame follows the [110] and [110] symmetry axes of the $c(4\times4)$ structure. Dimerized atoms in the chemisorbed surface layer are labeled with upper-case letters (A,B), while those in the bulk termination layer are labeled with lower-case letters (a,b,c).



FIG. 3. (a) Patterson map of interatomic correlations. The $c(4\times4)$ structure of the surface is clearly reflected in the 16-Å face-centered array of high correlation positions (i.e., correlation 00). These correspond to translation vectors among the neighboring dimer clusters illustrated in Fig. 1. Weaker unique correlations (01-05, inside dashed rectangle) correspond to atomic displacements within a single dimer cluster. These are labeled in correspondence with the interatomic vectors shown in (b). All other features in the Patterson map result from reflection and translation and symmetry operations. For clarity, only the positive values of the Patterson are illustrated. (b) Interatomic displacements corresponding to labeled peaks in the Patterson map. While some of the correlations result explicitly from the three-dimer cluster illustrated, others are common to the two- and one-dimer $c(4\times4)$ variants as well.



FIG. 5. Plot illustrating the mean size, shape, and orientation of $c4\times4$ reconstructed domain in relation to atomic steps and terraces in the GaAs surface. Each diametrically opposed pair of data points was obtained from a rocking-curve measurement. The ellipse drawn through the data points is a least-squares fit through the data. Atomic steps and terraces resulting from substrate offcut are indicated by successive light and dark regions. The step direction and terrace width were measured from CTR bifurcation. Note that the $c(4\times4)$ domain is aligned parallel to the step edges and extends nearly completely across the terrace.