Species intermixing and phase transitions on the reconstructed (001) surfaces of GaAs and InAs

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Scanning tunneling microscopy has been used to study the transition in surface structure between the As-terminated 2×4 and $c(4\times4)$ reconstructions on both GaAs(001) and InAs(001), as a function of surface temperature under an As_2 flux. For both materials, two-phase surface reconstructions exist through the transition regime. On GaAs, the two-phase surface consists of disordered (2×4)-like structures plus a $c(4\times4)$-like phase terminating one monolayer below the 2×4 surface. On InAs, a disordered asymmetric 1×3 phase occurs $\{a(1\times3)\}$ in addition to the main phases, one monolayer below each main phase. In both cases, simple addition of As via As-on-As chemisorption cannot account for the formation of the $c(4\times4)$ reconstruction from the 2×4 surface. The $c(4\times4)$ phase is inherently multilayered, which explains how the structure can form without the addition or removal of the group III component and still maintain its layering registry with the residual 2×4 or $a(1\times3)$ phase. One result of this formation process is the necessary intermixing of group III and group V species in the second layer of the $c(4\times4)$ reconstruction. Direct evidence of species intermixing on the top layer of the InAs(001)-$a(1\times3)$ structure is also shown and models for all of these reconstructions are proposed. [S0163-1829(99)00404-X]

I. INTRODUCTION

The (001) surface of GaAs has been widely studied and a general consensus has been achieved concerning the structural details of the As-stabilized reconstructions, most notably the 2×4 and the $c(4\times4)$ phases.[1–3] Scanning tunneling microscopy (STM) has played a vital role in achieving this understanding, but several other techniques such as isotope-resolved medium energy ion scattering[4] (MEIS) and photo-electron spectroscopy[5–7] (PES) have also provided valuable insights particularly relating to surface composition. Some controversy remains, however, concerning the intermixing of Ga and As in the individual layers of the 2×4 and $c(4\times4)$ surfaces.[4] There is no intermixing in the widely accepted models for these reconstructions, which consist of complete or partial layers of only one species. It should also be noted that these idealized models describe atomically flat surfaces and do not take into account the possibility of an inherently *multilayered* reconstruction. By this we mean a surface in which the terminating atomic layer varies in height by one or more layer spacings on a lateral length scale that is significantly shorter than the nominal terrace width. A full description of a surface reconstruction should include both the composition of the unit mesh and the typical surface morphology (e.g., surface roughness, terrace shape, and terrace width).

In addition to interest in the stable surface reconstruc-

tions, there has been considerable effort to understand the transitions between different structures. For GaAs(001), the majority of studies have concentrated on the transition between the Ga-stabilized 4×2 and the As-stabilized 2×4 reconstructions,[8,9] as well as between the 2×4 and the $c(4\times4)$ reconstructions.[10–12] The InAs(001) surface has been less comprehensively studied, although the InAs(001) 2×4 to 4×2 transition has been compared in detail with that on GaAs(001).[13] In this case, there is a distinct difference between the two materials, with a discontinuous transition with hysteresis occurring on InAs(001), contrasting with the continuous transition that occurs on GaAs(001). The difference has been explained by the differing relative interaction energies of the arsenic species on the two different surfaces.[13]

In this paper we focus on the phase transition between the As-stabilized $c(4\times4)$ and 2×4 reconstructions on both InAs and GaAs(001). There are significant differences in the transitional regime between the two materials, with InAs going through an intermediate asymmetric 1×3 phase $\{a(1\times3)\}$ that does not occur on GaAs. The presence of two-phase transitional surfaces provides strong evidence of species intermixing below the surface of the $c(4\times4)$ reconstruction and in the $a(1\times3)$ reconstruction.

II. EXPERIMENT

The experiments were carried out in a combined molecular beam epitaxy (MBE) chamber (DCA Instruments) and

TABLE I. Progression of surface reconstructions measured by RHEED and STM for GaAs(001) as a function of annealing temperature under a constant As$_2$ flux. In the range 460 °C–500 °C, two coexisting phases are observed in STM measurements.

Temperature (°C)	Reconstruction
>540	$\beta(2\times4)$
510–540	$\gamma(2\times4)$
500–510	2×4 dominant
490–500	$2\times4 + c(4\times4)$
460–490	$c(4\times4)$ dominant
<460	$c(4\times4)$

STM system (Omicron GmbH), which allows the growth of the samples and transfer to the microscope while under ultrahigh vacuum (UHV).[14] As$_2$ was used as the source of arsenic and was generated from a valved cracker cell.[15] The Ga, In, and As$_2$ fluxes were all calibrated using reflection high-energy electron diffraction (RHEED) specular beam intensity oscillations. Clean, singular (misorientation of $\pm0.2°$) GaAs(001) and InAs(001) substrates were prepared using standard MBE methods, with the growth and surface symmetry monitored using RHEED. Buffer layers of GaAs (InAs) were grown on each substrate and the samples were then cooled under a constant As$_2$ flux [$(2.0\pm0.5)\times10^{14}$ molecules cm^{-2} s^{-1}] to various temperatures and held for 5 min before rapid quenching to room temperature for observation by STM. Filled states images were obtained with a negative sample bias of 2–4 V and a tunneling current of 0.1–2.0 nA. The speed of the quenching process itself had very little effect on the observed surfaces (a typical quench comprised a few seconds in the MBE chamber followed by 2 min in the clean UHV environment of the STM chamber before initiating tip approach).[16] The sample temperature during growth and annealing was monitored using an infrared pyrometer and varied by no more than ±5 °C across the sample surface. The likely systematic error (consistent throughout these experiments) is around ±10 °C, based on monitoring oxide desorption temperatures.

III. RESULTS

A. GaAs(001)

As a guide to the general phase transitions occurring as the temperature is lowered, the GaAs surface structures observed by RHEED and STM are summarized in Table I. For GaAs(001), the $\beta(2\times4)$ RHEED pattern is observed at high temperatures, with equal intensity in the fourth-order diffraction rods. This RHEED pattern corresponds to the $\beta2(2\times4)$ surface reconstruction observed in STM.[1–3] As the temperature is reduced towards the transition region, the $\frac{2}{4}$-order diffraction rod becomes weaker and the $\gamma(2\times4)$ phase is produced (510 °C–540 °C). This is characterized in STM by increased disorder in the 2×4 structure, principally "kinks" in the dimer-pair rows for GaAs(001), although the density of top-layer As dimers remains at two per unit mesh.[17] At still lower temperatures (<500 °C), a two-phase surface is observed in STM, while the RHEED pattern changes in the fourfold azimuth. The fourth-order diffraction streaks all be-

come weaker, but the $\frac{2}{4}$-order streak gains in intensity at the expense of the $\frac{1}{4}$- and $\frac{3}{4}$-order features. The $\frac{2}{4}$-feature continues to gain in intensity as the temperature is reduced and the overall pattern becomes characteristic of the $c(4\times4)$ surface.[2,3] Once the temperature is reduced below 460 °C, the RHEED pattern shows sharp and intense fractional order features consistent with $c(4\times4)$ symmetry.

STM measurements indicate that regions of $c(4\times4)$ structure begin to develop in the dominant 2×4 surface at temperatures below 510 °C. A STM image of the GaAs(001) surface displaying a fully developed $c(4\times4)$ reconstruction is shown in Fig. 1(a); the surface was quenched from 445 °C, below the transition regime. The brickwork pattern of rectangular blocks of top-layer As atoms[2,3] is clearly seen in this image, with each lattice point of the large $c(4\times4)$ unit mesh being associated with a single block. The As atoms are highlighted with white circles for two adjacent unit blocks, one of which shows the full "ideal" complement of six atoms, while the other shows only three atoms arranged in a line parallel to the $[\bar{1}10]$ direction. In fact, the As atom content of each unit mesh varies considerably and at 445 °C around 45% of the atoms are missing from the ideal number of six per primitive mesh. This is consistent with the work of Avery et al.,[2] who found that for GaAs(001)-$c(4\times4)$ surfaces prepared by annealing under an As$_4$ flux, at 350 °C only 8% of the As atoms in the top layer are missing while at 400 °C nearly 30% are missing. This progression continues at higher temperatures into the transition regime, where the As content of each block is reduced to less than 50% of the ideal number. A STM image of the transitional surface is shown in Fig. 1(b) (quenched from 495 °C, in the middle of the transition regime). The surface consists of patches of $c(4\times4)$ phase surrounded by areas of disordered (2×4)-like structures. The $c(4\times4)$ patches are typically 500 Å across in the middle of the transition regime, but become larger as the temperature is reduced. This two-phase structure is identical to that recently observed by Kanisawa and Yamaguchi[12] for GaAs(001) annealed under an As$_4$ flux at similar temperatures. The $c(4\times4)$ phase is labeled in Fig. 1(b) and consists largely of strings of three As atoms such as the one highlighted in Fig. 1(a), although often the strings are only two As atoms long. The As content of the top layer is therefore below 50% of the ideal coverage. The 2×4 phase is highly disordered and consists of long chains of As dimer pairs separated by trenches that run in the $[\bar{1}10]$ direction. The general trend is that as the temperature is reduced, the coverage of the $c(4\times4)$ phase increases at the expense of the 2×4 phase (it should be noted that the temperature range for the two-phase structure is only ~40 °C). No additional surface structures exist, although the ordering and atomic details of the 2×4 and $c(4\times4)$ phases do change through the transition.

B. InAs(001)

The situation for InAs(001) is very different from GaAs(001) and is summarized in Table II. As the temperature is lowered from 430 °C, above which there is a sharp $\beta(2\times4)$ RHEED pattern, the same reduction of intensity in the $\frac{2}{4}$ streak occurs and the pattern becomes characteristic of $\gamma(2\times4)$. A further reduction in temperature from the $\gamma(2\times4)$
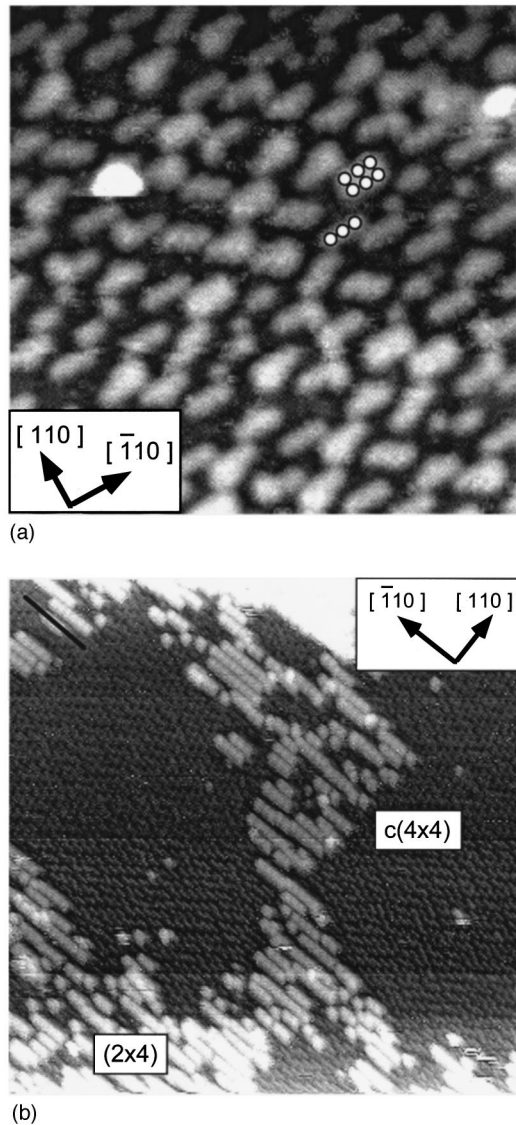
(a)

(b)

FIG. 1. (a) Filled state STM image (-3 V, 2 nA, and 100×100 Å^2) of a GaAs(001) surface quenched to room temperature after annealing at 445 °C under an As$_2$ flux. The RHEED pattern was sharp and showed $c(4 \times 4)$ symmetry. The top-layer As atoms are visible as bright features arranged with the characteristic brickwork pattern of the $c(4 \times 4)$ reconstruction. The variable composition of the unit mesh is indicated by white dots superimposed on two adjacent unit meshes. Each dot represents a single As atom and the top-layer content of the two unit meshes shown is three and six As atoms, respectively. Around 50% of the top-layer As atoms are missing compared to the ''ideal'' reconstruction of six atoms per unit mesh. (b) Filled state STM image (-3 V, 1 nA, and 600×600 Å^2) of a GaAs(001) surface quenched to room temperature after annealing at 495 °C under an As$_2$ flux. The RHEED pattern was a sharp $\gamma(2 \times 4)$ symmetry. Regions of both $c(4 \times 4)$-like and (2×4)-like reconstruction are shown. The black line (top left) indicates the position of the height section shown in Fig. 3(a).

regime results in the formation of a separate intermediate reconstruction before the onset of the $c(4 \times 4)$ structure. This intermediate phase shows 1×3 symmetry in RHEED, with the $\frac{1}{3}$- and $\frac{2}{3}$-order streaks closer together than their separation from the zeroth- and first-order features. The shift in the fractional order rods leads to the terminology for this pattern

TABLE II. Surface reconstructions measured by RHEED and STM for InAs(001) as a function of annealing temperature under a constant As$_2$ flux. In the ranges 280 °C–320 °C and 350 °C–370 °C, two phases are observed, while the pure $a(1 \times 3)$ phase exists only in a narrow temperature window between 320 °C and 350 °C.

Temperature (°C)	Reconstruction
>430	$\beta(2 \times 4)$
370–430	$\gamma(2 \times 4)$
350–370	$2 \times 4 + a(1 \times 3)$
320–350	$a(1 \times 3)$
280–320	$c(4 \times 4) + a(1 \times 3)$
<280	$c(4 \times 4)$

as an ''asymmetric'' 1×3 or $a(1 \times 3)$ structure. The pattern is very similar to that observed on InSb(001),[18] where it also exists at slightly higher temperatures than the Sb-terminated $c(4 \times 4)$ structure for a given Sb flux. However, for InSb(001) there is no equivalent 2×4 structure. There is a narrow temperature window for InAs(001) where the RHEED pattern shows no traces of either $c(4 \times 4)$ or 2×4 features (between 320 °C and 350 °C). Below this temperature range, fractional order features due to the $c(4 \times 4)$ symmetry begin to appear and by 280 °C the RHEED pattern is a sharp $c(4 \times 4)$.

The STM results reflect these changes in the RHEED pattern across the transition region. An image of the 2×4 surface quenched from a temperature of 455 °C is shown in Fig. 2(a). Very straight rows of As dimer pairs are clearly visible, the contrast between dimers being typically enhanced over that for the GaAs(001)-(2×4) structure due to the larger lattice spacing of InAs. However, defects consisting of missing As dimers are far more common than for GaAs(001), with around 30% of the dimers missing at 455 °C. As the temperature is lowered to 350 °C–370 °C, a new $a(1 \times 3)$ phase rapidly develops to coexist with residual disordered (2×4)-like domains. Figure 2(b) shows a STM image of the (2×4)-$a(1 \times 3)$ transitional surface. The $a(1 \times 3)$ phase consists of brighter meandering ''chains'' whose apparent height is significantly lower than that of the residual 2×4 patches. The local spacing of the chains in the $a(1 \times 3)$ phase varies between a twofold and a threefold periodicity and some corrugation is evident along them (see Sec. III C). The 2×4 phase appears as fairly straight rows of bright pairs separated by trenches, in a very similar manner to the well-ordered 2×4 surface. Interestingly, although the disorder in these 2×4 rows is significantly greater than for the complete 2×4 surface, there are very few missing dimer defects in the well-ordered regions.

At still lower temperatures (320 °C–350 °C), the residual 2×4 structure disappears and the entire surface is covered in the $a(1 \times 3)$ reconstruction. Although the temperature window is only 30 °C for the observation of a pure $a(1 \times 3)$ surface, this reconstruction does exist as an independent phase and therefore provides an intermediate step in the 2×4 to $c(4 \times 4)$ transition that is not present for GaAs. At higher temperatures than those where the pure $c(4 \times 4)$ reconstruction appears, the $a(1 \times 3)$ phase coexists with developing domains of $c(4 \times 4)$ that lie above the $a(1 \times 3)$ surface. A STM image of the $a(1 \times 3)$-$c(4 \times 4)$ two-domain surface is shown in
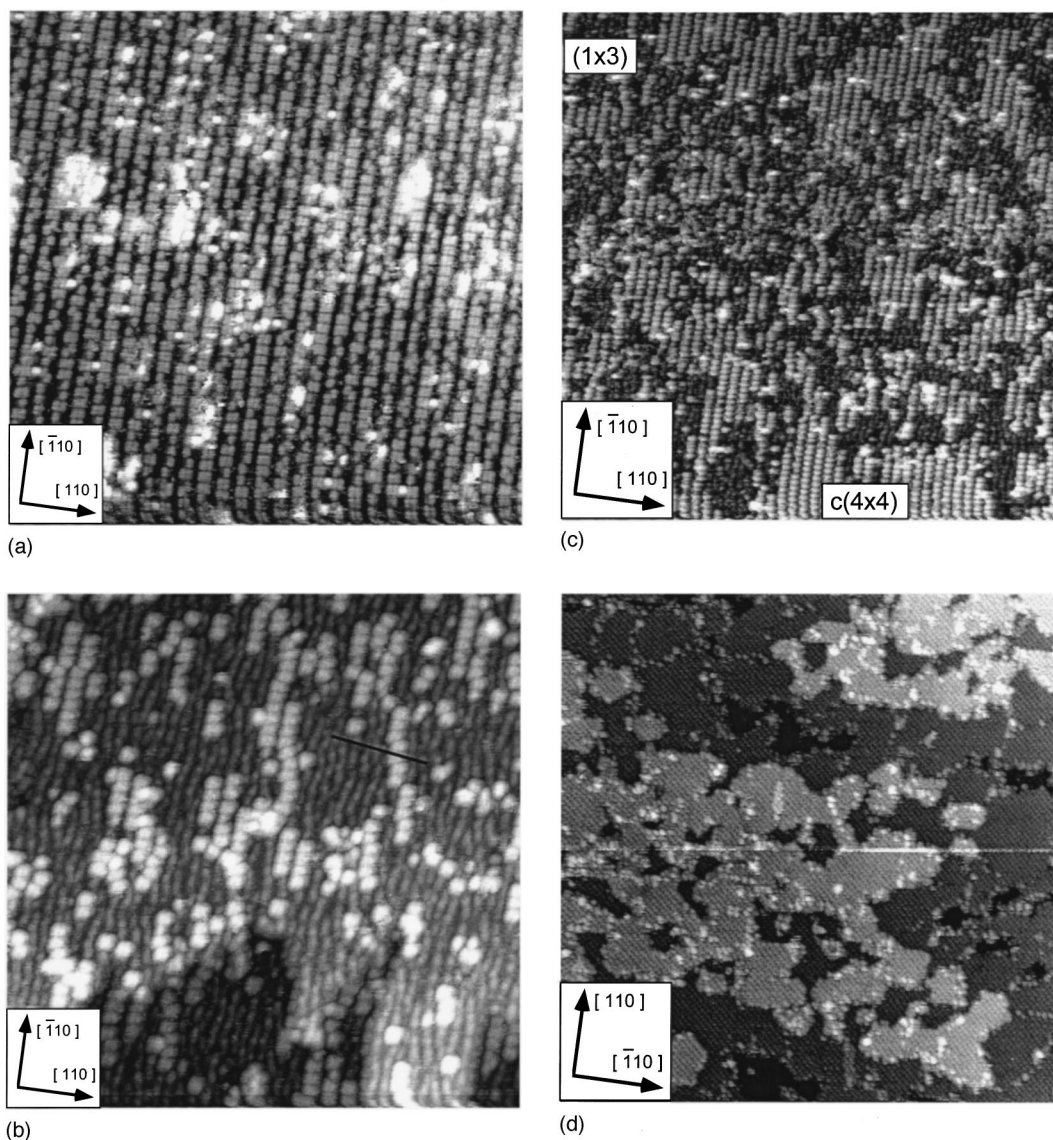
FIG. 2. (a) Filled state STM image (-2 V, 0.2 nA, and 400×400 Å^2) of an InAs(001) surface quenched to room temperature after annealing at 455 °C under an As$_2$ flux. A sharp $\beta(2 \times 4)$ RHEED pattern was observed during annealing. Bright cigar-shaped features due to the As dimer pairs in the top layer are clearly visible. The trenches between dimer pair rows are very straight, although missing top-layer As dimer defects are common ($\sim 30\%$ of the dimers are missing from the ideal structure on a typical surface). (b) Filled state STM image (-2 V, 0.2 nA, and 400×400 Å^2) of an InAs(001) surface quenched to room temperature after annealing at 365 °C under an As$_2$ flux. A meandering step edge runs along the bottom half of the image, while the terraces comprise both disordered chainlike structures [the $a(1 \times 3)$ phase] and (2×4)-like structures that terminate one atomic layer above the $a(1 \times 3)$ surface. The black line (upper right) shows the location of the section in Fig. 3(b). (c) Filled state STM image (-2 V, 0.1 nA, and 700×700 Å^2) of an InAs(001) surface quenched to room temperature after annealing at 300 °C under an As$_2$ flux. Regions of $c(4 \times 4)$ symmetry are visible and terminate one atomic layer higher than the underlying $a(1 \times 3)$ phase, which shows its characteristic disordered chainlike appearance. The top-layer atoms of the $c(4 \times 4)$ phase are not resolved even on higher magnification images. (d) Filled state STM image (-2 V, 0.2 nA, and 1000×1000 Å^2) of an InAs(001) surface quenched to room temperature after annealing at 250 °C under an As$_2$ flux. The entire surface is covered in the $c(4 \times 4)$ phase and shows a typically multilayered morphology.

Fig. 2(c). Units of $c(4 \times 4)$ structure can be very small (down to a single "block" of top-layer atoms), but in the larger domains, the characteristic brickwork pattern is maintained with good ordering. Unlike the GaAs(001)-$c(4 \times 4)$ surface at high temperatures there appears to be a rather small number of defects in the blocks of top-layer atoms [compare with Fig. 1(a)], with all the blocks appearing very similar. In fact, higher resolution images on both the transitional and pure $c(4 \times 4)$ surfaces show a slightly different appearance in the

blocks than on GaAs. Despite the larger lattice constant, the individual As atoms are not resolved on InAs and each block appears more barrel shaped.

A larger scale STM image of the pure InAs(001)-$c(4 \times 4)$ surface annealed to 250 °C is shown in Fig. 2(d). The scale is sufficiently large (2000 Å) that the $c(4 \times 4)$ periodicity is not clearly resolved, but the overall morphology of the surface is very different from that of the base 2×4 surface, which has large terraces (~ 1000 Å) separated by straight step edges.

On the $c(4\times4)$ surface, whether obtained by cooling a 2×4 surface under an arsenic flux or by growing directly at low temperatures, the morphology is "multilayered." Three terrace heights are clear in this image (three or four heights is typical for InAs annealed at this temperature), but the step edges separating them are meandering rather than straight and the terrace-terrace separation is only of the order of 100 Å. This morphology is also observed for GaAs(001)-$c(4\times4)$ surfaces prepared in different ways. For example, direct growth of ~50 monolayers on the $c(4\times4)$ surface, with or without subsequent annealing at the appropriate temperature, produces a multilayered reconstruction with many meandering step edges.

C. Layer structures and morphology

As discussed above, the $c(4\times4)$ reconstructions on both InAs and GaAs always show a multilayered morphology. This can be quantified a little more by defining an image size (1000 Å) somewhat smaller than the observed terrace width for the 2×4 surfaces and then counting the number of terrace heights represented in that image. This is typically three for both InAs and GaAs in the pure $c(4\times4)$ phase, but only one for the 2×4 reconstruction. Additionally, if the terraces are numbered in order of height, the area occupied by odd or even numbered terraces is always found to be 50 ($\pm10\%$) for both materials in the pure $c(4\times4)$ phase. The pure $a(1\times3)$ InAs surface, prepared by cooling a 2×4 surface under an As flux, is also multilayered, with islands around 200 Å wide often appearing on the otherwise flat terraces. However, when the areas of odd and even numbered layers are measured, the new islands only account for around 20% of the surface.

The morphology of the two-phase transitional surfaces on both GaAs [Fig. 1(b)] and InAs [Figs. 2(b) and 2(c)] varies as the temperature is changed. At higher temperatures, the terraces are large (>1000 Å), with fairly straight step edges, similar to the 2×4 phase. As the temperature is lowered, the morphology tends more towards the $c(4\times4)$-like structure [Fig. 2(d)]. It should be noted that the step edges are defined as two atomic layers high (2.8 Å for GaAs, 3.0 Å for InAs) and the two-phase surfaces include patches of different heights. However, it is clear from STM sections that the two different phases on a given terrace are separated in height by only a single atomic layer (1.4 or 1.5 Å in height). Two STM sections are shown in Fig. 3 for GaAs [Fig. 3(a), the section located in Fig. 1(b)] and InAs [Fig. 3(b), the section located in Fig. 2(b)] two-phase surfaces. The 2×4-like string of dimer pairs shown in Fig. 3(a) is clearly one atomic layer above the underlying $c(4\times4)$-like phase for the GaAs surface. For InAs, the 2×4-like island again lies one atomic layer (1.5 Å) above the underlying $a(1\times3)$ phase. In addition, the observed corrugation across the $a(1\times3)$ phase, shown in Fig. 3(b) in the range 0–50 Å along this section, is less than 1 Å and typically close to 0.5 Å. This low corrugation, less than one atomic layer in apparent height, may be due to electronic effects caused by the mixing of In and As species in the upper layer of this $a(1\times3)$ phase. A similar low corrugation has been observed for InSb(001) on the $a(1\times3)$ reconstructed surface.[18] Finally, we note that the surface structure transitions were found to be fully reversible, consistent with the results of Kanisawa and Yamaguchi.[12]
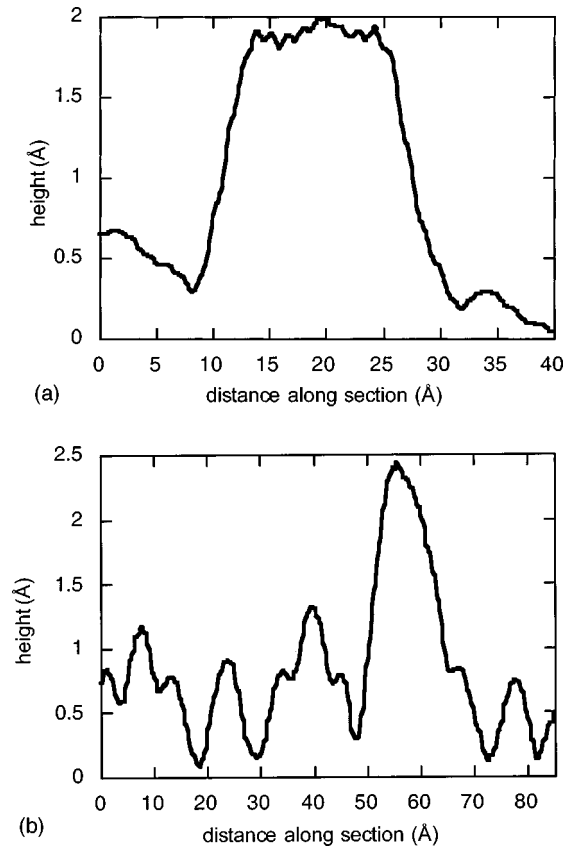

FIG. 3. (a) Height contour plot of the section marked in Fig. 1(b), corresponding to the two-phase GaAs(001) transitional surface. The height of the (2×4)-like dimer row chain through which the section passes is 1.4 Å above the underlying $c(4\times4)$ layer, i.e., one atomic layer. (b) Height contour plot of the section marked in Fig. 2(b), corresponding to the $a(1\times3)+2\times4$ InAs(001) transitional surface. The corrugations across the chains of the $a(1\times3)$ phase are small, typically less than 0.5 Å with some peaks at 1 Å above the trench depth between chains. In contrast, the (2×4)-like islands are 1.5 Å (one atomic layer) above the mean height of the underlying $a(1\times3)$ phase.

IV. DISCUSSION

A. 2×4 and $c(4\times4)$ phase

The first point to make concerning the 2×4 to $c(4\times4)$ transition on GaAs(001) is that it does not occur by simple adsorption of As on to the 2×4 structure. The layer registry of the coexisting phases, with the $c(4\times4)$ lying lower than the 2×4, clearly implies that this is not the case. Instead, the 2×4 phase must melt to allow As to condense on what was the third layer of the original 2×4 area.[12] A similar conclusion can be drawn for InAs(001) since there is an intermediate $a(1\times3)$ phase terminating one layer below both the $c(4\times4)$ and the 2×4 phases with which it coexists. Kanisawa and Yamaguchi[12] noted that simple adsorption of As onto the $\beta2(2\times4)$ structure cannot produce a $c(4\times4)$ structure due to the missing second-layer Ga atoms. They claimed that since simple adsorption does not occur, this was direct evidence for the validity of the $\beta2(2\times4)$ structure with an incomplete second layer as opposed to other possible structures with a complete second layer. However, a $c(4\times4)$ structure with a *mixed* third layer resulting from simple As adsorption is still

possible[2] and no such conclusion concerning the nature of the 2×4 structure can be drawn.

The second point concerns the nature of the $c(4\times4)$ reconstruction. The As coverage of this reconstruction is known to vary considerably with temperature and As flux. Direct observation of varying As coverage using STM is possible for GaAs(001) (Ref. 2 and this paper), with analogous results reported for InSb(001).[18] For GaAs(001), temperature programmed desorption (TPD) studies also indicate the presence of two separate desorption peaks from the $c(4\times4)$ surface.[11] These separate peaks were assigned to two different types of $c(4\times4)$ reconstruction, with well-defined atomic structures involving top-layer As "dimers."[3,11] However, the STM images reported here and in Refs. 2 and 13 clearly show a much more disordered array of top-layer As atoms. In particular, chains of three atoms and even single isolated atoms are very common [Fig. 1(a)], indicating that the top-layer atoms should not be described as "dimerized" in the usual sense (they are of course bonded to As atoms in the layer below rather than to group III atoms). Surface x-ray diffraction studies of the $c(4\times4)$-(2×4) transition also indicate strong disordering of the $c(4\times4)$ structure before the appearance of 2×4 diffraction features.[10] In contrast to GaAs(001) and InSb(001), the STM images of InAs(001) indicate much less clearly the atomic content of the upper layer [Fig. 2(c)]. The details of the InAs(001)-$c(4\times4)$ local atomic structure cannot therefore be inferred with similar confidence.

B. Phase transition regime: GaAs(001)

We have constructed a number of simple structural models for the transitional and $c(4\times4)$ surfaces. These models are presented only as side views of the layer structure to emphasize the importance of multilayered reconstruction and the strong possibility of species intermixing in a given layer, and also because both the $c(4\times4)$ and the $a(1\times3)$ phases are rather disordered around the transition regime. The structure of the 2×4 phases for both materials is assumed to be the "β2" form, with rows of As dimer pairs on the top layer and a missing Ga (or In) row in the second layer exposing As dimers in the third layer.[1,2] The atomic content of the top four layers is therefore $\frac{1}{2}$ As, $\frac{3}{4}$ Ga or In, full As, and full Ga or In, in descending order. The layer structure of this phase is shown in Fig. 4 for both InAs and GaAs. The following rules are employed to account for the surface structure transitions: (i) from the initial 2×4 structure, arsenic can adsorb and desorb freely; (ii) no loss or gain of the group III element is allowed above the fourth layer of the 2×4 phase, i.e., the uppermost full group III layer, (iii) group III atoms can migrate over a lateral distance of at least several unit mesh lengths; (iv) there are no step edges on the initial 2×4 surfaces; and (v) the $c(4\times4)$ phase initially terminates one atomic layer below the 2×4 phase.

Figure 4(a) shows a schematic layer model for the 2×4 and $c(4\times4)$ phases of GaAs. The content of the jth layer (j =1 being the uppermost layer) is given by a_j and g_j for the fractional arsenic and gallium content, respectively. The 2×4 phase is shown as completely flat (single layered), a good approximation based on the large terrace widths obtained experimentally (~2000 Å). The $c(4\times4)$ phase is shown as having two different terminating heights separated by two
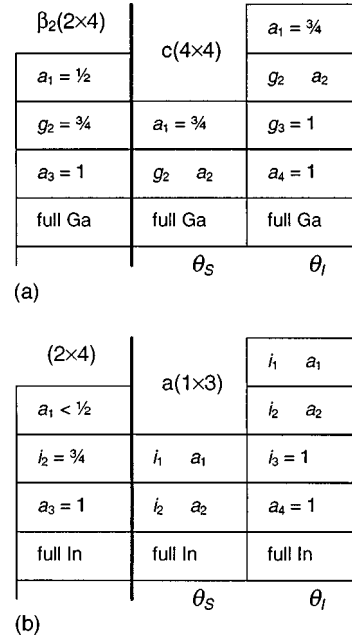

FIG. 4. (a) Schematic side view of the GaAs(001) 2×4 and $c(4\times4)$ surface reconstructions. The layer structure is shown with the variables a_j and g_j representing the arsenic and gallium content of the jth layer, respectively. The variables θ_S and θ_I represent the "substrate" and "island" layers of a multilayered reconstruction. (b) Schematic side view of the InAs(001) 2×4 and $a(1\times3)$ surface reconstructions. The layer structure is shown with the variables a_j and i_j representing the arsenic and indium content of the jth layer, respectively. The variables θ_S and θ_I represent the substrate and island layers of a multilayered reconstruction.

atomic layers, i.e., it is a multilayered phase. The fractional areas of the lower ("substrate") and upper ("island") layers of this phase are denoted by θ_S and θ_I, respectively. For the fully developed $c(4\times4)$ reconstruction it is reasonable to set $\theta_S = \theta_I = \frac{1}{2}$ since odd and even numbered layers have approximately the same area in all experimental images.

In order that the gallium content above the layer labeled "full Ga" be conserved over the transition, the following equation must be satisfied:

$$\tfrac{3}{4} = \theta_S g_2 + \theta_I(1 + g_2), \qquad (1)$$

where the terms from left to right represent the 2×4 phase, the lower $c(4\times4)$ layer, and the upper $c(4\times4)$ layer. If $\theta_S = \theta_I = \frac{1}{2}$, then g_2 is immediately obtained as $\frac{1}{4}$. This means that species intermixing in the second layer of the $c(4\times4)$ reconstruction is inevitable, with around one-quarter of the arsenic atoms replaced by gallium. In fact, this value is probably an upper limit since some of the gallium can be incorporated into step edges relaxing rule (iv) above. Note that gallium cannot be incorporated into a single-layered $c(4\times4)$ structure unless g_2 is exactly $\frac{3}{4}$, under the assumption that the new $c(4\times4)$ phase exists one atomic layer below the original 2×4. This high value would be inconsistent with PES and TPD data,[5–7,11] which show that As-As bonding is dominant in the upper layers. In fact, PES indicates a shifted Ga $3d$ component for the $c(4\times4)$ structure consistent with Ga atoms accepting more charge than in the bulk, which would be the case for second-layer substitutional Ga in the $c(4\times4)$ structure. Finally, if $\theta_I > \frac{1}{2}$ then the second layer of

the $c(4\times4)$ phase becomes less gallium rich ($g_2<\frac{1}{4}$), but since odd and even numbered layers in the experimental images occupy nearly equal areas, fixing $\theta_S=\theta_I=\frac{1}{2}$ seems to be most reasonable.

Our deduction of a gallium content of around $\frac{1}{4}$ in the second layer of the $c(4\times4)$ structure is broadly consistent with MEIS results obtained from arsenic-decapped GaAs(001)-$c(4\times4)$ surfaces.[4] These experiments showed that up to one-half of the second-layer As atoms must be replaced by Ga atoms to explain the measured relative ion yields for scattering from As to Ga. It is unlikely that a decapping procedure would produce precisely the same surface stoichiometries as *in situ* MBE growth[6] and so a quantitative comparison may be inappropriate. However, the STM data reported here provide strong additional evidence for a mixed second layer. The transition from the $c(4\times4)$ phase to the 2×4 surface reconstruction under MBE conditions requires both adsorption and desorption of As. This suggests that the 2×4 surface formed by thermal desorption of As alone may be significantly different from that formed under MBE conditions. Although our results indicate species intermixing for the $c(4\times4)$ surfaces, in agreement with the MEIS results of Falta *et al.*,[4] we find no evidence for intermixing in the MBE-grown 2×4 surfaces. Since the MBE-grown and decapped 2×4 surfaces may be substantially different (and noting that a three-As-dimer structural model was employed in the MEIS study), we do not believe this discrepancy to be particularly significant. It should be noted that the present model for the formation of the $c(4\times4)$ structure from the 2×4 structure differs from that of Avery *et al.*,[2] which was also based on STM observations. This model was constructed without STM images of the transitional two-phase surface and simply involves the addition of As to the 2×4 surface, failing to take into account the layer registry of the two phases observed both here and in Ref. 2. This model also involves species intermixing on the subsurface layers during and after the transition to $c(4\times4)$, but actually produces a more arsenic rich third layer rather than a more gallium rich second layer as in the present model.

The layer content of the two-phase surface is slightly more difficult to determine. If the surface is assumed to remain completely flat throughout the transition (from 510 °C–460 °C) then the second-layer gallium content of the high-temperature $c(4\times4)$ must be $\frac{3}{4}$, which is probably too large as discussed above. If the formation of additional bilayers is allowed, then the excess gallium can be accommodated without exceeding a value of $g_2=\frac{1}{4}$. However, in the temperature range 490 °C–510 °C, where there is still a very substantial amount of the (2×4)-like phase, the terraces remain rather wide with little evidence of a multilayered structure (very similar observations were made in Ref. 12 for this stage of the phase transition). This implies that the gallium fraction of the second layer should be $\frac{3}{4}$. To reduce this value requires a relaxation of the rules assigned above. In particular, some Ga may migrate to step edges after local melting of the 2×4 structure (Ga desorption is negligible). The amount of Ga that can be accommodated in this way depends on the migration length of Ga atoms during the annealing process, which may be enhanced during the phase transition.[13] We note that it is only in a very restricted temperature range (490 °C–510 °C) where the flat morphology of the surface

requires this migration. It may be possible to systematically vary the cooling rate and annealing time before quenching to further investigate this effect. It is also interesting to hypothesize that a larger second-layer Ga content may be related to the lower As content in the top layer for the high-temperature $c(4\times4)$ phase, which is revealed directly by STM for the high-temperature $c(4\times4)$ phase.

C. Phase transition regime: InAs(001)

The phase transition from 2×4 to $c(4\times4)$ on InAs(001) proceeds via an intermediate $a(1\times3)$ phase, but similar arguments to those used for GaAs can be applied for each individual transition. The transition between the 2×4 and $a(1\times3)$ phases is considered first. The low corrugation of the $a(1\times3)$ phase in STM images provides direct evidence for species intermixing on the top layer, with the apparent height contrast arising from electronic effects. A mixed top layer is also supported by analogy with the 1×3 reconstructions formed on InSb(001) (Ref. 18) and GaSb(001).[19] The favored models for these reconstructions comprise $\frac{2}{3}$ monolayer (ML) of Sb and $\frac{1}{3}$ ML of Ga or In on top of a full layer of Sb, and in the case of InSb(001) the surface appears very disordered in STM as well as producing an "asymmetric" RHEED pattern. This is very similar to the InAs(001) surface observed here [Fig. 2(b)].

Figure 4(b) shows a schematic diagram of the $a(1\times3)$ structure with its layer registry against the 2×4 structure indicated. The variables a_j and i_j represent the arsenic and indium content of the layers, respectively. For the model InAs surface, intermixing is also allowed in the second layer and conservation of indium above the "full In" layers leads to an equation for the total indium content of the upper two layers

$$i_1+i_2=\tfrac{3}{4}-\theta_I. \qquad (2)$$

STM images indicate that the pure $a(1\times3)$ surface is somewhat multilayered, with θ_I around 20% (in the form of irregular islands less than 100 Å wide). This means that the upper two layers should accommodate roughly 0.55 ML of indium. This is not consistent with the precise model employed for InSb and GaSb surfaces,[18,19] but requires some replacement of first- and second-layer arsenic atoms with indium. It is not possible, however, to judge whether such intermixing is restricted to the uppermost layer or to the upper two layers based on the STM images alone. The formation of islands on the two-phase $2\times4+a(1\times3)$ surface clearly requires some migration of indium atoms over several tens of nanometers. Since the 2×4 structure is melting during this transition in a similar way to GaAs, the same arguments concerning enhancement of migration lengths can be applied.[12] However, no STM images obtained in this study indicated that migration to step edges was essential as is the case for GaAs, merely the development of islands covering ~20% of the surface. If the rules for the phase transition outlined in Sec. IV B are again relaxed to allow indium incorporation at step edges, then the value of 0.55 ML for the indium content of the upper two ML would be reduced. There is therefore no evidence for intermixing on the second layer of the $a(1\times3)$ phase if the effects of step edges can account for ~0.22 ML of indium (leaving an "ideal" 0.33

ML in the top layer). It should be noted that if intermixing is allowed in the second layer, then second-layer indium atoms could be bonded to indium atoms in both adjacent layers.

For the transition from $a(1\times3)$ to $c(4\times4)$, simple adsorption of As cannot be invoked even though the uppermost layer of the $c(4\times4)$ structure is one atomic layer higher than the $a(1\times3)$ structure [Fig. 2(c)]. This is because there is too little indium in the upper two layers of the $a(1\times3)$ structure (0.33–0.55 ML) to form the 1 ML required for the third layer of the $c(4\times4)$ structure (plus any indium replacing arsenic in the second layer). Consideration of a layer model similar to Fig. 4(b) produces the conclusion that no replacement of arsenic by indium in the second layer of the $c(4\times4)$ structure is required. This could be directly tested by MEIS experiments similar to those carried out on GaAs(001);[4] to the authors' knowledge, no such experiments have been performed. It is interesting to note, however, that the STM images of the $c(4\times4)$ phase on InAs(001) appear much better ordered than the equivalent high-temperature $c(4\times4)$ phases on GaAs(001) [Fig. 2(c)]. In particular, the 2×4 blocks making up the brickworklike structure of $c(4\times4)$ all appear very similar on InAs at all temperatures, whereas on GaAs, missing As atoms are clearly visible [Fig. 1(a)]. This may reflect the perfect stoichiometry of the second layer in InAs even during the transition from $a(1\times3)$ to $c(4\times4)$ and the improving stoichiometry of the second layer as the temperature is reduced (and the degree of islanding increased) for GaAs.

D. Stability of small islands

We now make some comments on the smallest island structures observed on the transitional surfaces, where by ''island'' we mean a well-defined region of one phase surrounded by a different phase that terminates on a lower atomic layer. In the present cases, islands terminate one atomic layer above the surrounding phase and we discuss the following island types: (2×4)-like islands on GaAs(001) $c(4\times4)$, $c(4\times4)$-like islands on InAs(001) $a(1\times3)$, and (2×4)-like islands on InAs(001) $a(1\times3)$.

For two-phase GaAs(001) surfaces, STM observations indicate that the smallest (2×4)-like islands on the $c(4\times4)$ surface consist of just a single As dimer pair [Fig. 3(a)], in agreement with Kanisawa and Yamaguchi.[12] These structures are similar to one unit mesh of the $\beta2(2\times4)$ structure and electron counting arguments imply that they should be stable.[12] However, it is important to stress that a mixed second layer in the $c(4\times4)$ reconstruction may invalidate such arguments unless the presence of Ga is explicitly included. It should also be necessary to take into account the fact that the high-temperature $c(4\times4)$ surface, on which the islands lie, is itself highly disordered, with a much lower top-layer As content than the ideal $c(4\times4)$ structures (Fig. 1). Ito and Shiraishi[20] showed, using electron counting Monte Carlo (ECMC) simulations, that As desorption occurs when Ga is added to a perfect $c(4\times4)$ surface in order to allow the Ga dangling bonds to become empty of electrons. When more Ga atoms are added, a (2×4)-like island is produced since As dimers form on top of them, again ensuring that there are no electrons in the Ga dangling bonds. However, the calculations presented in Ref. 20 do not take into account either species intermixing in the second layer or missing As atoms on the top layer of the $c(4\times4)$ structure. It would be inter-

esting to include these in ECMC simulations and to see how they affect the predicted atomic configurations of islands on the $c(4\times4)$-(2×4) two-phase surface.

In the case of InAs(001), the (2×4)-$a(1\times3)$ surface is somewhat similar to the GaAs(001) two-phase surface, with the smallest common (2×4)-like island consisting of two As dimers or one 2×4 unit mesh [Fig. 2(b)]. In contrast to GaAs(001), occasional smaller units do exist comprising just a single As dimer and other non-(2×4)-like islands can also be observed. This is perhaps not surprising given that the $a(1\times3)$ surface is more disordered than the high-temperature $c(4\times4)$ surface and is very probably of mixed composition, allowing a wider variety of island structures to form. For this reason we have not attempted to deduce specific atomic structures for the observed islands based on electron counting rules. Nonetheless, the two-dimer structure is significantly more common than any other small island configuration. The $c(4\times4)$-$a(1\times3)$ mixed surface again shows very small islands, down to single isolated 2×4 blocks, each of which has the barrel-like appearance of the equivalent blocks in the well-developed $c(4\times4)$ structure [Fig. 2(c)]. These are particularly common at higher temperatures 310 °C–320 °C where the $a(1\times3)$ phase is dominant. Taking into account the three two-phase surfaces considered, the existence of very small stable islands on two-phase (001) surfaces seems to be a quite general phenomenon.

V. CONCLUSIONS

The structures of the (001) surfaces of InAs and GaAs in the transition regime between the 2×4 and $c(4\times4)$ reconstructions have been investigated using STM and RHEED. A two-phase structure is observed on GaAs(001) during the transition, while for InAs an additional $a(1\times3)$ phase is observed, existing independently in a narrow temperature window or coexisting with the main $c(4\times4)$ and 2×4 phases. The GaAs(001)-$c(4\times4)$ phase is shown to be inherently multilayered and initially arises on the 2×4 surface one atomic layer below the top layer of the 2×4 phase. The multilayered morphology of the $c(4\times4)$ structure allows the excess gallium of the 2×4 reconstruction to be accommodated only if around $\frac{1}{4}$ of the second-layer As atoms in this reconstruction are replaced by gallium atoms. A similar conclusion can be drawn concerning species intermixing on the second layer of the InAs $c(4\times4)$ reconstruction, which should be around $\frac{1}{4}$ In. For the InAs $a(1\times3)$ phase there is direct evidence from the STM images that the upper layer(s) are mixed, based on the corrugation of the surface, which is significantly lower than the spacing of the atomic planes (1.5 Å). Again, by considering the conservation of indium in the transition from the 2×4 to the $a(1\times3)$ layer, up to 0.55 ML of indium should be accommodated in the top two layers of the $a(1\times3)$ surface. These results highlight the importance of the surface morphology on a scale of tens of nanometers in determining the overall characteristics of a surface reconstruction, as well as highlighting the possibility of deducing details of subsurface atomic struggle by using STM images of surfaces undergoing phase transitions.

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