Commensurate and Incommensurate Phases at Reconstructed (In,Ga)As(001) Surfaces: X-Ray Diffraction Evidence for a Composition Lock-in

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Surface chemical ordering of group III elements in the ternary alloy $In_xGa_{1-x}As$, stabilizing the 2×3 reconstruction at the surface composition $In_{0.67}Ga_{0.33}As$, is demonstrated on the basis of x-ray diffraction data. An incommensurate $2 \times n$ reconstruction is observed for lower In surface concentrations, achieved by burying an InAs monolayer under a number of GaAs layers and letting the In surface segregation process operate. A quantitative account of the intensity measured in the incommensurate phase is obtained by using a probabilistic distribution of Ga- and In-rich structural elements.

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Ternary and quaternary III-V semiconductor alloys are key materials in advanced technology for optoelectronics and microwave devices. The ultimate performances are critically dependent on the quality of the interfaces at the various heterojunctions in terms of roughness and interdiffusion. While in most cases the topology of the interface can be tailored by selecting the proper growth conditions, the composition abruptness is impaired by the phenomenon of surface segregation which drives one of the constituents of an alloy preferentially to the surface. In the present example of (In,Ga)As ternary alloys, the surface segregation of indium has been evidenced by Auger and photoelectron spectroscopy [1,2] and correlated with the optical properties of heterostructures [3,4]. Since the effects are essentially damaging, a number of growth strategies have been operated to minimize the associated composition gradings [5]. Specific reconstructions, never observed in binary strain free materials, such as the commensurate 2×3 and incommensurate $2 \times n$, appear on pseudomorphic layers of $In_xGa_{1-x}As$, strained on GaAs(001) substrates for a range of nominal x values including unity [6,7]. Although a correlation was inferred between the indium surface concentration and the reconstruction, a full interpretation in terms of atomic distribution in the surface unit cell was not yet available.

Taking advantage of the unique ability of x-ray diffraction to probe the atomic ordering not only at the surface but also in the subsurface region, the present work establishes for the first time the existence of a cation ordering at the surface which stabilizes the 2×3 commensurate reconstruction at a minimal indium surface concentration of 0.67. Moreover, by using a diffuse scattering formalism, the transition to the incommensurate $2 \times n$ phase is interpreted in terms of an increased probability of gallium rich structural elements which are precursors of the pure GaAs(001)-$c(4 \times 4)$ symmetry. The experiment has been performed on a series of samples prepared *in situ* by molecular beam epitaxy (MBE) in a growth chamber coupled to the x-ray diffractometer within a single ultrahigh vacuum (UHV) system [8].

Thick gallium arsenide substrates ($13 \times 13 \times 2.5$ mm^3), cut within 0.1° of the nominal (001) orientation and mechanochemically polished, were deoxidized in a 10% HCl-ethanol solution prior to the introduction in the UHV system. A 5000 Å GaAs buffer was grown in standard conditions [580 °C, 1 monolayer (ML) per 3 s] and resulted in an extremely well ordered 2×4 reconstructed surface whose structural properties are presented in a separate paper [9]. One molecular layer of InAs was then deposited with a calibrated In cell, in As rich conditions, at 450 °C and a deposition rate of 1 ML/13 s. From this stage, four different procedures have been followed: Sample I was simply cooled under an As flux and transferred to the diffractometer stage after controlling by reflection high-energy electron diffraction (RHEED) the presence of a clear commensurate $\times 3$ reconstruction in the [110] direction. Sample II was first covered by one molecular layer of GaAs at 450 °C at a rate of 1 ML/3 s before cooling under the As flux; the RHEED pattern was again a commensurate $\times 3$. Sample III was covered by 5 ML of GaAs at the same rate, temperature, and As pressure as sample II, and the pattern developed after cooling was then clearly an incommensurate $\times n$. Finally, sample IV was covered with 10 ML of GaAs, and, in that case, a diffuse streaky RHEED pattern was observed. In any of the first three samples, half-order streaks in the $[1\bar{1}0]$ direction were barely visible, denoting a weak correlation for the $\times 2$ periodicity. The preparation procedure is known to produce an indium composition profile with a surface peak whose intensity depends on the thickness of the GaAs cap [2,4]. The x-ray diffraction data presented in the following will provide a direct

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correlation between the reconstruction and the surface In concentration.

The data have been collected at room temperature in the UHV surface diffractometer (base pressure low 10^{-10} mbar) installed on the Wiggler beam line DW12 at the LURE synchrotron radiation facility (Orsay, France). The samples were set at the critical angle for total reflection ($\alpha = 0.2°$) for the incoming x-ray energy of 12.4 keV (0.1 nm). 28 independent in-plane third order reflections and 7 integer orders have been measured for samples I and II, whereas for sample III only 15 fractional and 5 integer peaks were found above the background level due to the increased disorder in the surface. Half-order lines related to the twofold periodicity in the $[1\bar{1}0]$ direction were too diffuse to be measured. The configuration of the diffractometer at the time of the experiment did not allow the collection of out-of-plane data. The measured integrated intensities were corrected according to the standard procedure for the Lorentz and geometrical factors in order to obtain a set of observed structure factors for the three samples; a 2×3 surface basis was used with the following relationship with the bulk fcc basis:

$$\mathbf{a}_1 = [1\bar{1}0]_{\mathrm{cub}}, \quad \mathbf{a}_2 = 3/2[110]_{\mathrm{cub}}, \quad \mathbf{a}_3 = [001]_{\mathrm{cub}} .$$

Prior to any structural analysis, the comparison between the observed structure factors in samples I and II showed that their differences did not exceed the experimental accuracy estimated at about 10%. The structural features responsible for the reconstruction must then be identical in both samples, a result which can be interpreted in two ways: The reconstruction is only due either to arsenic rearrangement in the topmost layers, irrespective of the atomic nature of the underlying cation layer, or to the In surface segregation trend; an exchange has taken place between In and Ga, leading to identical cation distribution in both samples.

The refinement was then performed first on sample I data. The key feature of the As saturated $c(4 \times 4)$ surface is the presence of chemisorbed As dimer arrays, first demonstrated by x-ray diffraction [10] and further confirmed by scanning tunneling microscopy experiments [11,12]. A trial model involving such dimers along [110] was thus used for one part of the unit cell and completed with an As dimer along $[1\bar{1}0]$ in the second part to achieve a 2×3 periodicity (Fig. 1); the subsurface cation layer was assumed to be pure indium. No attempt was made at this stage to satisfy the requirements of surface neutrality [13].

The free parameters for the fitting procedure were an overall scale factor, the coordinates for As(1), As(2), As(3), In(1), and In(2) reducing to four displacement parameters to preserve a 2 mm symmetry, one Debye-Waller factor for the atoms in the three surface layers, and an occupancy factor for the As(2)-As(2) dimer whose disorder accounts for the poor $\times 2$ periodicity along $[1\bar{1}0]$; the bulk Debye-Waller factor was taken equal at 0.5 as in the previous GaAs structure determination [10]. The normalized

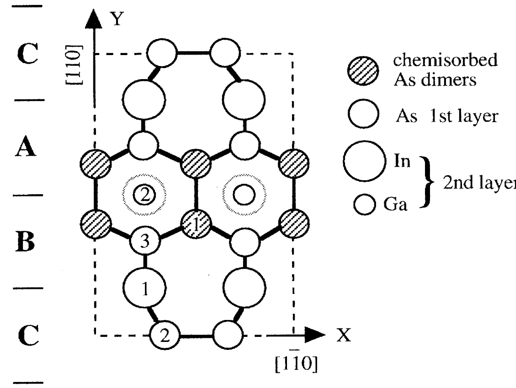

FIG. 1. Projected model of the atomic arrangement in the surface 2×3 unit cell. Labels refer to the atoms whose coordinates are listed in Table I.

χ^2 value [14] for such a model remained above 6.8, and it was only by allowing for a fractional occupancy for the In(2) site that χ^2 went further down. Instead of a distribution of indium vacancies, this effect is better interpreted as a preferential occupancy of this site by gallium atoms, and a refinement performed with this assumption led to a χ^2 value of 2.4 for an occupancy of 0.8 Ga and 0.2 In. The minimum in χ^2 being rather flat between 0.7 and 1 for the gallium occupancy of this site, the value 1 will be considered in the following. The number of independent integer orders was not sufficient to address a possible indium composition profile in the bulk, and, if one accepts the single (2,6) integer peak, the agreement between the observed and calculated structure factors displayed in Fig. 2, especially in view of the large dynamic range of the data, assesses that the model carries the essential features of the reconstructed surface. The most important one is the surface chemical order among indium and gallium, compatible with the triply periodic bulk ordering detected in $Al_{0.48}In_{0.52}As$ [15], and obviously driven by the As saturated (001) surface geometry: Gallium sits in a pure GaAs(001)-$c(4 \times 4)$ configuration, whereas indium lies in a more open arrangement, allowing for normal strain accommodation. The in-plane data do not carry information on the z coordinates; however, by considering reasonable interatomic distances, a tentative displacement pattern in the normal direction can be proposed which involves quite large rearrangements (Table I). An out-of-plane diffraction experiment scheduled in the near future with the upgraded version of the UHV diffractometer presently in the commissioning phase will allow these assumptions to be checked.

The refinement of sample II data with the same model led to a χ^2 value of 2.6 with free parameter values within the accuracy of the present determination (see Table I). This result demonstrates that a full exchange toward the stable 2×3 configuration is achieved when a single GaAs layer is deposited at 450 °C with the selected growth rate of 1 ML/3 s. No trends for an increased indium concentration in the deeper layers

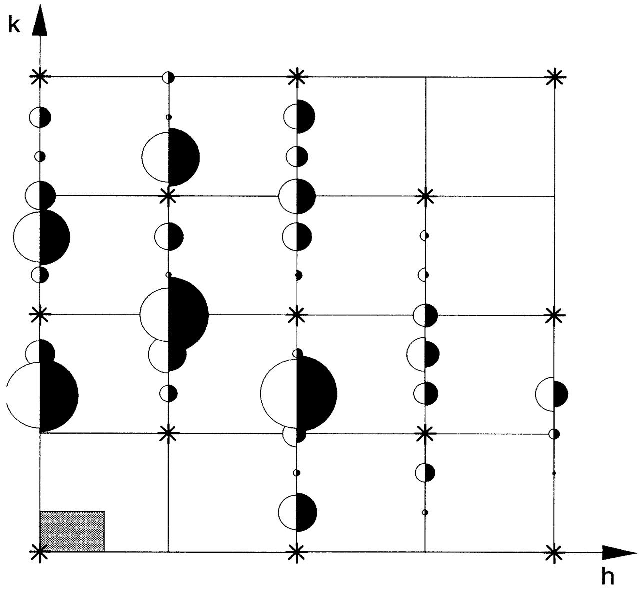

FIG. 2. Comparison between observed (black semicircles) and calculated (white semicircles) structure factors for the best fit in sample I. A square grid outlines the 1×1 bulk derived reciprocal lattice, where stars mark the location of bulk allowed nodes. The shaded rectangle indicates the 2×3 reciprocal unit cell used for the *hk* indexation.

could be detected in sample II. Since a similar 2×3 reconstruction had been observed on ternary alloys $In_xGa_{1-x}As$ [1,2,4] with nominal compositions x as low as 0.20, a further confirmation of the indium surface segregation is provided. Indeed, x-ray data collected in a previous experiment [16] on nominal $In_{0.2}Ga_{0.8}As$ and $In_{0.28}Ga_{0.72}As$ alloys, reconstructed 2×3, scaled fairly well with the present data sets.

A line-shape analysis performed on pure surface peaks after deconvolution of the experimental resolution function effects led to an isotropic coherent domain size of about 150 Å in both samples, not taking into account the mentioned disorder in the As dimer sequence along the $[1\bar{1}0]$ direction which has no influence on the measured reflections. This size corresponds to the average distance between the InAs rich 2D nucleation centers, coalescing at the completion of the monolayer with a random phase relationship for the $\times 3$ reconstructed domains, and supports the determination of the InAs quantum dots radius performed by Marzin *et al.* on a similar surface [17]. The terrace size, derived from the linewidth of the integer order peaks (in a 1×1 basis), is about 1600 Å and corresponds to what is measured on the GaAs substrate [9], which means that, at this stage, there is no increase of the surface roughness. It should be remarked that although the substrate has been exposed to 1 ML In, only two-third has been incorporated in the surface. Another peculiarity of the model is that a default in electrons is present in the top two arsenic layers; this could be neutralized by a random distribution of 25% undimerized arsenic along the disordered $[1\bar{1}0]$ direction.

The case of sample III is more complex: As was already obvious in the RHEED pattern, the reconstruction is no longer commensurate, and the peaks are shifted along the k axis by about one-tenth of the commensurate unit vector, resulting in a pseudo 2×2.7 periodicity. To account for this shift and to reproduce the observed structure factor changes, the diffracted intensity has been calculated in the framework of diffuse scattering formalism [18]. The starting assumptions and guide lines for the calculation will be presented here together with the main results, whereas the extended treatment will be the object of a forthcoming publication [19]. A commensurate-incommensurate transition appears when a multiplication of faulted sequences takes place in a periodic stacking. The surface unit cell of the 2×3 structure can be decomposed in the three building blocks (A, B, and C) outlined in Fig. 1. The normal sequence in the 2×3 is $ABCABCABC\ldots$, the other extreme case being the sequence $ABABAB$ which leads to the pure GaAs $c(4 \times 4)$ surface if an ordered distribution of missing As dimers is introduced. An intermediate case can be described by a probability p of finding a C block after and AB pair. The general formula for the intensity diffracted at a momentum transfer $\mathbf{Q}$ reads

$$I(\mathbf{Q}) = \sum_n \sum_{n'} F_n(\mathbf{Q}) F_{n'}^*(\mathbf{Q}) e^{-i\mathbf{Q}\cdot(\mathbf{r}_n - \mathbf{r}_{n'})}, \qquad (1)$$

where $\mathbf{r}_n$ and $\mathbf{r}_{n'}$ denote generic lattice sites in a 1×1 bulk derived basis and $F_{n(n')}$ stands for the structure factor of the element at $\mathbf{r}_{n(n')}$, namely, F_A, F_B, or F_C. Setting $m = n' - n$ and $\mathbf{r}_m = \mathbf{r}_{n'} - \mathbf{r}_n$, expression (1) can be written

$$I(\mathbf{Q}) = \sum_m \left(\sum_n F_n F_{n+m}^* \right) e^{i\mathbf{Q}\cdot\mathbf{r}_m}. \qquad (2)$$

The inner summation is proportional to the average value of the structure factor product between two blocks separated by the vector $\mathbf{r}_m$, and it can be expressed in

TABLE I. Atomic coordinates in unit $a_0/\sqrt{2}$ along X, $3a_0/\sqrt{2}$ along Y, and a_0 along Z with $a_0 = 5.6532$ Å. The Z coordinates are tentatively chosen to keep Ga-As and In-As distances close to their strain-free values, 2.45 and 2.63 Å, and are given only to show the displacement trends from GaAs bulk derived positions marked in parentheses.

Atom	In (1)	Ga,In (2)	As (1)	As (2)	As (3)
X	0.25	0.25	0.5	0.345 ± 0.015	0.25
Y	0.150 ± 0.003	0.50	0.400 ± 0.004	0	0.350 ± 0.004
Z	−0.42 (−0.50)	−0.50	0.045 (0.0)	−0.10 (−0.25)	−0.21 (−0.25)

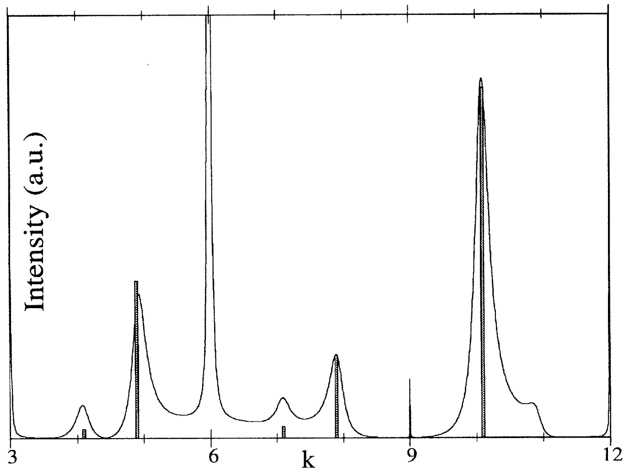

FIG. 3. Calculated intensity distribution along the reciprocal row $h = 2$ as a function of k in the incommensurate phase. Measured satellite integrated intensities are marked by bold bars.

terms of the pair probabilities $P_{XY}(m)$ for a block X (A, B, or C) to have a block Y (A, B, or C) as mth neighbor. Using the specific constraints of the model, namely, B always following A and C following B with probability p, one is able to extract with some algebra the required $P_{XY}(m, p)$. The diffuse scattering given by expression (2) can then be obtained for any location $\mathbf{Q}$ in reciprocal space by use of structure factors F_A, F_B, and F_C, calculated with the position parameters found in the commensurate phase. Figure 3 displays the calculated variation of $I(\mathbf{Q})$ along the k axis at $h = 2$ for the value $p = 0.6$, which gives the optimal account of the position, relative intensity, and linewidth of the diffuse scattering features measured at the incommensurate phase satellite locations along this axis, indicated by bold bars. The quality of the overall agreement between this description of the surface and the experimental data is remarkable since, at this stage, the only free parameters are the probability p and the scale factor.

An estimate for the In surface concentration is obtained as a function of p according to the formula, $[\mathrm{In}] = 2p/2 + p$, which gives 0.46 in the present sample. This value compares satisfactorily with the concentration 0.35 deduced from the data of Gérard and Marzin [4] when one takes into account the difference in the growth conditions: lower growth rate and uncertainty on the exact substrate temperature. The occurrence of the commensurate-incommensurate transition as a function of temperature or (and) As over pressure, observed by Moison, Guille, and Bensoussan [6] in a strained InAs layer grown on $In_xGa_{1-x}As$, can be understood as controlled by the InAs versus GaAs surface stability; the reversibility being only obtained thanks to the In reservoir provided by the ternary buffer.

The present experiment has thus established for the first time the existence of a chemical order at the (In,Ga)As(001) surface with a composition lock-in at $In_{0.67}Ga_{0.33}As$ for the commensurate 2×3 reconstruction. Making use of the resources of x-ray diffuse scattering methods, the incommensurate phase could be interpreted in terms of faulted sequences with an enriched gallium content which accommodate a range of surface stoichiometries leading continuously to the pure GaAs $c(4 \times 4)$ surface.

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