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STRUCTURE OF IN-SITU GROWN GaAs(001) RECONSTRUCTED SURFACES BY GRAZING INCIDENCE X-RAY DIFFRACTION

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The atomic structure of GaAs(001) reconstructed surfaces prepared in-situ by molecular beam epitaxy (MBE) has been determined by grazing incidence X-ray diffraction (GIXD) using a synchrotron radiation source. The c(4×4) phase is described as a mixture of two limiting structures with clusters of 4 or 6 As atoms chemisorbed on a full As layer. The atomic arrangement in the 2×4 reconstruction is still controversial: the present GIXD data imply a predominance of As terminated bulk whereas previously published data are in favour of a Ga bulk top layer.

1. Introduction

GaAs surfaces prepared by molecular beam epitaxy (MBE) [1] are known to present a large variety of reconstructions produced by a proper selection of the growth conditions. For such compound semiconductors, reconstruction is often correlated to stoichiometry and it is thus possible to go through a series of phase transitions on the (001) surface from the As saturated c(4 × 4) to the Ga stabilized c(8 × 2) structures [2] by adjusting the substrate temperature or (and) the ratio of As and Ga partial pressures in the MBE chamber.

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For each surface symmetry a range of composition has been determined by coupling electron diffraction and spectroscopic techniques [3]. The very existence of extended composition ranges [4] suggest the possibility of different atomic arrangements preserving the surface symmetries.

From a technological point of view, the most important surface reconstructions are the 2×4 and $c(4 \times 4)$ phases, respectively stable at high (600 °C) and low (below 300 °C) temperature, at the end of the standard MBE growth procedure under As stabilized conditions. Accordingly both surfaces have been the subject of several experimental and theoretical studies, and structural models have been proposed on the basis of reflection high energy electron diffraction (RHEED) [5] and angular resolved photoemission [6–8] results. In addition, a direct space experiment by scanning tunneling microscopy (STM) [9] has recently produced images of a local atomic ordering showing the 2×4 symmetry which confirms total energy calculations and RHEED intensity data [10].

No STM data are available on the $c(4 \times 4)$ surface structure and the present grazing incidence X-ray diffraction (GIXD) gives the first structural information on the atomic arrangement. Indeed, electron diffraction methods such as RHEED are mostly used to establish the surface symmetry and phase diagram, but quantitative intensity analysis is made difficult by multiple scattering effects which can be neglected in the case of thin layer X-ray diffraction. Moreover, the grazing incidence geometry ensures a high surface sensitivity since the penetration depth is reduced to a few tens of ångströms.

In the particular field of III–V semiconductor reconstructed surfaces, GIXD structural determination has been performed on the InSb(111)2×2 [11] and GaSb(111)2×2 [12] surfaces but none of these studies was concerned with in-situ processing of the surface state. To allow such surface conditioning, an experimental set-up coupling a MBE growth chamber, equipped with the standard surface characterization techniques, to a 4-circle diffractometer under a continuous ultra-high vacuum (UHV) in the low 10^{-10} mbar range, has been developed at the LURE-DCI synchrotron radiation facility (Orsay, France) [13].

GIXD data have been obtained for both $c(4 \times 4)$ and 2×4 GaAs(001) surface phases. The As chemisorbed nature of the $c(4 \times 4)$ surface proposed by Larsen et al. [7] has been confirmed but a two-domain description of the actual surface was necessary to fit the data. The two structure bases are sketched in figs. 1a and 1b and correspond respectively to an As coverage of 0.5 and 0.75, on top of a full bulk-like As layer. The structure in fig. 1a was already suggested by Larsen et al. [7]. Varying the ratio between these two limiting cases accounts for the range of stoichiometry attributed to the $c(4 \times 4)$.

The 2×4 unit cell derived from STM images [9] is shown in fig. 2: the structure basis consists in three adjacent As dimers followed by a missing

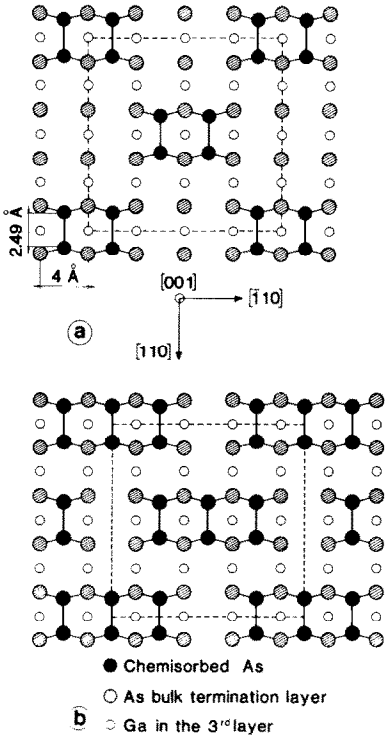

Fig. 1. Structure bases for the c(4×4) phase: (a) 4-atom chemisorbed As clusters on a centered square lattice – As coverage 0.5 (after ref. [7]); (b) 6-atom chemisorbed As clusters – As coverage 0.75. The atom coordinates in the first two layers, determined by X-ray diffraction are found in ref. [14].

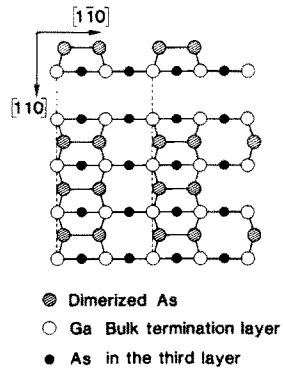

Fig. 2. The 2×4 unit cell (after refs. [9,10]).

dimer row, the As coverage is then 0.75, on top of a full bulk-like Ga layer. Energy calculations [10] have shown that a basis made of two dimers followed by two missing dimer rows (As coverage 0.5) would be nearly as stable, which might account for the composition range over which the 2×4 symmetry is observed.

The first results collected by GIXD on the 2×4 phase do not agree with this description since the Ga nature of the bulk termination layer is questioned. However STM images have clearly shown the high inhomogeneity of this surface and areas with an As bulk termination might be present as well.

2. Experimental

GaAs layers have been grown following the standard MBE procedure under As stabilized conditions: the stable state at the growth temperature (580 °C) is the 2×4 phase. By cooling under As pressure one obtains the c(4 × 4) structure whereas decreasing the As pressure when keeping the sample around 450 °C enables one to retain the 2×4 symmetry. This procedure was found to yield a better 2×4 order than annealing a c(4 × 4) surface in UHV. The sample was transferred in situ to the diffractometer stage where the normal to the surface (within 0.1° of the [001] direction) was first laser aligned with the diffractometer ϕ axis by means of an in-vacuum orientation tool.

Diffracted intensities have been collected at a constant grazing incidence angle α kept within 2% of the critical value α_c for total external reflection ($\alpha_c \approx 5 \times 10^{-3}$ rad for $\lambda = \lambda_{KNi} = 0.1488$ nm) in order to optimize the signal while preserving the surface sensitivity. The α value was controlled by monitoring the specular beam on an X-ray sensing video detector. The sample was kept at 200 °C during the whole data collection in order to avoid surface contamination; a reference peak measured at regular intervals showed no significant drift and a room temperature measurement performed at the end of the session demonstrated that no changes had been introduced by working at 200 °C.

3. The c(4 × 4) structure

A set of 38 independent fractional reflections has been used to derive a model for the atomic structure which involves a two-domain description: two structure bases have been identified (see figs. 1a and 1b). Either of these taken separately led to a rather poor fit with the experimental structure factors, F_{obs}. When using a reliability factor R defined by

$$R = \frac{\sum | F_{obs} - | F_{calc} | |}{\sum F_{obs}},$$

where F_{calc} are structure factors calculated according to a given model, one found that refining model 1a led to a minimum R value of 32% whereas model 1b led to 24%. Since either value was still significantly larger that the 15% accuracy estimated for the experimental data from the comparison of symmetry equivalent reflections, the refinement was pursued by allowing a mixing of the two structures. This procedure brought the R value down to 17.5% when 50% of the surface was reconstructed as in fig. 1a and 50% as in fig. 1b. The expression used for the value $|F_{calc}|$ was then:

$$|F_{calc}| = \left(0.4\,|F_{calc}|_a^2 + 0.6\,|F_{calc}|_b^2\right)^{1/2},$$

subindices a and b refering respectively to the models presented in figs. 1a and 1b. Introducing random vacancies in either model did not improve the fitting and the above description was thought to display the essential features of c(4 × 4) GaAs surfaces: an adjustable stoichiometry via the mixing of two structural forms and the non-fourfold symmetry of the phase, clearly evidenced by the different intensities of the two fractional peaks (3/2, ±3/2, 0.03) shown in fig. 3 and expected for a (001) surface in a III–V semiconductor, the true symmetry induced by dangling bond orientation being mm2.

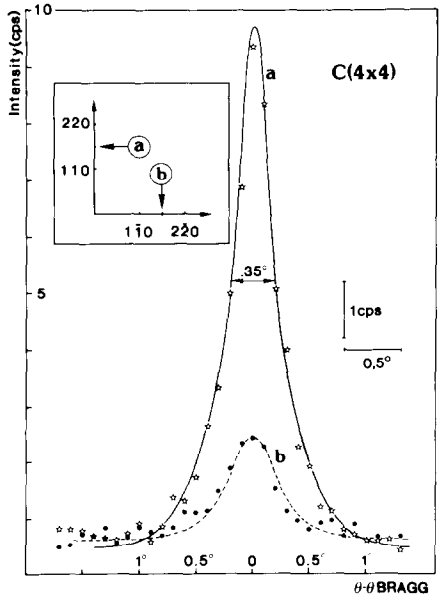

Fig. 3. c(4×4) diffraction data: fractional surfaces peaks (3/2, 3/2, 0.03) curve a, and (3/2, $\bar{3}$/2, 0.03) curve b. Evidence for the non-fourfold symmetry of the structure. The inset shows the location of nodes in reciprocal space. Coherent domain size of about 20 nm deduced from the FWHM. For all experimental curves presented in figs. 3–6, counting rates are normalized to a current of 100 mA in the DCI storage ring.

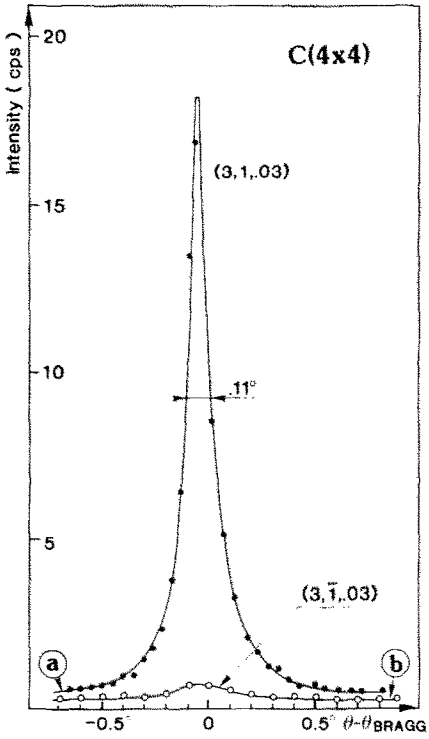

Fig. 4. c(4×4): integer orders (3, 1, 0.03) and (3, $\bar{1}$, 0.03). The narrow width of the (3, 1, 0.03) order is an evidence for a strong volume contribution in agreement with the As nature of the bulk termination layer.

Further details concerning the structure refinement are published in a separate paper [14].

The registry of the chemisorbed layers with respect to the bulk is assessed by considering integer order reflections (h, k, l) which are surface allowed but bulk forbidden (h, k both odd, $l \approx 0$). Owing to the strong damping in grazing incidence geometry, the interference between successive bulk layers is no longer totally destructive and the resulting amplitude has to be added coherently to the reconstructed layer scattering [15]. It can be shown that for (001) III–V semiconductor surfaces, these reflections are a very sensitive indicator of the back-bond orientation in the bulk termination layer: for example a strong contribution, proportional to the sum of the scattering factors ($f_{As} + f_{Ga}$) is expected at the reciprocal point (3, 1, 0) whereas a vanishingly small effect, proportional to ($f_{As} - f_{Ga}$) is due at point (3, $\bar{1}$, 0) in the case of an As bulk termination layer, which is indeed observed in the c(4 × 4) surface diffraction data (fig. 4). Moreover the surface structure

coherence being of shorter range than the bulk coherence, integer orders with a strong volume contribution have a smaller full width at half maximum (FWHM) than fractional surface peaks (compare (3/2, 3/2, 0.03) and (3, 1, 0.03) in figs. 3 and 4, respectively). In the present sample the reconstructed domain size was about 20 nm.

4. The 2 × 4 structure

The preliminary data analysis concerning 23 fractional reflections and 5 integer orders does not support the STM derived unit cell [9] (fig. 2). Discrepancies lie not only in the fractional intensities compared to the model predictions but also in the volume contribution to integer orders. Following the same lines as in the previous section it can be deduced that a Ga bulk termination layer (as is proposed in fig. 2) should lead to a major volume contribution to the (3, $\bar{1}$, 0) peak and to nearly no volume contribution in the (3, 1, 0) order, which is not observed experimentally (fig. 5). Our results imply

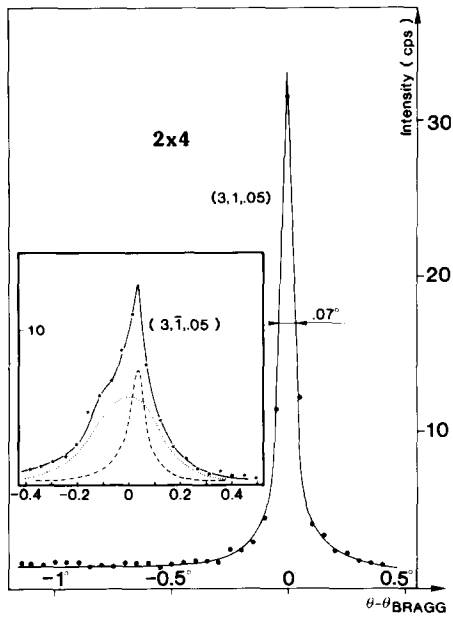

Fig. 5. 2×4 diffraction data: the same integer orders as in fig. 4. The quasi exclusive volume contribution (identified by the narrow FWHM) to the intense (3, 1, 0.05) peak contradicts the assumption of a Ga bulk termination layer (see fig. 2). No satisfactory explanation is available yet for the angular shift between volume (narrow curve) and surface (broad curve) components present in the reflection (3, $\bar{1}$, 0.05) as roughly sketched by the dotted lines. A similar shift has been observed for reflection (5, $\bar{1}$, 0.05).

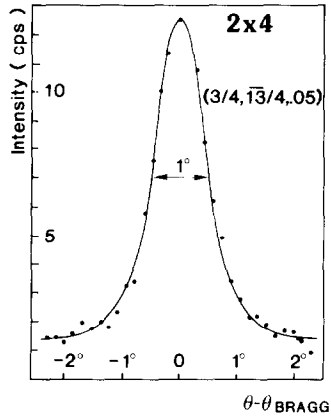

Fig. 6. The strongest fractional peak in the 2×4 diffraction data set, a predominance not predicted by the model shown in fig. 2. The broad FWHM corresponds to a coherent size of 5 nm for the reconstructed domains.

that a large fraction of the sample area corresponds to an As terminated bulk while Ga terminated regions are only present to a lesser extent.

As was already known from electron diffraction data [5], half order reflections due to the doubling of periodicity in the [1$\bar{1}$0] direction have been found very diffuse, whereas fourth order reflections were well defined (fig. 6). When compared to the c(4 × 4) surface, the shorter range of coherent reconstruction is assessed by the larger FWHM of fractional orders (fig. 6). The average coherent domain size is estimated to be 6 nm.

5. Conclusion

These two GIXD studies on in-situ MBE grown GaAs(001) surfaces have demonstrated the existence of several atomic arrangements preserving the surface symmetry while allowing a finite composition range.

A two-structure description has been unambiguously established for the c(4 × 4) phase, whereas the actual atomic ordering for the 2 × 4 reconstruction is still an open question. For the latter case, the high disorder and the different preparation conditions may explain the discrepancy between the results obtained by the various techniques. The full X-ray diffraction data analysis of the 2 × 4 structure is in progress and will presumably lead to a multi-structure description

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