Multiple-scattering evaluation of RHEED intensities from the GaAs(001)2×4 surface: Evidence for subsurface relaxation

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Experimental reflection high-energy electron-diffraction (RHEED) rocking curves in the $[\bar{1}10]$ azimuth from the molecular-beam-epitaxy (MBE) grown As-rich GaAs(001)2×4 surface have been analyzed by fitting rocking curves computed using elastic multiple-scattering (dynamical) theory. The surface is assumed to be composed of unit cells having the "missing row" structure in which the 2× periodicity arises from symmetrically dimerized As atoms and the 4× periodicity from a regular array of missing dimers, such that the As surface coverage is three-quarters of a monolayer. The surface model permits relaxation in both the surface layer (As) and the second layer (Ga). The best fit to the experimental data occurs for a surface unit-cell structure in which the triplets of surface As dimers are "rumpled" and the second layer (Ga) atoms relax in both the in-plane and perpendicular directions. The effect upon the fit of tilts and twists of the As dimers has been studied by imposing small displacements on the dimerized surface As atoms away from the best-fit configuration. We find evidence to suggest that the As dimers are symmetrical to within possible tilt angles of ~ 1° and/or twist angles of ~ 1°.

I. INTRODUCTION

The (001) surface of the molecular-beam-epitaxy (MBE) grown GaAs system exhibits a large family of reconstructions, different members of which occur as a result of different growth conditions (i.e., substrate temperatures and III/V flux ratios).[1,2] One surface may possess a range of different coexisting surface unit cells, each with a different surface stoichiometry, yet each of which has the same reconstruction symmetry (as revealed, e.g., in a surface diffraction experiment).[3-5] Because of these complexities it has proved extremely difficult to determine the correct surface unit-cell models for these surfaces, let alone to determine accurately the structural parameters of the reconstruction in any one of the given models. Among these reconstructed (001) surfaces, the most useful for the fabrication of device structures is the As-rich (2×4) [or c(2×8)] system. The (2×4) system was first subject to scanning tunneling microscopy (STM) studies by Pashley *et al.* These studies confirmed that, for the case of a surface As coverage, Θ_{As}, of 0.75 monolayers (ML) (known as the β phase[5]), the surface unit cell has the "missing row" structure.[6] This structure, in which the 2× periodicity arises from dimerization of

surface As atoms and the 4× periodicity from a regular array of missing dimers, had been proposed in a number of earlier theoretical studies.[3,7,8] Theoretical work has also suggested that the As dimers are symmetrical (i.e., not tilted or twisted),[3,8-10] but, because of limited resolution, STM studies have not been able to confirm this.

The structural parameters of the (2×4) "missing row" reconstruction are not well known. X-ray photoelectron diffraction (XPD) has been used to provide estimates of the As dimer bond length and the perpendicular displacement of the As surface layer from the adjacent Ga second layer and also suggested that the As dimers are symmetrical.[11] Earlier fits, performed by the present authors, of sets of calculated dynamical (multiple scattering) reflection high-energy electron-diffraction (RHEED) rocking curves to experimental rocking curves[12] for the $[\bar{1}10]$ azimuth have provided estimates of these same structural parameters.[13] (The rocking curve is the curve of the elastically diffracted intensity as a function of primary electron-beam angle of incidence.) These two studies produced reasonable consistency in their estimates of the As dimer bond length (2.2±0.2 Å from XPD and the range 2.2–2.6 Å from RHEED). However, using XPD the perpendicular relaxation of the surface As layer was found to be 0.1±0.2 Å in an inward direction (i.e., to-

wards the Ga second layer) and, although the RHEED analysis yielded perpendicular relaxation estimates lying within the quoted error on the XPD estimate, the relaxation was found to be in the opposite direction. The outward relaxation indicated by the RHEED analysis agrees with a number of earlier theoretical proposals.[7,9,14] However, the most sophisticated theoretical analysis reported so far, recently carried out by Ohno using *ab initio* total-energy calculations, has suggested a more complicated picture.[10] Here the dimers are symmetrical and the two end dimers of the As dimer triplets have dimer bond lengths of 2.72 Å while the central dimer has a bond length of 2.60 Å. Additionally, the second-layer Ga atoms are all relaxed inwards, with those adjacent to the "missing row" moving in further than those Ga atoms lying beneath the central As dimer. The central As dimer moves outwards by 0.05 Å and the two end ones move inwards by 0.04 Å ("rumpled" dimers). These discrepancies between different studies serve to indicate the present uncertainties concerning the detailed surface structure of this system.

Knibb and Maksym performed the first comparison of experimental RHEED rocking curves with calculated rocking curves for the GaAs(001)2×4 surface.[15] The STM studies mentioned earlier[6] subsequently showed, however, that the surface unit-cell model used in this initial RHEED study was incorrect since it assumed an As surface coverage of $\Theta_{As} = 1$ ML, with four tilted, twisted dimers per unit cell. As would be expected, our earlier RHEED intensity analysis employing the more correct missing-row structure produced a better fit to the experimental data than did the work of Knibb and Maksym. However, residual discrepancies in our fit suggested that too few fitting parameters were being considered in the surface model. Consequently, the values of the structural model parameters obtained could be regarded as provisional only. In particular, relaxation was assumed to be limited only to the surface As layer and to exist only in the perpendicular direction. In this paper we report an analysis of the experimental [$\bar{1}10$] azimuth RHEED rocking curves by comparison with dynamical calculations but using a more complex surface model in which both in-plane and perpendicular relaxation in the surface layer and the second layer are permitted. This work constitutes one of the few reported applications of RHEED for quantitative structural determination. Using the new model, a strikingly improved fit has been obtained. Under the assumptions of a missing-row surface unit cell with $\Theta_{As} = 0.75$ ML and symmetrical As dimers, the fit produces estimates of the surface structural model parameters and provides evidence derived from experimental data for subsurface relaxation in the GaAs(001)2×4 system. The fit reveals features in the surface structure which are not evident from using the simple model considered in the aforementioned XPD and RHEED studies. Finally, an analysis of the effect on the fit in the [$\bar{1}10$] azimuth of small displacements of the surface As atoms away from the best-fit positions suggests that the As dimers are symmetrical to within possible tilt angles (from perpendicular displacements) of $< 1°$ and/or twist angles (from in-plane displacements) of $< 1°$.

II. RHEED COMPUTATION AND FITTING PROCEDURE

RHEED is used routinely in MBE and related thin-film growth techniques both to monitor growth to within monolayer accuracy (using intensity oscillations) and to provide such surface information as the presence of disorder and the reconstruction symmetry.[16] Its use as a tool for quantitative structural determination requires the comparison of experimental rocking curves with rocking curves calculated using one of the formulations of the theory of dynamical RHEED.[17–20] In this work we use the theory of Maksym and Beeby[17] and more details of its use for the GaAs(001)2×4 surface are given in Refs. 13 and 15. The experimental RHEED rocking curves analyzed here were measured by Larsen *et al.*[12] Their experiment used a 12.5-keV primary electron beam and a substrate temperature of 838 K. In the [$\bar{1}10$] azimuth they recorded rocking curves for the six zeroth-order Laue zone reflections (0,0), (0,1), (0,2), $(0,\frac{1}{4})$, $(0,\frac{1}{2})$, and $(0,\frac{3}{4})$. Although experimental RHEED rocking curves were also reported for the [110] and [010] azimuths in Ref. 12, the [$\bar{1}10$] azimuth data have certain advantages for the present fit. More experimental rocking curves (corresponding to inequivalent reflections) were recorded for the [$\bar{1}10$] azimuth than for the other two azimuths. The [$\bar{1}10$] azimuth also provides RHEED data which are the least susceptible to the effects of the one-dimensional surface disorder known to occur from the presence of both (2×4) and c(2×8) domains,[6] and which, in the form of streaks, strongly affects RHEED patterns measured in the [110] and [010] azimuths.[3,12,21] Of course, provided that the influence of disorder is treated adaquately in dynamical RHEED calculations, fits to rocking curves measured in the [110] and [010] azimuths may also, in principle, yield quantitative surface structural information.

For the fits reported in Ref. 13, 131 beams from five integral-order Laue zones were required for convergent results. However, we found that, by using only the 51 beams in the zeroth-order Laue zone, a very good approximation to the fully converged 131 beam results could be obtained, with a consequent significant reduction in the computational demands. Use of only zeroth-order Laue zone beams, however, produces a situation in which variations in surface structural parameters in the direction parallel to the primary electron-beam azimuth have no effect on the rocking curves. The present calculations use this reduced beam set, permitting only structural parameters perpendicular to the direction of the primary beam azimuth to be fitted. As in Ref. 13, the 51 beams are made up of the 21 integral-order beams (0,0), (0,±1),..., (0,±10), the 20 quarter (with odd numerator) order beams $(0,\pm\frac{1}{4})$, $(0,\pm\frac{3}{4})$,..., $(0,\pm\frac{19}{4})$, and the 10 half (with odd numerator) order beams $(0,\pm\frac{1}{2})$, $(0,\pm\frac{3}{2})$,..., $(0,\pm\frac{9}{2})$.

The GaAs(001)2×4 surface model is shown in Fig. 1. Results of total-energy calculations for a number of model GaAs(001) surfaces suggest that surface relaxation extends at least as deeply as the third layer.[9] In our present
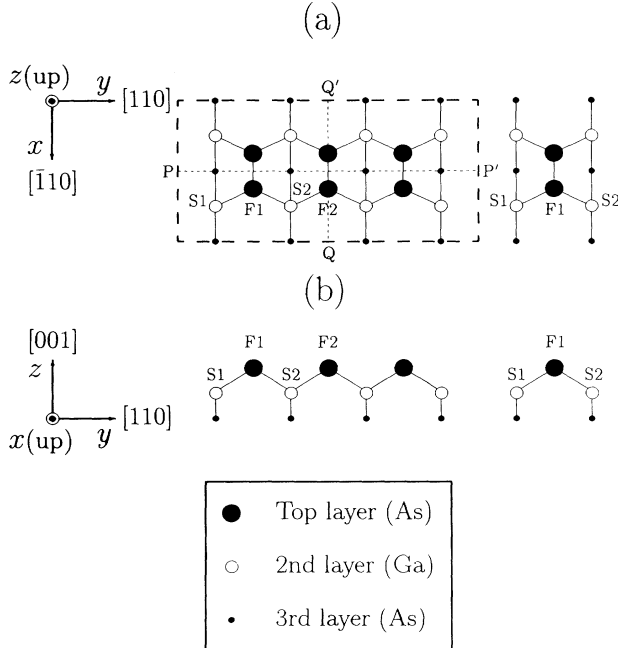
MULTIPLE-SCATTERING EVALUATION OF RHEED . . .

FIG. 1. Model of the GaAs(001)2×4 surface unit cell used for dynamical RHEED calculations, also showing the crystallographic directions and the Cartesian coordinate system with respect to which relaxations are specified. The dashed box in (a) encloses one (2×4) unit cell. Atoms $F1$, $F2$ are top layer As atoms and $S1$, $S2$ second-layer Ga atoms. The dotted lines PP' and QQ' indicate the two assumed mirror reflection symmetry planes of the unit cell described in the text. The surface is viewed along (a) the [001] direction and (b) the [$\bar{1}$10] direction (the direction of the primary electron beam).

analysis we assume that relaxation extends no further than the second layer. This simplification is adopted in order to avoid reliability problems arising from attempting to fit too many parameters to what is a rather small experimental data set. We adopt a labeling convention in which surface (first-) layer atoms (As) and second-layer atoms (Ga) have labels prefixed by F and S, respectively (Fig. 1). The positions of atoms are specified with respect to their ideal, unrelaxed, bulk-terminated positions by relaxations in the y and z directions given by Δy and Δz, respectively. As mentioned earlier, we cannot treat relaxations in the x direction (i.e., parallel to the primary electron beam) since only zeroth-order Laue zone beams are being considered. Initially we assume that each of the three As dimers per (2×4) unit cell is symmetrical. By making use of two assumed but perfectly reasonable mirror symmetries of the unit cell [the dashed rectangle in Fig. 1(a)], it is possible to reduce the number of independent structural parameters. The first mirror reflection symmetry plane is that yz plane which lies midway along the three As dimer bonds [i.e., along line PP' in Fig. 1(a)], while the second is that xz plane intersecting the As atom $F2$ [i.e., along line QQ' in Fig. 1(a)]. Hence it is sufficient only to consider the positions

of the surface As atoms $F1$, $F2$, and the second-layer Ga atoms $S1$, and $S2$ (Fig. 1). By symmetry, the positions of the remaining (unlabeled) atoms in the unit cell are also specified. A further simplification arising from symmetry is $\Delta y_{F2} = 0$. Therefore, the seven independent structural parameters are Δz_{F1}, Δz_{F2}, Δy_{F1}, Δz_{S1}, Δz_{S2}, Δy_{S1}, and Δy_{S2}. The final fitting parameter employed is the correction which is added to the model scattering potential (derived from the Fourier transform of the electron scattering factors for Ga and As, as tabulated by Doyle and Turner[22]) in order to match it to the real GaAs volume average potential ("inner potential"). More details of this correction are given in Ref. 13. The value of this correction obtained in our earlier analysis resulted in a volume average potential of −13.03 eV.[13]

As is usual in dynamical RHEED calculations, the effect of inelastic scattering processes is incorporated by using an optical potential. As in Ref. 13, the ratio of the imaginary to the real part of the optical potential is taken to be 0.237. In contrast to Ref. 13, this ratio was excluded from being a fitting parameter as calculated rocking curves are rather insensitive to its exact value. Finally, in order to approximately correct the calculated rocking curves for the effect of the loss of primary beam intensity (and consequent diffracted intensity) at very low angles of incidence (for the geometrical reasons discussed in detail in Ref. 13), calculated rocking curves are multiplied by the function $s(\theta) = 1 - \exp(-\beta\theta^2)$. As in Ref. 13, the value of β is taken to be 2.48 deg^{-2}. Again this functional form of $s(\theta)$ used is only approximate and this correction (and the exact value of β used) has little effect upon the fitting procedure. We use the same efficient multiple-parameter fitting procedure (the Marquardt algorithm[23]) as in Refs. 13 and 24–26. Errors on the best-fit parameters have been estimated using the new method developed to be used in conjunction with this fitting procedure which is described in Ref. 26. (In error estimates we have assumed the same value for the typical uncertainty in the experimental data as in Ref. 26.) Our measure of metric distance $D(f, g)$ between two rocking curves $f(\theta)$ and $g(\theta)$ (e.g., corresponding to an experimental and a calculated rocking curve, respectively) is given by

$$D(f,g) = \left[1 - \frac{\left(\sum_{i=1}^{N} f_i g_i \right)^2}{\sum_{i=1}^{N} f_i^2 \sum_{i=1}^{N} g_i^2} \right]^{\frac{1}{2}}, \qquad (1)$$

where f_i and g_i are the values of the curves $f(\theta)$ and $g(\theta)$, respectively, at the points given by θ_i ($i = 1, \ldots, N$). This has the properties $D(f, g) = 0$ if f is proportional to g and $D(f, g) = 1$ if there is no correlation between f and g. Finally, in order to correct for the effect of systematic errors in the measurement of the angle of incidence in the experimental rocking curves,[13] a maximum relative angle shift of ±0.22° has been permitted between individual experimental and theoretical rocking curves during the fitting procedure.

III. RESULTS AND DISCUSSION

In Fig. 2 are shown the results of our earlier fit to the experimental RHEED rocking curves reported in Ref. 13. This fit is shown for comparison with the fit presented in this paper. Figure 3 shows the experimental and the theoretical rocking curves obtained from the best fit using our surface model (with the reflection coefficient R_{lm} in all cases having been normalized). The average metric distance between the experimental and theoretical rocking curves for this best fit (calculated using a weighting corresponding to the number of experimental data points available for each reflection) is $D = 0.34$. This compares with a value of $D = 0.40$ obtained in our earlier reported fit (Fig. 2).[13] Numerically this is a modest improvement. However, what is most significant, and what may not be readily perceived by considering only the numerical value of the metric distance, is the striking improvement in the qualitative agreement displayed in Fig. 3 over that in Fig. 2. Generally, high-intensity peaks are well reproduced in the calculated curves and some features largely absent from the fit in Fig. 2 are present. The parameters producing this new fit are $\Delta z_{F1} = 0.01 \pm 0.03$ Å, $\Delta z_{F2} = -0.21 \pm 0.03$ Å, $\Delta y_{F1} = -0.01 \pm 0.06$ Å, $\Delta z_{S1} = -0.28 \pm 0.03$ Å, $\Delta z_{S2} = -0.17 \pm 0.03$ Å,

$\Delta y_{S1} = -0.00 \pm 0.06$ Å, $\Delta y_{S2} = 0.12 \pm 0.05$ Å, and a volume average potential of -13.86 ± 0.05 eV. Figure 4 summarizes the in-plane and perpendicular relaxations in the surface model obtained from the fit. The volume average potential of -13.86 ± 0.05 eV from this fit provides better agreement with the estimate of this quantity in Ref. 12 (-14.5 eV) than does our earlier estimate of -13.03 eV.[13] It is important to be clear that the errors quoted on the best-fit parameters provide error estimates *only within the surface model used*[26] and they can say nothing about whether the surface model used is correct. The best-fit surface model shows a number of features which have not been proposed before. One of the most striking features is that the perpendicular relaxation of the middle As dimer is significantly larger than that of the end ones (rumpling of the As dimers). Moreover, the difference in perpendicular displacement of these dimers from the second layer indicates that this is a prominent characteristic. Although we cannot directly determine relaxations in the x direction it is possible to postulate, at least qualitatively, given the y and z relaxations we have obtained, the likely sign of x relaxations of certain of the atoms. This is because a general property of covalent bonds between two given types of atom is that, whatever the structure and overall stoichiometry, bond lengths tend to remain fairly constant, as shown, e.g., in
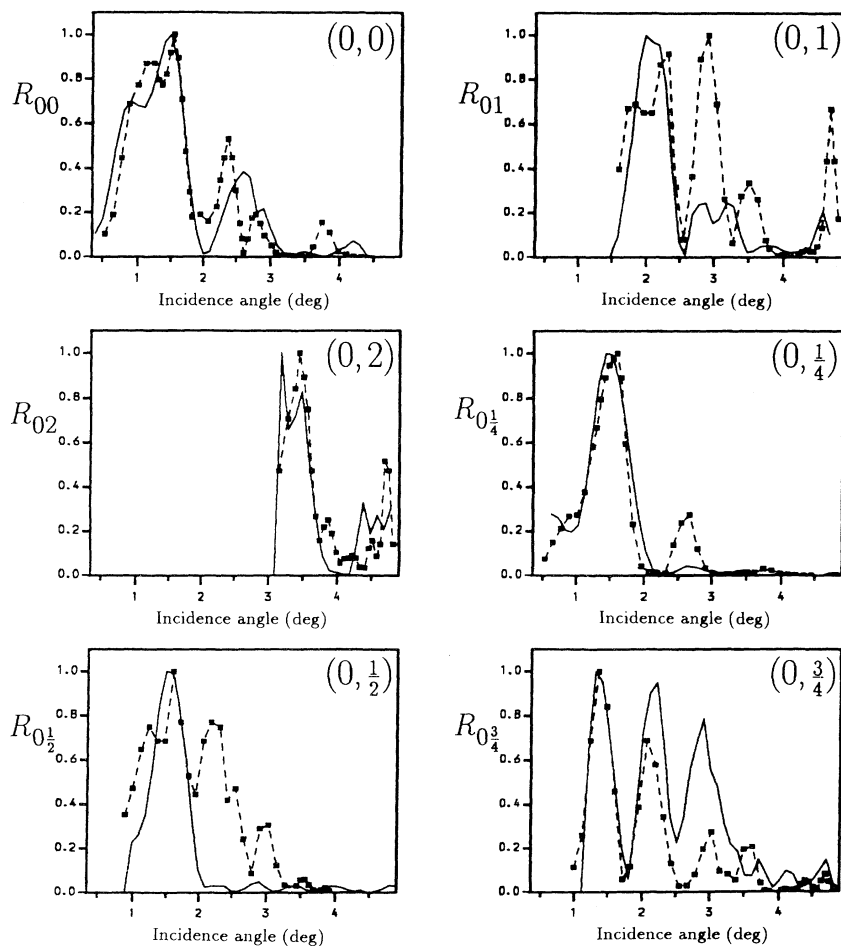

FIG. 2. Normalized experimental (dotted lines) and fitted calculated (full lines) rocking curves for the zeroth-order Laue zone reflections (0,0), (0,1), (0,2), $(0,\frac{1}{4})$, $(0,\frac{1}{2})$, and $(0,\frac{3}{4})$ reported in Ref. 13. The primary beam has energy 12.5 keV and is incident in the $[\bar{1}10]$ azimuth. The fitted curves were calculated using 131 beams and a surface model in which the only structural fitting parameters were the As dimer bond length and the perpendicular displacement of the surface As layer from the Ga second layer.
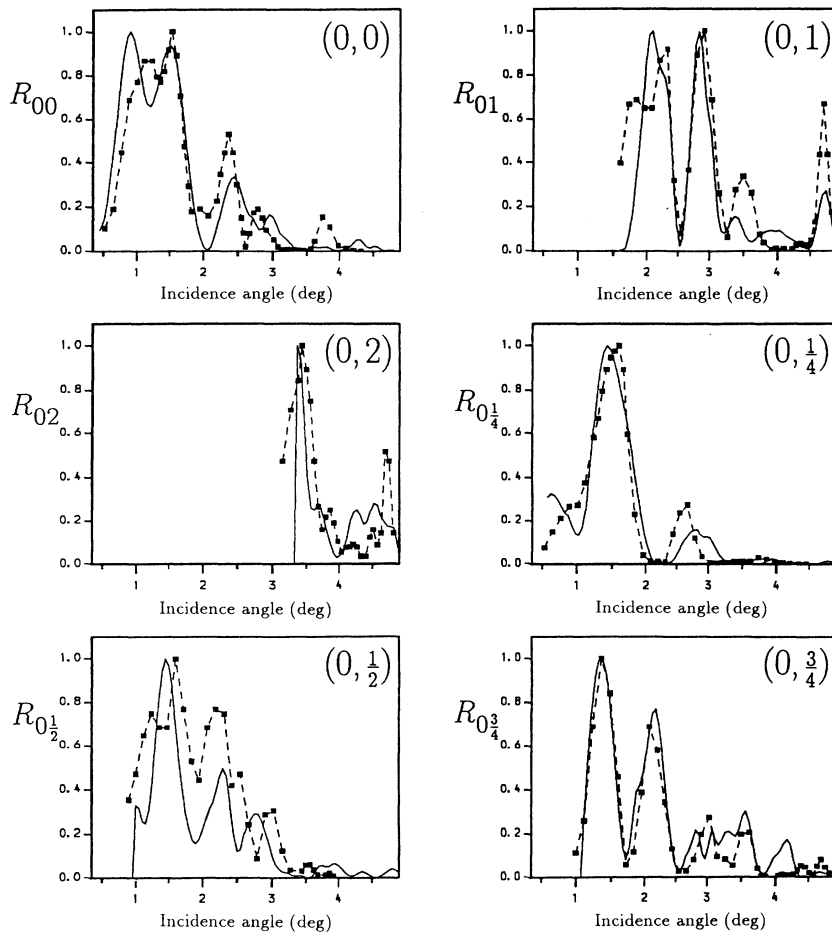
FIG. 3. Normalized fits to the same experimental data as in Fig. 2, except that here fitted curves are obtained using fewer (51) beams and a surface model in which surface relaxation is allowed in two atomic layers (see text).

the structure of amorphous compound semiconductors.[27] Applying this constraint to the relaxations we have obtained, we can infer that, since the z relaxation of the surface As atom $F2$ and the y relaxation of the Ga second-layer atom $S2$ tend to move these atoms together in the yz plane (Fig. 4), it is likely that the second-layer atom $S2$ moves in the x direction in compensation to approximately preserve the $F2$–$S2$ bond length. This suggests that the Ga atom $S2$ has a relaxation in the x direction such that $\Delta x_{S2} > 0$ [in the coordinate system of Fig. 1(a)].

As mentioned in the Introduction, the GaAs(001)2×4 surface has been the subject of a recent study by Ohno using *ab initio* total-energy calculations.[10] This computational method is extremely powerful and can provide very accurate results. Here we compare our best-fit structure with the structure proposed by Ohno. As described in the Introduction, Ohno's structure possesses rumpled As dimers and it therefore shares a common feature with ours. However, Ohno's rumpling is less prominent: the two end dimers of the As dimer triplet move inwards 0.04 Å and the central dimer moves outwards 0.05 Å. Furthermore, the sense of the rumpling in Ohno's structure is opposite to ours in that, in our structure the two end dimers move *outwards* while the central one moves *inwards*. There is also a large disagreement in the in-

plane relaxation of the end two dimers in the As dimer triplet (Δy_{F1}): our fit gives a value of -0.01 ± 0.06 Å for this parameter while Ohno's structure gives a value of 0.27 Å. Better agreement exists for the perpendicular relaxations of the second-layer atoms, the directions of these relaxations agreeing between the two models: the two parameters Δz_{S1} and Δz_{S2}, which have the values -0.28 ± 0.03 Å and -0.17 ± 0.03 Å, respectively, in our fit, take the values -0.24 Å and -0.06 Å, respectively, in Ohno's model. Finally, the overall agreement between the two models for the second-layer in-plane relaxations
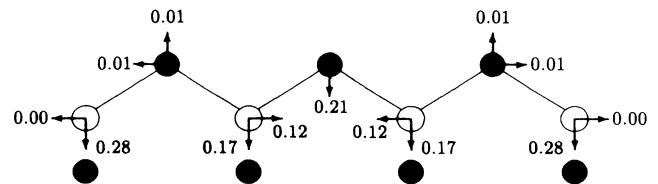

FIG. 4. Summary of atomic relaxations in the GaAs(001)2×4 surface as viewed along the $[\bar{1}10]$ azimuth [i.e., as in Fig. 1(b)]. The magnitudes of the displacements are given in units of angstroms. The displacements were determined using a surface model allowing relaxation in two atomic layers.

is rather poor, with our fit taking the values -0.00 ± 0.06 Å and 0.12 ± 0.05 Å for the two parameters Δy_{S1} and Δy_{S2}, respectively, while Ohno's model takes the values 0.72 Å and and 0.21 Å, respectively. The average metric distance between the experimental RHEED rocking curves and rocking curves calculated using Ohno's parameters is significantly worse than that obtained from our best-fit parameters, the value being $D = 0.42$. In order to understand more of the origins of the disagreement between our best-fit parameters and Ohno's parameters, it is necessary to consider in detail the sources of error entering our analysis. This is done in detail in the next paragraph. Finally, we note here that a best-fit average metric distance as large as $D = 0.34$ is compatible with the presence of significant error and this means that our main conclusions concerning evidence for the presence of subsurface relaxation may be qualitative rather than quantitative.

We now consider the sources of error in our analysis. The fitting procedure and associated method for estimating errors in the best-fit parameters provide reliable estimates provided that the typical error in an experimental rocking curve is known and that the surface structural model employed is correct.[26] (Possible errors in the experimental rocking curves have been more fully discussed in Ref. 13.) However, there are also further sources of error which may affect the fitted parameters, but in a manner which is difficult to quantify. Specifically, the effects of possible disorder present on the real surface[6,21] are neglected and surface relaxation is assumed to be limited to two layers only. It is likely that these factors, in particular the former, increase the error ranges on the best-fit parameters above our quoted values, but we cannot assess the magnitudes of these increases. Possible surface stoichiometry variation (i.e., deviations from a uniform As surface coverage, Θ_{As}, of exactly 0.75 ML) in the sample upon which the experiments were performed may be suggested as a further factor contributing to an increase in quoted error ranges. However, this is unlikely to contribute significantly since for the temperature at which the experimental data were collected (~ 838 K) the three As dimer β phase is believed to predominate.[5] It is important to be clear at this point that none of these postulated sources of error arises from deficiencies in the dynamical theory of elastic RHEED from a perfect surface. They are all associated with possible deviations of the real surface from the perfect surface model assumed in the calculations. Indeed, we know that existing dynamical elastic RHEED theories have proved perfectly capable of providing excellent agreement with experimental data (e.g., Refs. 24–26 and 28–30).

While errors are present and indeed provide uncertainty in quantitative details, the qualitative features of our resulting best-fit surface model, such as the rumpling of the As dimers and subsurface layer relaxations, are clear. Furthermore, our present fit (Fig. 3), taken in conjunction with our earlier reported one (Fig. 2),[13] shows clearly the improvement in the experiment/theory comparison (i.e., reduction in the metric distance) when both in-plane (y direction) and perpendicular (z direction) relaxation of increased depth from the surface is in-

corporated into the surface model. We conclude that this result provides very strong evidence, derived from experiment, for the existence in the GaAs(001)2×4 system of in-plane and perpendicular surface relaxation extending beyond the known perpendicular relaxation of the surface atoms (As) with respect to the second-layer (Ga), which we mentioned in the Introduction.

It is interesting to consider the relevance of the surface structural model proposed here and, indeed, that proposed by Ohno[10] (both having rumpled dimers) to STM studies of the GaAs(001)2×4 β phase surface. A recent STM study of this surface by Gallagher, Prince, and Willis performed with extremely high lateral resolution has found an interesting modulation in image brightness running in the [110] direction along the middle of the As dimer triplets [i.e., along line PP' in Fig. 1(a)].[31] The origin of this feature is unclear, but we speculate that it may be related in some way to the rumpling of the As dimers suggested in these surface models and it may, perhaps, be independent evidence for this structural feature. However, since the STM measures charge density, which often has no simple relationship to atomic positions, this must be regarded as an open question.

In an attempt to further improve our fit, we have extended our surface model to permit third-layer (As) in-plane and perpendicular relaxations. Using this model it has been possible to perform the fitting procedure and to reduce the metric distance to $D = 0.25$. However, this is only achieved at the cost of unreasonably large relaxations of the third-layer atoms which are, typically, larger than the relaxations present in the second layer. This is unsatisfactory as the magnitude of relaxations is expected to reduce with increasing distance from the surface.[9] The reason for this result is currently unknown. However, all the main qualitative features of the structure we have proposed using the model permitting relaxation in two layers only (i.e., the rumpling of the As dimers and the directions of the relaxations of atoms in the first two layers) are also present in the best-fit structure obtained from the three-layer relaxation model, although the magnitudes of relaxations are different.

In the Introduction we referred to the results of theoretical studies of (2×4)-reconstructed and simpler GaAs(001) surfaces which suggested that in all cases the As dimers are symmetrical. The XPD study mentioned earlier also found that the best experiment/theory agreement in the (2×4) system was obtained using symmetrical As dimers. Hence it is of interest to determine whether the experimental RHEED rocking curve data provides evidence confirming the symmetrical As dimer picture suggested by these other studies. The most reliable way, in principle, of addressing this question would be to perform the fit to the experimental data with the assumption of symmetrical dimers removed so that dimers are free to tilt and twist. However, this would further increase the number of independent structural parameters it would be necessary to consider, particularly if each dimer were permitted to tilt and twist independently of the others. Additionally, the symmetries of the second-layer relaxations employed in Sec. II could no longer be assumed, increasing further the number of independent

parameters. This would result in a large increase in the computational demands and possibly in reliability problems through attempting to fit too many parameters to the experimental data. Therefore, we have adopted a simpler approach which provides evidence which is suggestive rather than conclusive.

In this approach we take as the starting point the surface model with structural parameters corresponding to those of the best fit with two layers of atoms permitted to relax. In order to describe dimer tilts, additional displacements in the z direction, of $+\Delta z_t$ and $-\Delta z_t$, are respectively added to both of the As atoms making up one dimer. All three dimers in the unit cell are tilted by the same amount and, because of the insensitivity of rocking curves to x coordinates, it is irrelevant which of the two atoms in the dimer is "up" and which is "down." These z displacements constituting the imposed tilt, in the absence of imposed additional compensating x displacements, do not preserve absolutely the dimer bond length of the symmetrical dimer. However, for tilt angles of the order of a few degrees this is unimportant and it is sufficient that z displacements only are necessary to satisfactorily describe small tilts and still effectively preserve the dimer bond length, with the tilt angle being simply defined as the angle the line joining the two atoms of the dimer makes with an xy plane. Exactly the same considerations apply to describe dimer twists, except that additional displacements in the y direction of $+\Delta y_t$ and $-\Delta y_t$ are, respectively, added to the two atoms of a dimer pair. Again all three dimers in a unit cell are twisted and it is again irrelevant which atom is "left" and which is "right." We find that any possible tilts and twists of the dimers must be by angles less than 1° and 1°, respectively, before the average metric distance between sets of experimental and theoretical curves increases above $D = 0.34$ (to the two decimal place accuracy within which all metric distances are quoted). This shows that such models with dimers tilted and/or twisted by angles in these ranges are consistent with the experimental data and so cannot be excluded from being present in the real system. Equivalently, within our assumptions, the experimental data support a symmetrical dimer structure to within these small, well-defined limits in angle.

Finally, a recent suggestion has been made, on the basis of high-resolution medium-energy ion scattering using a Li$^+$ ion source, that in the (2×4) missing-row surface unit cell having three surface dimers one of the dimers may in fact be a Ga dimer.[32] We have investigated the effect of such a surface model by repeating our fitting procedure using a three-dimer missing-row model, but with the middle one of the three dimers changed to a Ga dimer. We have found that this change in the surface has little effect upon the results of the fit. This result is to be expected since the electron scattering factors for Ga and As atoms are rather similar.[22]

IV. SUMMARY

Multiple-scattering RHEED theory has been used to analyze RHEED rocking curve data in the [$\bar{1}$10] azimuth

from the MBE grown As-rich GaAs(001)2×4 surface. The analysis involves fitting calculated rocking curves obtained from a model of the surface to experimental rocking curve data. The surface model assumed is the (2×4) missing-row structure with a three-quarter monolayer surface coverage of As in the form of symmetrical dimers. Subsurface in-plane and perpendicular relaxation extending as deeply as the second layer (Ga) is permitted in the model. We find that, in comparison to previously considered surface models, allowing this two-layer relaxation gives an improved fit to the experimental data, providing evidence for subsurface in-plane and perpendicular relaxation in the real system. Furthermore, the middle one of the three As dimers in the surface unit cell has a large perpendicular relaxation directed towards the second layer, while the remaining two dimers have much smaller perpendicular relaxations. The presence of such rumpling of the dimers has been suggested independently, on the basis of *ab initio* total-energy calculations, by Ohno. However, the rumpling we have found is larger and directed in the opposite sense to that suggested from these *ab initio* total-energy calculations. The best fit gives estimates of the values of the surface structural model parameters. Errors in these parameters arise from possible errors in the experimental data and the neglect of relaxation extending more deeply than the second layer. A further factor is the neglect of the effects of surface disorder. Possible surface stoichiometry deviations from a uniform As surface coverage of 0.75 ML are not thought to be a major source of error. Finally, by considering the effect upon calculated rocking curves of small tilts and twists of the As dimers from their best-fit positions, we find that the agreement between experiment and theory is not significantly reduced provided the angles of tilt and/or twist are less than 1° and 1°, respectively. This suggests that, within the assumptions adopted, the experimental data support the symmetrical As dimer picture to within these quoted limits.

It will be interesting to see whether future studies using different probes confirm details of the GaAs(001)2×4 surface model proposed here. One difficulty with this work is our ignorance of the quantitative effect of surface disorder on the sample from which the experimental data was collected. We suggest that for studies of this kind one way of overcoming this problem would be for one sample to be subject to a combined STM and RHEED rocking curve study. This would also assist in providing information about the sample surface stoichiometry. Theoretical analysis of the rocking curve data, in the manner described here, could then be performed with improved information about the quantitative effects of any surface disorder which may be present.

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