Surface structures of MnAs grown on GaAs(111)B substrates

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Atomically flat MnAs epilayers grown on GaAs(111)B substrates by molecular-beam epitaxy present surface structures depending on the sample temperature and on the surface stoichiometry: the known (2×2) reconstruction and two new phases, i.e., a (3×1) reconstruction and a mixed phase of (2×2) and (3×1). By monitoring the reflection high-energy electron-diffraction diagram evolution as a function of the annealing temperature, it was possible to ascribe the (3×1) as being the As richest phase and the (2×2) as the As poorest phase. Two structural models for the observed reconstructions [i.e., (3×1) and (2×2)] are proposed.

INTRODUCTION

Combining a magnetic metal film with a semiconductor substrate to obtain an efficient electrical injection of spin-polarized carriers represents one of the major challenges for material science today.[1] Future devices could use not just the charge of electrons but also their spin, if well-characterized and efficient hybrid magnetic metal/semiconductor heterostructures could be realized. *Condicio sine qua non* for the development of these devices is the understanding, the reproducibility and the mastery of film growth. In particular, during growth, knowledge of the thin-film morphology and of the atomic structure of its surface provides useful information concerning the interfaces of the constructed heterostructures.

In this paper we focus on the morphology and on the surface structure of MnAs/GaAs, a promising ferromagnetic metal/semiconductor heterostructure. Indeed MnAs is ferromagnetic at room temperature with a NiAs-type hexagonal structure ($a=3.72$ Å and $c=5.71$ Å),[2] and is studied by many experimental groups.[3–6] Moreover, it grows epitaxially on the technologically well-known GaAs.[7]

The studies performed on MnAs grown on both GaAs(111) (Refs. 3 and 8) and GaAs(001) (Ref. 9) have shown a strong dependence of film's morphology on growth conditions and a rich variety of surface reconstructions depending on annealing temperature and on the As overpressure. Findings concerning growth conditions of MnAs on GaAs(111) substrates are reproduced in this work. Moreover, we present a detailed study of the MnAs/GaAs(111) surface and of its reconstructions. The stability domain and the stoichiometry of the observed surface structures are investigated. The study of these surface reconstructions is not only "academic" but also technologically relevant, since they affect the growth of multilayer structures[7] and, during growth, they are a fingerprint of the actual phase of the sample.

EXPERIMENT

The MnAs films were grown in a III-V molecular-beam epitaxy (MBE) chamber on a GaAs(111)B substrate with samples mounted with indium on a molybdenum plate. The sample temperature was checked using a thermocouple placed at the back of the plate and double checked with an infrared pyrometer. Before the growth of MnAs, a 150-Å-thick GaAs buffer layer was deposited at 580 °C under an As overpressure (P_{As}) of 10^{-6} Torr. The streaky and intense reflection high-energy electron diffraction (RHEED) pattern attests the flatness of the buffer layer, which displays a $(\sqrt{19}\times\sqrt{19})R23.4°$ reconstructed surface during growth.[10] While cooling, the well known (2×2) reconstruction is found at ~480 °C. The As shutter is then closed at 400 °C.

MnAs films were grown with substrate temperature of $T_{sub}=280$ °C and growth rates of ~25 Å/min, as determined by RHEED specular intensity oscillations (growth conditions similar to Refs. 8 and 11) and confirmed by the analysis of cross-sectional TEM (transmission electron microscopy). Under these conditions, film surfaces are flat, as will be shown later.

The growth starts by opening the As shutter, followed after few seconds by the Mn shutter. 1000-Å-thick films were grown, presenting the following epitaxial relations as
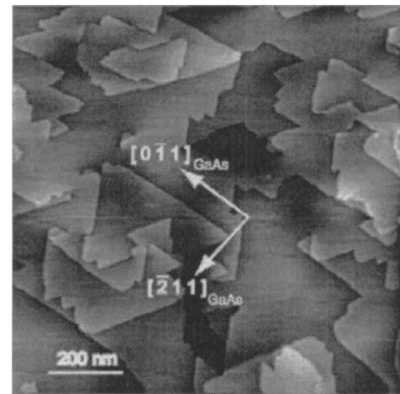

FIG. 1. STM image of the MnAs(0001) surface. The image was recorded at $+1.895$ V sample bias and 0.204 nA tunneling current. The surface is (2×2) reconstructed. White arrows indicate GaAs substrate directions.
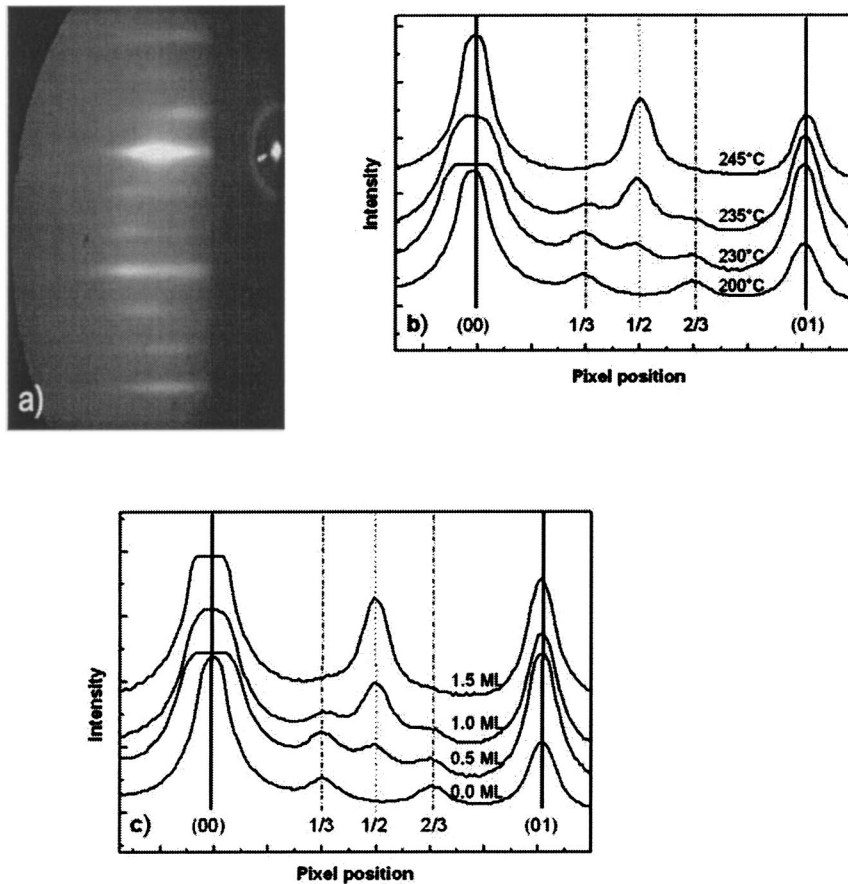
FIG. 2. RHEED patterns taken in the $[0\text{-}11]_{GaAs}$ azimuths of differently reconstructed MnAs(0001) surfaces: (a) Initial threefold reconstructed surface at a substrate temperature T_{sub} $\sim 200\,°C$; (b) cross-sectional cut of RHEED patterns as a function of the substrate temperature; (c) cross-sectional cuts of RHEED patterns as a function of Mn coverage.

determined by TEM and in agreement with Ref. 12: $(0001)MnAs//(111)GaAs\text{-}B$ and $[2\text{-}1\text{-}10]MnAs//[0\text{-}11]GaAs$.

RESULTS AND DISCUSSION

RHEED studies

The films are (2×2) reconstructed during growth and present flat surfaces (Fig. 1). This type of surface is stable at room temperature after closing the Mn and As shutters and switching off the substrate heating power, as pointed by Kastner *et al.*[3] A new (3×1) reconstructed surface has been observed when sample is cooled down to $200\,°C$ under As overpressure. This result is important and original, since Sadowski *et al.*[8] have claimed a (3×3) reconstructed surface for the same temperature range. Indeed the surface threefold symmetry is broken locally, in differently (3×1) oriented domains, as it will be shown later in scanning tunnel microscope (STM) images. Also a mixed phase $[(2\times2)+(3\times1)]$ [previously reported as (3×2) in Ref. 13] is observed at $250\,°C$ and can also be stabilized down to room temperature by closing the As shutters and by switching off the power of the substrate heater. This mixed phase can present a technological importance for magnetic heterostructures since Tanaka *et al.*[13] reported that epitaxial monocrystalline GaAs can be grown on a (3×2) MnAs surface at $T_{sub}<250\,°C$, whereas polycrystalline GaAs was grown on the (2×2) reconstructed surface.

Temperature evolution of the atomic surface structure

The nature of the MnAs (0001) surface reconstruction depends on substrate temperature and on As overpressure. Some simple experiments were performed in order to obtain information about the different surface structures. Reconstruction changes as function of temperature and/or overpressure have been monitored by RHEED. First, the (3×1) surface was stabilized [Fig. 2(a)] at room temperature and then UHV annealed. The (3×1) surface remains stable up to $235\,°C$ where a mixed phase shows up, followed by a complete evolution toward the (2×2) that is reached at $245\,°C$ [see cross-sectional cuts of RHEED patterns in Fig. 2(b)]. One should stress that the stability temperature range for the mixed phase is quite narrow. Our first guess is that the observed structural evolution must be related to thermally induced As desorption, which would imply that the (3×1) surface is an arsenic rich surface.

In order to verify this point, the annealing of the the (3×1) surface from 200 to $300\,°C$ has been performed with different arsenic overpressures. It turns out that the transition temperature for both mixed and (2×2) phases show an augmentation which follows the As overpressure. For example, annealing under an As overpressure of 5×10^{-7} Torr produces the mixed phase at $245\,°C$ and the (2×2) reconstruction at $255\,°C$ while for an As overpressure of 10^{-6} Torr, the phase transition temperature is shifted up by $15\,°C$. In these experiments no hysteresis has been detected during the cooling cycle.

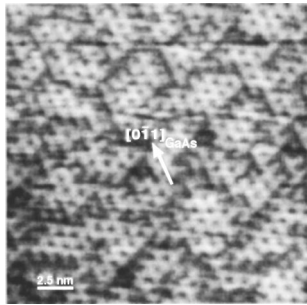FIG. 3. STM image of the MnAs (0001)-(2×2) reconstruction. The image was recorded at −1.794 V sample bias and 0.183 nA tunneling current.

These experiments confirm that the transition from the (3×1) to the (2×2) reconstruction results from arsenic desorption, implying that *the (3×1) reconstruction is the As richest phase and the (2×2) reconstruction is the poorest.* Coherently, during film growth, the (3×1) reconstruction is obtained by cooling the (2×2) reconstruction under As overpressure.

Depositing Mn on a (3×1) reconstructed surface

In order to both confirm the previous results and get some more quantitative information on the surface stoichiometry, we have deposited Mn with low evaporation rate (0.003 monolayer/s), calibrated after RHEED oscillations, on an As rich (3×1) surface kept at temperature of 200 °C. At this temperature, the (3×1) surface is stable. The substrate temperature is smaller than the transition temperature but at the same time, it allows enough atomic mobility on the surface. The result, displayed in Fig. 2(c), shows that ∼0.5 monolayer (ML) of Mn are required to change the (3×1) surface to the mixed phase (twofold and threefold), and ∼1.5 ML of Mn to saturate the signal of the (2×2) reconstructed. Further deposition of Mn beyond this point is detrimental to the surface flatness.

This experiment confirms that the lowering of the surface stoichiometry As/Mn ratio drives the (3×1) structure to the mixed phase and finally to the (2×2) reconstruction. The difference in stoichiometry between the (3×1) and the (2×2) reconstructions is of about 1.5 monolayer, the (3×1) being the As richest.

STM and LEED studies: Surface reconstruction

STM images of the (2×2) reconstructed surface show atomically flat terraces more than 2000 Å wide (Fig. 1). The step edges, clearly resolved, are parallel to the ⟨110⟩ directions of the GaAs substrate. Atomically flat terraces separated by bilayer height steps are clearly resolved. At atomic scale, our STM images of the (2×2) reconstruction (Fig. 3) are in good agreement with those of Kastner *et al.*[3] Low-electron energy diffraction (LEED) pattern confirms the presence of a homogenous (2×2) reconstructed surface, characterized by isotropic (circular) $\frac{1}{2}$ fractional spots [Fig. 4(a)].

Let us now focus on the first observation of the MnAs (3×1) reconstructed surface. As previously anticipated, this surface is characterized by three (3×1) reconstructed do-
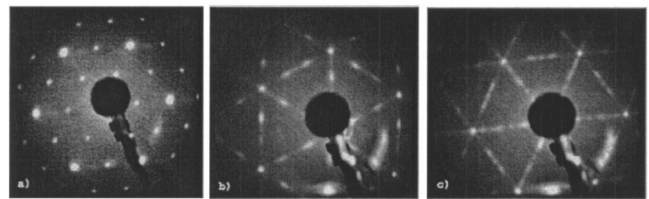

FIG. 4. LEED patterns (60 eV) of the MnAs surface after different reconstruction: (a) twofold surface reconstruction; (b) threefold surface reconstruction; (c) mixture of two- and threefold surface reconstruction.

mains, rotated by 120°. Large-scale STM images on this surface show a very flat surface characterized by elongated terraces [Fig. 5(a)]. The bulk threefold axis is locally lost in the surface structure.

In STM images, a pile of sticks is visible [Fig. 5(b)], aligned along the ⟨110⟩ GaAs substrate directions and with a period of 9.7 Å. The comparison with the images obtained on the (2×2) surface shows the strong anisotropy of the (3×1) surface. These features are confirmed by the LEED pattern [Fig. 4(b)] where the absence of two intermediate spots for all voltages attests clearly that the surface is not (3×3) reconstructed, as previously believed. Moreover, the elongation of the LEED fractional spots reflects the anisotropic character of the domains observed by STM.

Let us now focus on the mixed phase produced by heating the (3×1) phase at 250 °C and stabilized to room temperature. Two contributions can be clearly distinguished in the LEED diagram [Fig. 4(c)], the first one arising from the (3×1) reconstructed surface with elongated spots at the 1/3 and 2/3 positions, and the second one from the more isotropic (2×2). The STM picture shown in Fig. 6 corroborates the mixture of phases scenario, with two clearly distinguished atomic structures: the first, hidden among the long and narrow structures, is the typical (2×2) lozenge with 7.42±0.3 Å sides (coherent with the ideal value of 7.39 Å). Above the terraces, we can still observe the same type of sticks as for the (3×1) surface, still oriented along the ⟨110⟩ directions of the GaAs substrate. In the image the distribution of these rows is not regular, due to defects produced by the annealing. Elsewhere, the same surface presents domains of sticks with the densest possible arrangement, i.e., the (3×1) reconstruction.
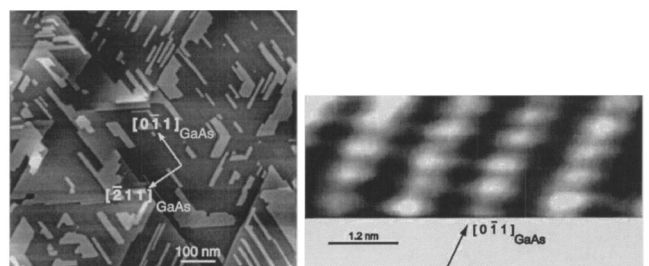

FIG. 5. (a) STM image of the MnAs (0001)-(3×1) reconstruction. The image was recorded at +1.667 V sample bias and 0.137 nA tunneling current. (b) Detail of a STM image of the MnAs (0001)-(3×1) reconstruction. The image was recorded at −2.493 V sample bias and 0.212 nA tunneling current.
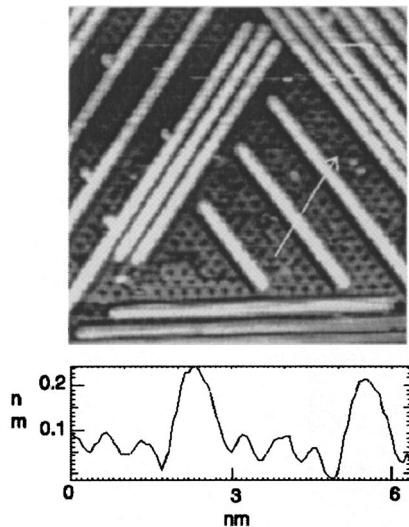
FIG. 6. Detail of a STM image of the MnAs (0001)-(2×2) and (3×1) reconstruction. The image was recorded at -2.234 V sample bias and 0.193 nA tunneling current. The white arrow indicate the GaAs substrate [0-11] direction. A cross-sectional cut is shown below.

As anticipated, the results on the (3×1) reconstruction are original. Sadowski *et al.*[8] claimed that within growth conditions, the (2×2) reconstruction evolves to a phase mixture $[(2\times2)+(3\times3)]$ in the temperature range 205–$200\,°C$ and to the (3×3) reconstruction at $195\,°C$. It is worthwhile to notice that their MnAs films were grown at a lower growth temperature ($200\,°C$ instead of $280\,°C$) leading to a rougher surface. In order to exclude a dependence of surface reconstructions with respect to growth parameters, we have prepared MnAs thin films at $200\,°C$. STM images show a rougher surface. An identical surface transition sequence has been found for these surfaces.

The surface model

In the following we will underline some features observed on the STM images. Two structural models for the observed reconstructions [i.e., (3×1) and (2×2)] will be proposed, taking into account the following observations:

(i) The more As covers the surface, the denser is the stick distribution, leading to the conclusion that sticks are As constituted. The densest configuration for sticks is found in the (3×1) reconstruction [see Fig. 5(b)]. The high-resolution image shows that these sticks are composed of As atoms aligned at $60°$ with respect to the stick direction.

(ii) RHEED experiments have shown that the deposition of ~1.5 ML of Mn drives the As-rich (3×1) surface to the (2×2) reconstruction. As a consequence, the structural models must take into account that the (3×1) reconstructed surface exceeds the (2×2) by an amount of ~1–1.5 As layers.

(iii) Since As sticks covering a (2×2) surface are observed also in the phase mixture's STM images (see Fig. 6), the structural model must describe the matching and the morphology of the observed features.
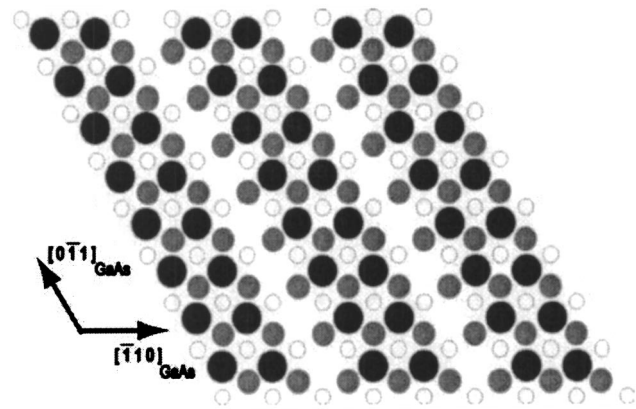

FIG. 7. Structural model for the (3×1) reconstructed surface. Large filled circles correspond to the As first layer, gray circles to the As second layer, small open circles correspond to the Mn third layer.

The (3×1) structure that we propose is obtained by adding two As adatoms every three unit cells (Fig. 7) on an As terminated MnAs surface. The bright and dark features, observed at $60°$ with respect to the stick direction, can be interpreted respectively as As and Mn atomic lines. This arrangement has been suggested by an analogy with a single crystal of arsenic;[14] the sites chosen for the two As adatoms in the (3×1) unit cell correspond to those of an As crystal which presents a rhombohedral structure and a lattice parameter very close to MnAs ($a=3.76$ Å rather than 3.72 Å in the a,b plane and $c=10.55$ Å).

This surface structure presents a large amount of As atoms: two As adatoms occupy three sites of the As-terminated surface unit cell leading to 1.67 ML of arsenic covering the bulk Mn-terminated surface of a MnAs crystal.

Let us now focus on the (2×2) surface structure. To be consistent with the proposed model of the (3×1) surface structure, the As coverage of the (2×2) is expected to be bounded by 0.2 ML and 0.7 ML since 1–1.5 ML of Mn drive the (3×1) surface to a (2×2). Two models seem most likely to us: the As-trimer model and the As-adatom model. The former, proposed by Kästner *et al.*,[3] is an As-trimer model similar to the $GaAs(2\times2)B$-(2×2) reconstruction. The As atoms in the trimer are each bonded to one As atom in the first layer. For the $GaAs(2\times2)B$-(2×2) reconstruction Biegelsen *et al.*[10] have calculated that the remaining first-layer As atom is 1.89 Å below the plane of the trimer. This model presents a very high As coverage—1.75 ML of As above the Mn layer—outside the $[0.2$–0.7-ML$]$ range. The latter model is presented in Fig. 8: 0.25 ML of As adatoms are adsorbed on a Mn-terminated surface in their bulk-like sites and define a (2×2) unit cell. The surface is As terminated but Mn rich. This model is coherent with the proposed (3×1) structure since the As coverage is 0.25 ML. About 1.4 ML of supplementary As adatoms distinguish the As rich (3×1) from the Mn rich (2×2), in reasonable agreement with the Mn amount which drives the (3×1) to the (2×2) reconstructed surface (i.e., ~1.5 ML).

Indeed, a careful look at the main features of the phase-mixture STM images corroborates the atomic surface struc-
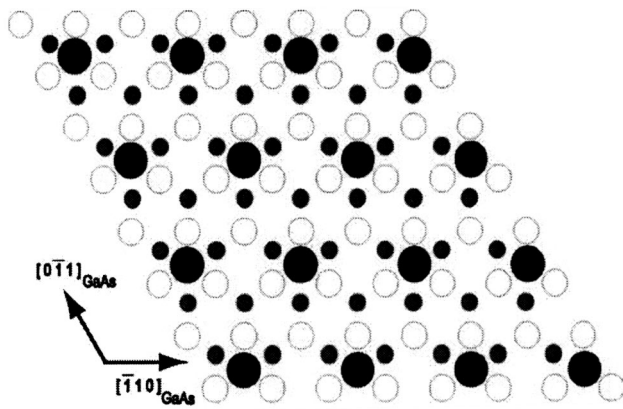
FIG. 8. Structural model for the (2×2) reconstructed surface. Large filled circles correspond to the As first layer, open circles to the Mn second layer, and small black circles correspond to the As third layer.

tures proposed above, i.e., the As adatom and the (3×1) models. In Fig. 6, two different height levels can be noticed: the first corresponds to terraces where the (2×2) reconstruction is still predominant. Triangular protusions and pits are observed in the (2×2) unit cell. The height differs by less than 0.6 Å. These reconstructed terraces are not affected by the presence of a large amount of sticks aligned along the $\langle 110 \rangle$ GaAs substrate directions. They are centered on lines joining protrusions and pits and are surrounded by similar lines. This allows us to evaluate precisely the width of an elementary stick, since its width matches with the $\times 2$ periods (ideal value of 7.39 Å). This observation has been taken into account in the construction of the (3×1) model proposed above.

Also the height of the observed structures is helpful (Fig. 6):

(i)   The cross-sectional cut shows that the outermost atoms of the (2×2) terraces are 1.3 Å below the top of the sticks. This value matches nicely with the distance between As planes in the arsenic crystalline structure (1.27 Å) that we have used to propose the (3×1) model, where only one partially filled As layer is adsorbed on a As-terminated surface (see large filled circles in Fig. 7). This confirms the RHEED experiments attesting that $\sim 1-1.5$ ML of Mn distinguish the As rich (3×1) from the Mn rich (2×2).

(ii)   Similar to the GaAs surface,[15] the expected corrugation of the trimer model for the (2×2) surface is ~ 2 Å. This is at odds with the corrugation found in the (2×2)

reconstructed terraces where the height difference between triangular protrusions and pits is smaller than 0.6 Å.

Although the STM images cannot provide a definitive model for the surface, the models for the (2×2) and (3×1) reconstructed surfaces presented in Figs. 8 and 7 match nicely with the main features observed during STM and RHEED experiments.

CONCLUSIONS

MBE-grown MnAs/GaAs(111)B thin films present an atomically flat surface and a rich variety of surface reconstructions. During growth they display a (2×2) reconstruction. At room temperature three surfaces can be stabilized: (2×2), (3×1), and a phase mixture $[(2 \times 2) + (3 \times 1)]$.

RHEED patterns attest that the surface phases depend on the substrate temperature and the As overpressure. Moreover, the deposition of Mn drives the (3×1) reconstructed surface towards the mixture phase (~ 0.5 ML of Mn) and then to the (2×2) reconstruction (~ 1.5 ML of Mn). These experiments have clearly shown that the (3×1) reconstruction is the As-richest phase and the (2×2) reconstruction the poorest.

STM images show that the (3×1) reconstruction is composed of a pile of long and narrow structures (sticks) aligned along the $\langle 110 \rangle$ GaAs substrate equivalent directions. In the case of the phase mixture, STM images show that the surface presents both (2×2) and (3×1) reconstructed domains.

After RHEED and STM experiments, we propose that: (i) The coverage of the (3×1) reconstructed surface exceeds the (2×2) by $1-1.5$ As layers. (ii) The sticks observed on the (3×1) reconstructed surface and on the phase mixture are As constituted. (iii) In the (2×2) unit cell, 0.25 ML of As adatoms are adsorbed on a Mn-terminated surface in their bulklike sites. The (3×1) unit cell is obtained by "filling" the As layer and by adding above two As adatoms in the unit cell. A simple scenario can describe the experimental findings: the lowering of the stick density by As desorption permits us to uncover (2×2) reconstructed terraces (phase mixture) and finally to obtain a (2×2) reconstructed surface.

Surface reconstruction and morphology of the MnAs/GaAs(111)B film are not only reference points for growth (temperature of the substrate, stoichiometry of the surface, etc.) but they can also affect the growth of multilayers structures and, consequently, the output of future electronic devices.

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