X-ray diffraction analysis of the gallium-rich surface of GaAs(001)

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We have performed an x-ray diffraction analysis of the gallium-rich reconstruction of GaAs(001). The results clearly support the $\zeta(4\times2)$ model, which was recently proposed by Lee *et al.* [Phys. Rev. Lett. **85**, 3890 (2000)] in order to explain the atomic structure of this surface. We obtain precise values of the atomic coordinates and we analyze the chemical bonds between the first atomic layer and the underlying layers.

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The microscopic description of the gallium-rich surface of GaAs(001) is important from a technological point of view, since this surface is used for epitaxial growth. In spite of electron diffraction experiments,[1] x-ray diffraction experiments,[2] and scanning tunneling microscopy (STM) experiments,[3,4] the microscopic structure of this surface is still controversial.[5] Many authors assume that the β_2 model, the unit cell of which contains three gallium dimers, describes the Ga-rich $(4\times2)/c(8\times2)$ reconstructed GaAs surface. However, it has been shown recently that this structure, in the same way as other structures proposed in the past, does not account for the x-ray diffraction and STM experiments.[6] It has also been found that structures containing more complex structural elements such as mixed Ga-As dimers can be energetically as stable as the β_2 model.[7] A new structure containing two Ga dimers in the second atomic layer and one Ga dimer as well as threefold-coordinated Ga and As atoms in the topmost layer has been proposed recently.[8] This so-called $\zeta(4\times2)$ model is shown in Fig. 1. It has the same stoichiometry as the β_2 model, but has been found to be lower in energy.[8] It has also been demonstrated that this structure can explain the STM images measured for Ga-rich GaAs(100)(4×2) surfaces. A very recent analysis[9] has come to the conclusion that models similar to the $\zeta(4\times2)$ model can interpret the x-ray diffraction data for the cation-rich (001) surfaces of GaAs, InAs, and InSb. In view of the complexity of this model, it might be thought, however, that other related structures, combining similar structural elements, could as well describe the Ga-rich GaAs surface.

Here, we present an x-ray diffraction analysis of the gallium-rich $(4\times2)/c(8\times2)$ reconstruction, and we compare the experimental atomic positions with positions obtained from an *ab initio* calculation. Our analysis gives strong evidence for the $\zeta(4\times2)$ structure. The experiments were performed at the DCI storage ring of the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE). A clean gallium-rich surface was *in situ* prepared by molecular beam epitaxy by growing a GaAs buffer layer in standard As-rich conditions, and followed by vacuum annealing at 600 °C until a sharp 4x pattern was observed using reflection high energy electron diffraction (RHEED). After growth, the sample was transferred and aligned onto the

x-ray diffractometer, connected under Ultra-High Vacuum (UHV) to the growth chamber. The x-ray diffraction pattern was referred to a 1×1 surface basis related to the bulk fcc unit vectors by

$$\mathbf{a}=1/2[1\bar{1}0]_{\text{cubic}} \quad \mathbf{b}=1/2[110]_{\text{cubic}} \quad \mathbf{c}=[001]_{\text{cubic}}.$$

From the presence of half-order spots shown in the x-ray diffraction pattern in the k direction, we deduced that the surface reconstruction was $c(8\times2)$, where the unit cell is built from two 4×2 subunits. These spots are more diffuse, which is indicative of some disorder in the [110] direction of the surface, and were not used in the analysis. For integer values of k, the diffraction spots are sharp, from which we calculate a coherence length of 700 Å. The intensities of 65 independent diffraction spots in the $l\sim0$ plane were monitored. The intensities of five fractional diffraction rods were also taken, which corresponds to a total number of 83 independent out-of-plane data.

In a first stage, we calculated the atomic coordinates of the $\zeta(4\times2)$ unit cell, and of the reference β_2 one. This was performed using *first-principles* total-energy calculations employing the density functional theory in the local density approximation. A massively parallel, real-space finite-difference method was used to deal efficiently with the large
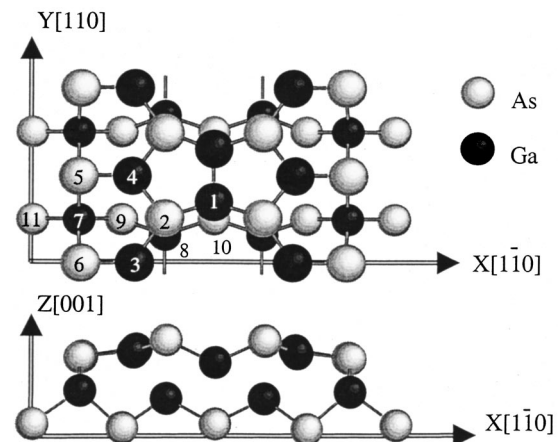

FIG. 1. Ball and stick model of the $\zeta(4\times2)$ unit cell, as proposed in Ref. 8.

unit cell needed to describe the surface.[10] The surface was modeled by periodic supercells containing material slabs consisting of 12 atomic GaAs layers separated by vacuum regions equivalent in thickness to eight atomic layers. Further computational details can be found in Ref. 8. The atomic coordinates were calculated using both a 4×2 unit cell and a $c(8 \times 2)$ one, and the results were very similar. We also probed the adsorption of additional Ga adatoms on top of the $\zeta(4 \times 2)$ unit cell, as suggested in Ref. 9. This configuration turns out to be energetically unstable, however.

In a second stage, the quality of the agreement between the measured data and the theoretical model was evaluated using the ROD software.[11] First, comparison between theory and experiment was performed by computing the factor χ^2 given by

$$\chi^2 = \Sigma_{hkl} \frac{1}{\sigma_{hkl}^2} [F_{hkl}^{obs} - F_{hkl}^{calc}]^2, \quad (1)$$

where F_{hkl}^{obs} and F_{hkl}^{calc} are the measured and calculated structure factors, respectively, and the quantity σ_{hkl} is equal to unity for all structure factors. Such a choice corresponds to a σ value of 5% for the strongest reflection and 100% for the lowest and gives a stronger weight to larger structure factors.

TABLE I. Comparison of the β_2 and $\zeta(4 \times 2)$ models with the x-ray diffraction data in the $l \sim 0$ plane. The second column shows the starting values of the quality factor χ^2 obtained using the experimental data together with atomic coordinates derived from the *ab initio* calculations, before any fitting procedure. The third column shows the reduced χ^2 after adjustment, and the fourth column shows the number p of adjustable parameters.

Starting model	χ^2 at beginning	χ^2_{red} after adjustment	Number p of adjustable parameters
β_2	1240	9.4	12
$\zeta(4 \times 2)$	130	1.3	15

Secondly, selected parameters in the model were allowed to vary in order to minimize the reduced quality factor $\chi^2_{red} = \chi^2/(N-p)$, where p is equal to the number of degrees of freedom which are let free, and N is the number of independently measured structure factors. The results in the $l \sim 0$ plane of the reciprocal space are compared in Table I with the reference case of the β_2 model.

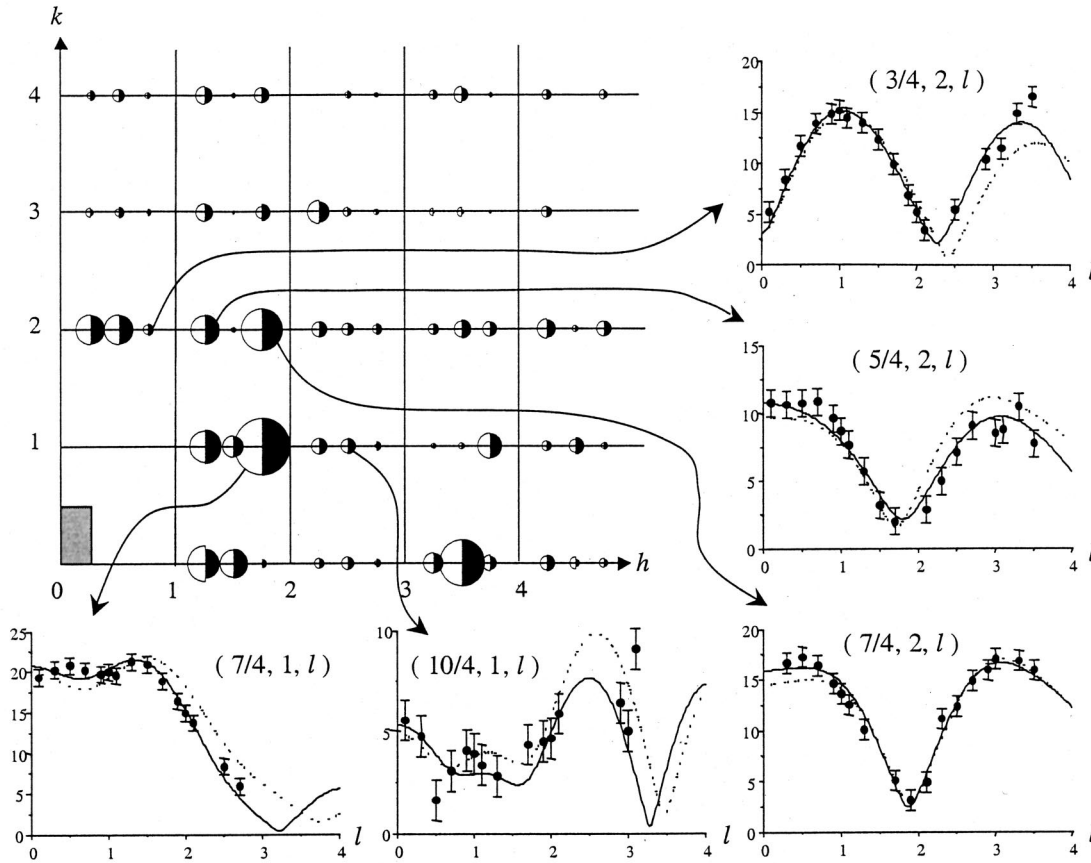Immediately apparent from the table is the fact that, before any fitting procedure, the correspondence between the

FIG. 2. Comparison between experimental (full semicircles) and calculated (open semicircles) structure factors in the $l \sim 0$ plane. The 1×1 reciprocal lattice is outlined by the square grid. The shaded rectangle at the origin displays the 4×2 unit cell. Also shown is the comparison between measured structure factors as a function of l, for specific values of h and k, indicated by arrows, with the behavior predicted by using the theoretical z atomic coordinates and the fitted atomic coordinates in the x and y direction (dotted curves), and after adjustment of the z atomic coordinates (solid curves).

experimental data and the calculations was significantly better for the $\zeta(4\times2)$ model than for the β_2 model, since the quantity χ^2 was one order of magnitude lower. Moreover, for the β_2 model, the fitting procedure had a tendency to induce the breaking of the gallium surface dimers. If we avoided these unphysical distortions, the final value of χ^2_{red} was still large. Consequently, although this model has often been proposed as the correct one for the Ga-rich surface, it can be excluded on the base of these results. In strong contrast, for the $\zeta(4\times2)$ model, the fitting procedure led to a rapid improvement of the quantity χ^2_{red}, with very small values of the displacements concerning only the first and second atomic layers, and converged to a small value of χ^2_{red}. Figure 2 shows the comparison between the experimental and calculated structure factors for the $\zeta(4\times2)$ model, and indeed displays a perfect agreement between theory and experiment. In the fit, we adjusted 15 independent atomic coordinates, corresponding to all the displacements of the first three atomic layers allowed by symmetry, and the uncertainty of the determination of these displacements was of the order of 10^{-3} of the unit cell. Only seven of these displacements have a value larger or equal to this value. Table II gives the resulting x and y atomic coordinates. It is obvious that the discrepancies between the experimental and theoretical values are very small. Indeed, the largest displacements, concerning the first atomic layer all have values smaller than 8×10^{-3} of the unit cell, whereas the maximum displacement of the second atomic layer is 4×10^{-3} of the unit cell and the only displacement of the third layer has a value equal to the uncertainty. Because of the very good fit, it was not necessary to adjust the atomic positions in the underlying layers. This very good agreement proves the relevance of the $\zeta(4\times2)$ model.

Also shown in Fig. 2 are the dependences as a function of l of the experimental values of the *out-of-plane* structure factors, together with their calculated values (dotted curves), using the fitted x, y atomic coordinates and the theoretical z values. The agreement with the experimental values is quite good, if we except slight discrepancies at large l. We performed a fitting procedure by liberating all the z atomic coordinates, apart from the one of atom 11, which defines the origin of the z axis. The z atomic displacements induced by the fitting procedure are shown in Table II. The precision in the determination of the z value was of the order of 10^{-2} of the unit cell, and in the table, asterisks show the displacements which have a value smaller than this quantity. This procedure has allowed us to obtain a satisfactory fit to the experimental data (solid curves in Fig. 2). The strongest atomic displacements introduced by the fitting procedure concern the vertical positions of gallium atoms 3 and 4. Atom 4 moves upwards, whereas atom 3 moves downwards. The z positions of these atoms appear quite physical, and corresponds to a quasiplanar $sp2$-like configuration as observed classically on III-V reconstructed surfaces.[12,13] (While for a perfectly planar configuration, the sum of the three bond angles should be 360°, this sum is, for atoms 3 and 4 equal to 341° and 357°, respectively, whereas the *ab initio* calculation finds values of 354° and 357°.) The bonds be-

TABLE II. Atomic coordinates of the model, in fractions of the 4×2 unit cell. (1.5988 nm, 0.7994 nm and 0.56532 nm along the x, y and z direction, respectively). The atom numbers refer to Fig. 1. For each atom the table gives the theoretical values, whereas the small correction gives the difference between the experimental values and the theoretical ones. Also shown are, for each atom, the number of equivalent atoms in the unit cell. The asterisks show atomic coordinates which were let free in the fit, but gave displacements smaller than 5×10^{-4} in the xy plane and than 1×10^{-2} in the z direction.

Atom Number	Atom type	x	y	z	Eq. Atoms
First layer					
1	Ga	0.500	0.347*	0.48+0.02	2
2	As	0.364*	0.263−0.007	0.65+0.02	4
3	Ga	0.288+0.008	0.000	0.58−0.07	2
4	Ga	0.274*	0.500	0.56+0.09	2
5	As	0.123−0.004	0.500	0.52+0.02	2
6	As	0.138+0.005	0.000	0.52*	2
Second layer					
7	Ga	0.127*	0.250*	0.26*	4
8	Ga	0.365+0.002	0.156+0.004	0.20+0.01	4
Third layer					
9	As	0.245+0.001	0.244*	−0.03*	4
10	As	0.500	0.247*	0.000−0.01	2
11	As	0.000	0.247*	0.000	2

tween atoms 4 and 5 are slightly buckled since the gallium atom protrudes above the arsenic atom by 0.05 nm. We find that, within experimental uncertainty, there is no buckling for the bond between atoms 3 and 6.

We now discuss some relevant interatomic distances. The length of the gallium dimers in the first atomic layer, of 0.244 nm, is the same as in the starting model. This quantity is slightly smaller than its corresponding value for the gallium dimers in the second atomic layer, which is of 0.249 nm in the starting model and of 0.250 nm after the fitting procedure. The distance between the As and Ga atoms of the first layer is slightly larger for atoms labeled 4 and 5 in Fig. 1 (experimental value 0.250 nm, theoretical value 0.242 nm) than for atoms labeled 3 and 6 (experimental value 0.242 nm theoretical value 0.240 nm), but is in all cases very close to the Ga-As distance in the volume of GaAs, of 0.245 nm.

The present detailed analysis of interatomic distances gives a deeper insight on the existent chemical bonds between the first and second atomic layers. We recall here that Ref. 8 proposed that the only bonds were between atoms 5 and 7 and between atoms 6 and 7, whereas Ref. 9 suggests the presence of additional bonds between atoms 2 and 8. The distance between atoms 5 and 7, of 0.254 nm (theoretical value 0.250 nm), is compatible with the existence of a chemical bond between these atoms, whereas the distance between atoms 2 and 8 is larger (experimental value: 0.272 nm, theoretical value: 0.266 nm). These values confirm the chemical bonds proposed by Ref. 8, rather than the ones of Ref. 9.

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