Fractional Stoichiometry of the GaAs(001)$c(4\times4)$ Surface: An *In-Situ* X-Ray Scattering Study

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Synchrotron x-ray diffraction analysis of GaAs(001) epilayers grown *in situ* by molecular-beam epitaxy shows clear evidence of As-As dimers on top of the outermost As layer. These dimers are ordered in a variable way between two structures which both show a $c(4\times4)$ symmetry but have different As content. Both structures have twofold symmetry although the unit cell is square.

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Compound-semiconductor surfaces are fundamentally different from their elemental counterparts because they have an additional composition degree of freedom. GaAs(001) is a good example with a sequence of surface symmetries starting with the most As-rich $c(4\times4)$ and ending with the 4×6 on the Ga-rich side.[1,2] Change of symmetry is certainly an indication of change of structure, but it is entirely possible that several structures have the same symmetry. For example, total-energy calculations performed on a 2×4 surface cell[3] have demonstrated that two structures with As coverages equal to 0.5 and 0.75, respectively, were equally stable; the latter being primarily observed by scanning tunneling microscopy,[4] together with small patches of other arrangements. Here we show that the $c(4\times4)$ state of GaAs(001) adjusts its structure between two extremes to accommodate different amounts of As.

The $c(4\times4)$ is the only reported GaAs(001) reconstruction exhibiting an apparent fourfold symmetry which seems to disregard the "native" twofold symmetry induced by the dangling bond orientation on this polar surface; it actually corresponds to an excess of As and may be considered a chemisorbed-type phase produced by chemisorption of either (As)4 or (As)2 molecules. Previous work by LEED in conjunction with molecular-beam epitaxy and later by reflection high-energy electron diffraction on the $c(4\times4)$ GaAs(001) surface[5-7] has not identified a structure. The only model proposed so far comes from photoemission studies which clearly identify As-As covalent bonding not present in the bulk and suggest the presence of As-As dimers.[8-10] While LEED or reflection high-energy electron diffraction are useful for surveying surface symmetry, they are difficult to apply for quantitative evaluations because of multiple scattering. On the contrary, in the case of grazing incidence x-ray diffraction,[11] the diffracted intensities can be interpreted in the simple framework of the kinematical theory and concerning clean semiconductor surfaces, reliable results have been obtained for Si(111)7×7,[12,13] Ge(001)2×1,[14] InSb(111)2×2,[15] and GaSb(111)-2×2.[16]

The present results on GaAs(001)$c(4\times4)$ are the first dealings with a GaAs reconstructed surface obtained by grazing incidence x-ray diffraction. The presence of As-As dimers is confirmed with a dimer bond length of 2.59 ± 0.06 Å, significantly longer than the value for bulk As. Moreover, direct inspection of the x-ray data demonstrates that the true symmetry of the reconstructed surface is not fourfold but belongs to the $mm2$ two-dimensional symmetry group, in agreement with the bonding scheme in the As bulk termination layer.

The experiment was made possible by coupling a molecular-beam-epitaxy growth chamber (base pressure

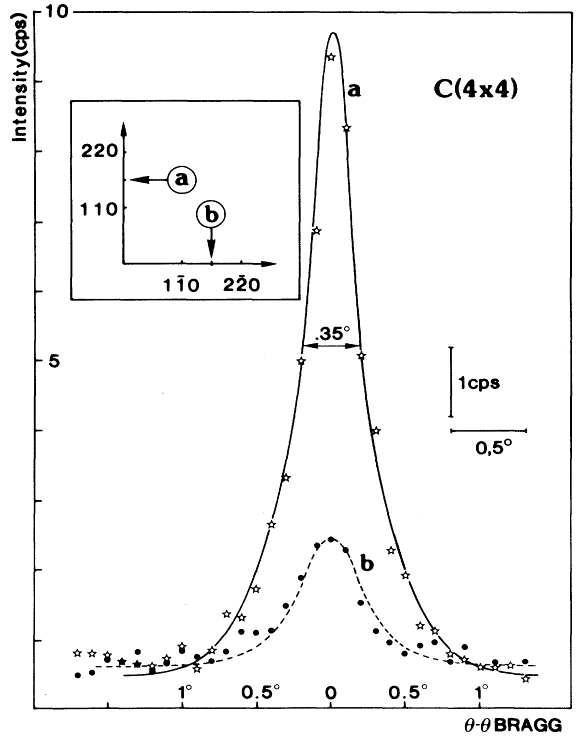

FIG. 1. Experimental rocking curves (θ scans) for two fractional orders whose intensity ratio is critical in model selection; $(\frac{3}{2},\overline{\frac{3}{2}},0.03)$: absent with the position parameters proposed in Ref. 8. $(\frac{3}{2},\frac{3}{2},0.03)$: strongest pure surface peak.

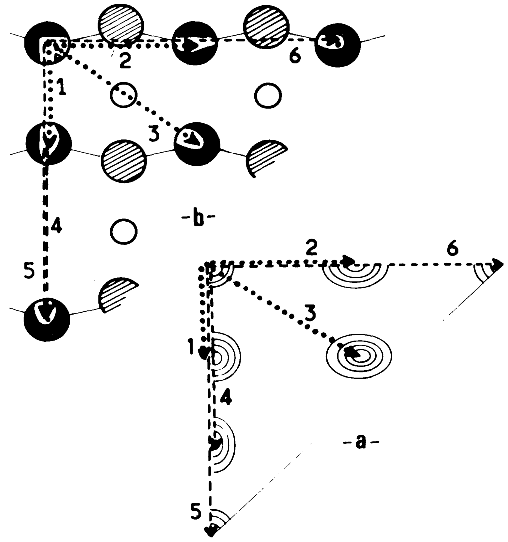

FIG. 2. (a) Asymmetric unit of the experimental Patterson map. (b) Blowup of Fig. 3(b): interatomic vectors compatible with (a).

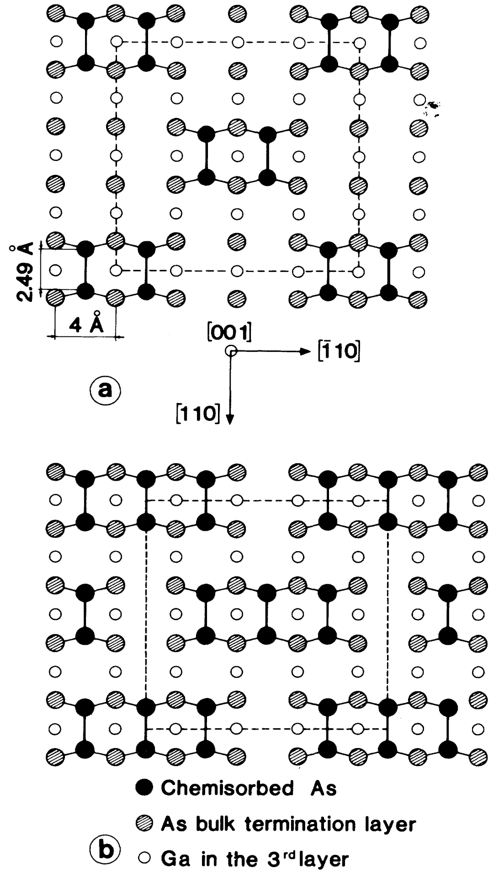

FIG. 3. Possible models for the $c(4\times4)$ surface unit cell with parameter $a_s=4a_v/\sqrt{2}=16$ Å. (a) Four-atom cluster basis (from Ref. 8). (b) Six-atom cluster basis. Notice the different registry of the surface cell (dashed square) with respect to the bulk when the origin is chosen at the center of symmetry for the structure basis.

10^{-10} mbar) with an ultrahigh-vacuum-compatible four-circle diffractometer set at the bending-magnet beam port D25 of the LURE synchrotron radiation facility (Orsay, France).[17] The GaAs substrates were submitted to a light chemical etching (H_2SO_4-H_2O_2-H_2O) prior to the introduction in the growth chamber. Growth was performed at 580 °C under As stabilized conditions and proceeded with the 2×4 As-rich surface. At the end of the epilayer growth, the $c(4\times4)$ reconstruction was obtained on cooling down to 300 °C under the As flux. After being transferred to the diffraction chamber (base pressure 5×10^{-10} mbar) the sample was kept at 200 °C during the whole data collection to prevent surface pollution. A reference surface diffraction peak ($\frac{3}{2},\frac{3}{2},0$) was monitored and found to change neither in intensity nor in width. At the end of the experiment several surface reflections were recorded at room temperature and found identical to the measurements performed at 200 °C. The data set used in the present work has been collected on three surfaces: two successive epilayers grown on the same substrate, and one independent growth run on a different substrate, under the same pressure and temperature conditions, thus ensuring a constant chemical potential environment.

The sample normal (cut to with 0.1° of [001]) was aligned with the diffractometer Φ axis by means of a laser and an in-vacuum goniometer stage. The data were recorded with a Si(Li) detector with a constant incidence angle α, kept within 2% of the critical angle for total external reflection α_c ($\alpha_c=5\times10^{-3}$ rad for $\lambda=0.1488$ nm) by our monitoring the specular beam on a video camera. The resolution function is highly anisotropic since a quasiparallel incident beam is used ($\Delta q/q$ parallel transverse $\sim10^{-4}$) and a (5×5) mm^2 slit is placed in front of the detector ($\Delta q/q$ parallel radial $\simeq\Delta q/q$ perpendicular $\simeq2\times10^{-2}$).

A total of 79 integrated intensities were measured, which reduced to 44 crystallographically independent values. The reproducibility of symmetry equivalents was

TABLE I. Atom fractional coordinates in $c(4\times4)$ unit cells of parameter $a_s=16$ Å with origin at the inversion center of the basis for the two structures leading to the best fit (see Fig. 4).

Six-atom cluster			Four-atom cluster		
	u	v		u	v
As_1	0	0.085(3)	As_1	0.121(2)	0.080(2)
As_2	0.244(2)	0.083(2)	As'_1	0	0.122(3)
As'_1	0.111(2)	0.128(2)	As'_2	0.249(2)	0.117(2)
As'_2	0.373(2)	0.120(2)	As'_3	0.5	0.125(3)

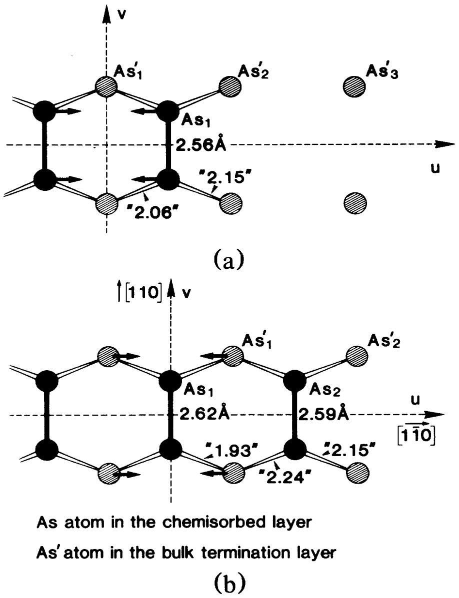

FIG. 4. Atomic positions used in the refinement; u and v are fractional coordinates in the fourfold square cells sketched in Fig. 3. Primed and nonprimed labels refer to As atoms in the second and top layers, respectively. Arrows mark the sense of displacement from bulklike sites for the As' atoms. The projected lengths of out-of-plane bonds are indicated between quotation marks.

15% which is taken to be the overall systematic error. Six of the data with integral indices in the reciprocal lattice contain contributions of crystal truncation rods[18] from the bulk. The intensities of these show a dramatic departure from fourfold symmetry (see Fig. 5) in the direction that indicates As termination of the bulklike crystal lattice; only a random mixture of Ga and As termination could give a fourfold symmetric pattern due to the bulk $\bar{4}3m$ symmetry. Depending on the sample, the angular FWHM of the surface peaks in Q space ranged between 3×10^{-2} and 0.1 Å^{-1} which corresponds to a size of 20 to 6 nm for the coherent reconstructed domains.[19] Fractional peaks $(\frac{3}{2},\frac{3}{2},0.03)$ and $(\frac{3}{2},\overline{\frac{3}{2}},0.03)$ are displayed in Fig. 1 and clearly reveal the nonfourfold symmetry of the reconstruction.

The set of 38 surface reflections has been used to produce a Patterson map, Fig. 2(a), which indeed showed all the interatomic vectors (labeled 1, 2, and 3) predicted by the four-atom cluster model[8] [Fig. 3(a)]. However, additional interatomic vectors [labeled 4, 5, and 6 in Fig. 2(a)] could only be interpreted in terms of a new model involving a six-atom chemisorbed As cluster basis arranged on an identical centered square lattice [Fig. 3(b) and blowup 2(b)]. A similar structure has been proposed for a $c(4\times4)$ reconstruction of Si(001) observed under very stringent preparation conditions.[20]

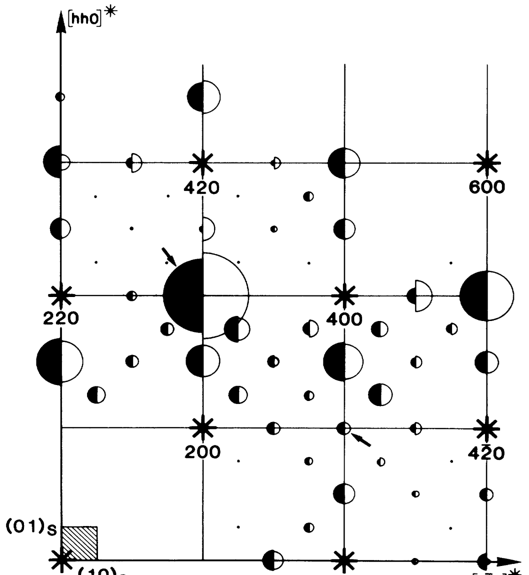

FIG. 5. Observed (empty semicircles) and calculated (full semicircles) structure factors (radius proportional to the numerical value). The square grid outlines the 1×1 reciprocal lattice, the shaded square marks the 4×4 reciprocal cell with unit vector $(10)s$ and $(01)s$. The lack of fourfold symmetry is demonstrated by the absence of a mirror along $[h00]^*$: the arrows point to the nonequivalent integer orders 310 and 3$\bar{1}$0, whose intensity ratio would be reverse in case of a Ga bulk termination layer.

Both structures in Fig. 3 were least-squares refined for the best fit with the data. Displacements, consistent with the $mm2$ (c_{2v}) symmetry, were permitted in the top two layers. The final parameters are listed in Table I with the numbering scheme of Fig. 4 where "primed" labels refer to As atoms in the second layer. Both models showed clear minima in R factors[21] of 32% [two dimers, Fig. 3(a)] and 24% [three dimers, Fig. 3(b)] but neither was satisfactory at the level of experimental errors (15%). Statistical disorder was introduced in the topmost layer without substantial improvement. Only when a *mixture* of the two ordered models was considered did a satisfactory fit emerge, for the proportion 50-50 ($R=17.5\%$), yielding the correspondence between observed and calculated structure factors displayed in Fig. 5. This model is then considered a fairly good description of the surface structure for the samples studied in the present experiment. Changing the partition between the two types of domains allows for a variable surface coverage from 0.5 to 0.75 which corresponds well to the range over which the $c(4\times4)$ reconstruction is actually observed.[2] Moreover, when one considers the scanning tunneling microscope images obtained for GaAs(001)-2×4,[4] or Si(001)2×1,[22] it is quite realistic to assume that several ordered atomic arrangements are simultaneously present on the surface.

The projected bond lengths in the two refined models show the same chemical trends: the As−As bond of the dimer is systematically (3-5)% larger than in bulk As (2.51 Å)[23]; the interlayer As−As bonds [$\mathrm{As}_1-\mathrm{As}_1'$ and $\mathrm{As}_1-\mathrm{As}_2'$ in Fig. 4(a); $\mathrm{As}_1-\mathrm{As}_1'$ and $\mathrm{As}_2-\mathrm{As}_1'$ in Fig. 4(b)] are asymmetric in their projections. We note that even though we cannot distinguish directly between the almost isoelectronic Ga and As atoms in the structure, the agreement for the integer order reflections is very sensitive to the stacking of the layers and the registry of the overlayer (see Fig. 5). We have assumed bulk composition up to the As layer containing the displaced atoms As_1' and As_2'. Different registries of the dimer layer gave worse agreement for these reflections.

Our surface-sensitive grazing-incidence x-ray diffraction experiment has established two models for the $c(4\times4)$ reconstruction of GaAs(001) containing different numbers of As adatoms but showing the same twofold symmetry. The actual state of the surface is a combination of these two limiting structures indicating that the stoichiometry varies across the surface. This result neatly explains how the $c(4\times4)$ state can occur over a range of As coverages. The same stoichiometry was found to occur for all three preparations of the surface used. We believe this to be dictated by the choice of growth conditions and would expect it to vary with the As chemical potential; experiments are planned to investigate this effect.

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