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Unreconstructed As atoms mixed with (3×2) cells and (6×6) supercells in low As pressure epitaxy on GaAs(001)

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Since the early days of GaAs molecular beam epitaxy, it has been understood that on the As-stabilized growth surface, As lies in the form of As_2 building blocks. At lower As pressure however, there is a transition to a (3×1) growth surface observable by reflection high-energy electron diffraction. Using *in situ* scanning tunneling microscopy, we provide an atomically resolved observation of this still As rich surface that displays unreconstructed As atoms in (1×1) cells as well as (3×2) and (6×6) reconstructed areas. Most surface As atoms do not display any dimer bonds. From the statistics of surface Ga atoms in sp^2 hybridization we propose that the background carbon acceptor impurities content is significantly reduced in the (3×1) growth.

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During the last 25 years, the increase in the electronic mobility of two-dimensional electron systems (2DES) in AlGaAs/GaAs heterostructures has been a springboard for the discovery of important quantum physics phenomena in two dimensions.[1] In structures with a sufficiently large spacer, the Si doping ionized impurity scattering can be reduced by optimizing the AlGaAs barrier modulation doping.[2,3] The 2DES low temperature (LT) electron mobility is found to be inversely proportional to the content of carbon background acceptor impurities.[4,5] Attempts to reduce this C content require optimizing the molecular beam epitaxy (MBE) reactor, pumping system, and baking procedure.[5,6]

Alternatively, the As pressure growth on GaAs(001) can be reduced, while still keeping it in the As rich growth mode. This is monitored by a transition of the reflection high-energy electron diffraction (RHEED) pattern from the well-known (2×4) to a diffuse (3×1) reconstruction. This (3×1) surface is a weakly As-stabilized state in between the higher As pressure As-stabilized (2×4) and the too low As pressure Ga-stabilized (4×2), but its atomic structure remains fully unknown.[7,8] Although widely discussed privately to be of importance for obtaining high mobility 2DES heterostructures, an understanding of the (3×1) growth is still lacking in the literature. In this paper, using atomic resolution scanning tunneling microscopy (STM) images of the (3×1) surface, we explain why this surface state provides a further benefit for high mobility heterostructures.

Previously, the atomic structures of various (2×4) surface reconstructions on GaAs(001) surfaces obtained during MBE growth under strong As flux were measured by grazing incidence x-ray diffraction,[9] and by STM in ultrahigh vacuum (UHV).[10,11] Molecular dynamics models[12] confirm the stability of the two As-dimers $\beta2(2\times4)$ atomic structure, in which all surface As atoms, sp^3 hybridized are paired in dimers along $[1\bar{1}0]$. On the upper As plane, which has only half a monolayer (ML) of As atoms, these dimers are paired into rows aligned along the $[1\bar{1}0]$ direction. On each edge of these rows, Ga atoms are in a planar sp^2 hybridization with the three As-Ga-As angles close to 180°.[9] The Ga sp^2 hybridization is also present on $[1\bar{1}0]$ step edges. On the (3×1) surface stabilized down to room temperature, our filled states STM images show that this is actually a complex surface with spatially separate (3×2) and (6×6) reconstructed areas. Furthermore, outside these cells, As surface atoms are not involved in reconstruction but remain in their bulk position, in (1×1) cells without dimerization. Knowing the As atoms configurations, we infer the hybridization of the Ga underneath. These, sp^3 bonded with 4 As, cannot bind directly any C acceptor, in contrast to those sp^2 bonded with only 3 As. We propose that the observed significant reduction in Ga sp^2 atoms with respect to the same surface but $\beta2(2\times4)$ reconstructed leads to a proportional reduction in the residual C acceptors incorporation rate.

STM images are obtained at room temperature (RT) and $P=8\times10^{-11}$ torr, using an Omicron UHV-AFM-STM connected under UHV to a Riber 32 MBE chamber, dedicated to RHEED controlled growth of high mobility 2DES in AlGaAs/GaAs heterostructures. We use undoped GaAs nominally (001) substrates, thermally deoxidized, covered with a 3-μm GaAs buffer layer grown at 620 °C and 1 Å/s in the standard high As pressure (2×4) reconstruction. This layer is slightly Si doped (10^{16} cm^{-3}) in order to achieve STM imaging. Reducing the As beam from a valved cracker cell to 2.3×10^{-6} torr beam equivalent pressure, in order to get a (3×1) RHEED pattern, we grow a 200-nm-thick layer. The cooling process under As flux is controlled by RHEED to maintain this (3×1) surface state down to RT. Filled states STM images are obtained with an electrochemically etched tungsten tip with a sample bias ≈−2.5 V and a tunneling current ≈250 pA. After STM experiments, the samples were reinserted into the MBE reactor: the RHEED remained (3×1) and was unchanged when heating up the samples to growth condition, and even when restarting the growth. No difference in the atomic organization of the (3×1) surfaces is observed using an As sublimation cell instead of the As cracker cell.

As shown in Fig. 1, the (3×1) surface exhibits several narrow up-down steps (one GaAs monolayer=2.83 Å), indicating a disordered flat surface already identified in Ref. 13. The surprising information obtained here is an almost complete spatial demixing of two different surface reconstruc-

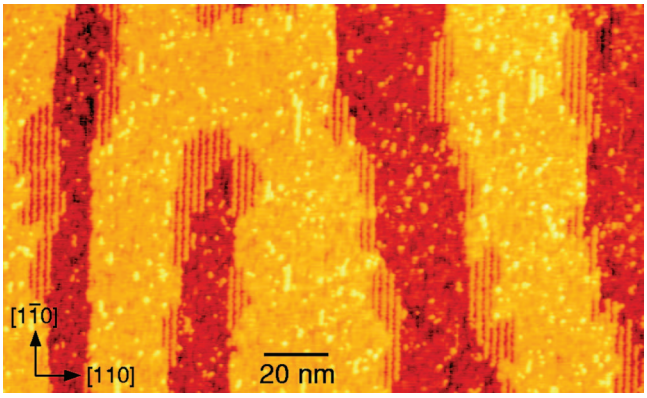

FIG. 1. (Color) 200 nm $\times$ 120 nm filled states STM image of the mixed reconstructed two terrace levels (upper yellowish, lower reddish) surface obtained after growth of GaAs at 620 °C, 1 Å/s and an As flux of 2.25×10^{-6} torr. The [1$\bar{1}$0] rows close to the step edges are the signature of the $(n\times6)$ area.

tions: the upper and lower terraces exhibit the same aspect on the surface except on areas close to step edges. A few rather long dimer rows are conspicuous only in restricted areas close to the [1$\bar{1}$0] oriented step ledges (within 150 Å). These As rows always seem to nucleate at some [110] oriented kink or larger protrusion, run along [1$\bar{1}$0], and may end up either freely on the terrace or at another protrusion. Outside these As-dimer rows, the terraces appear as rather homogeneously As covered, with some quite short pieces of dimer rows appearing as bright features, scattered everywhere.

The closer view STM scan, Fig. 2, confirms this organization of the low As pressure surface reconstructions, which now can be identified. On the lower terrace of the STM image presented Fig. 2(a), the [1$\bar{1}$0] running As dimer rows have a periodic spacing of 24 Å along [110], corresponding

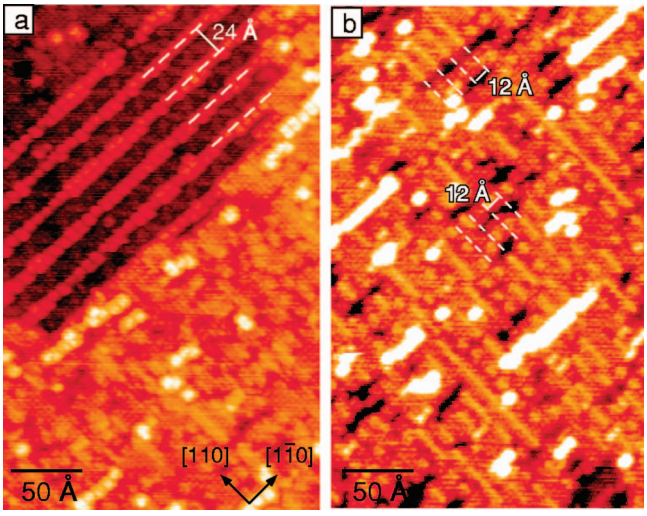

FIG. 2. (Color) (a) Filled states STM image (−2.4 V, 270 pA) of a terrace ledge: the As-dimer rows on the lower terrace are separated by 24 Å corresponding to the $\times6$ periodicity along [110]. (b) Filled states image (−2.88 V, 370 pA) of an As-covered upper terrace: brighter As [110] rows are separated by 12 Å, corresponding to the $\times3$ order visible on the RHEED pattern during growth.

to a $\times6$ reconstruction. The occupation rate of these $(n\times6)$ areas is between 8% and 20% with the As_4 cell and As cracker cell respectively. This may well explain the diffuse RHEED pattern in the [1$\bar{1}$0] azimuth around the integer streaks. On the As-covered terraces, some fine parallel bright lines can be distinguished running in the orthogonal [110] direction. They are best seen Fig. 2(b), having a periodic separation of only 12 Å along [1$\bar{1}$0], corresponding perfectly in azimuth and fractional order to the $\times3$ RHEED feature. Furthermore these patches comprise quite numerous defects of one ML depth, appearing in the form of [1$\bar{1}$0] oriented short and narrow dark features, having in some occurrences a 24-Å spacing. This may indicate remnants of a previous $(n\times6)$ reconstruction. This claim is further supported by observing on Fig. 2(a), the onset of the filling of the first dark stripe of the $(n\times6)$ area on the lower terrace, a remarkable atomic scale testimony of some local step flow process as the ledge is flowing locally ahead towards [110] by filling the space between two As-dimer rows of the $(n\times6)$ area. On these three STM images, brighter [1$\bar{1}$0] oriented rows of one ML height are present on the flat terraces and are formed of As dimers; these are the nucleated seeds for the growth of the $(n\times6)$ area.

Figure 3(a) shows an atomically resolved STM image of the As-covered terrace. Within the faint bright lines a cross-shaped pattern may be clearly resolved, allowing the identification of (3×2) cells. The line profile along [110] presented in Fig. 3(b) reveals well-resolved peaks, two corresponding to As atoms in faulted position that are around 0.8 Å higher than the unreconstructed As atoms. A proposed atomic structure for this cell is displayed in Fig. 3(c). The important point is that two displaced Ga atoms in a planar sp^2 hybridization become bound to three As atoms leading to the two As sp^3 atoms in faulted position. This planar pattern of three As and one Ga is also the building block for the Ga-rich $\zeta(4\times2)$ reconstruction.[12] On our atomic structure we try to place the atoms keeping the As-Ga length bonds between 2.35 and 2.51 Å (bulk value: 2.45 Å), and also to have bond angles close those for ideal planar or tetrahedric configurations of each atom. Although not relaxed, this model gives 0.73 Å for the height difference between faulted As atoms and surface As, a value close to the experimental 0.8 Å. The (3×2) cell depicted in Fig. 3(c) displays full mirror symmetry around a (110) plane. Considering the cell structure factor it is easy to show that such a symmetry implies a perfect cancellation of the half order streak intensity. Therefore, although the (3×2) cells may happen to be ordered along [110], the RHEED remains (3×1) without any hint for the twofold periodicity, which can only be revealed by STM. So there is a complete agreement between the *in situ* (3×1) RHEED pattern and the *ex situ* STM images. Such a model based on symmetry has also explained the lack of one-fourth and three-fourth features in the $c(4\times4)$ RHEED pattern.[14]

Outside these (3×2) cells many unreconstructed (1×1) cells involving a single As atom can be resolved. They do not bind in dimers as would be the case on the higher As pressure (2×4) surface, but have two Ga bonds and one *sp*

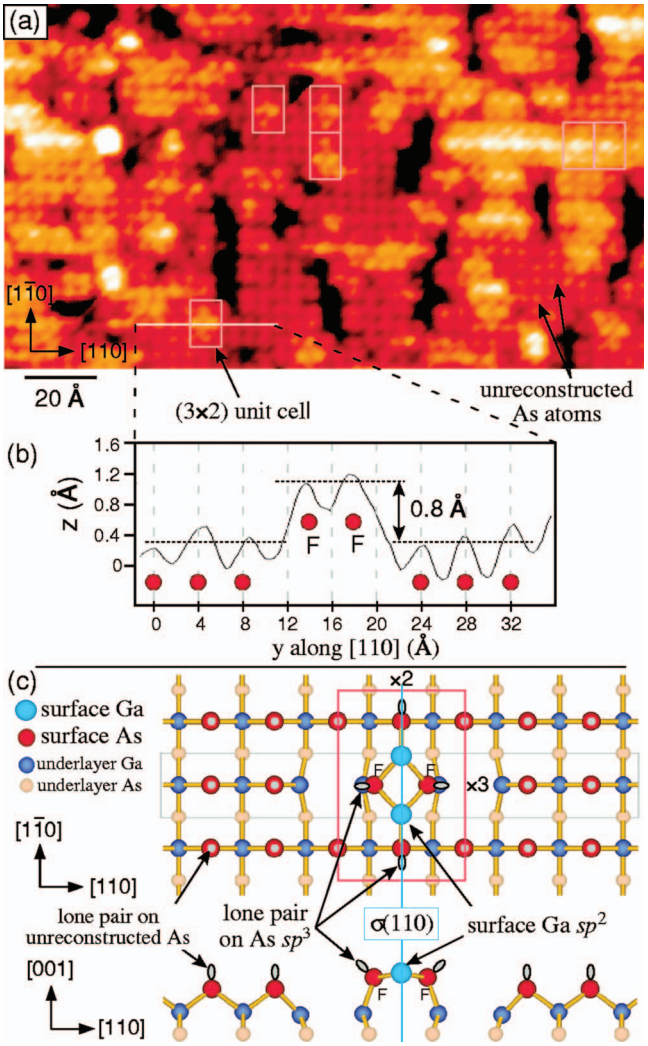

FIG. 3. (Color) (a) Filled states STM image showing the organization of the atomic As plane: 45% of As atoms are unreconstructed and 13% of As atoms are in faulted position leading to the formation of a local (3×2) cell (a few are highlighted with pink frames). (b) Height profile along the white [110] line passing through As atoms in faulted position. (c) Atomic structure for the (3×2) cell: the faulted As atoms are linked to two planar Ga sp^2 atoms.

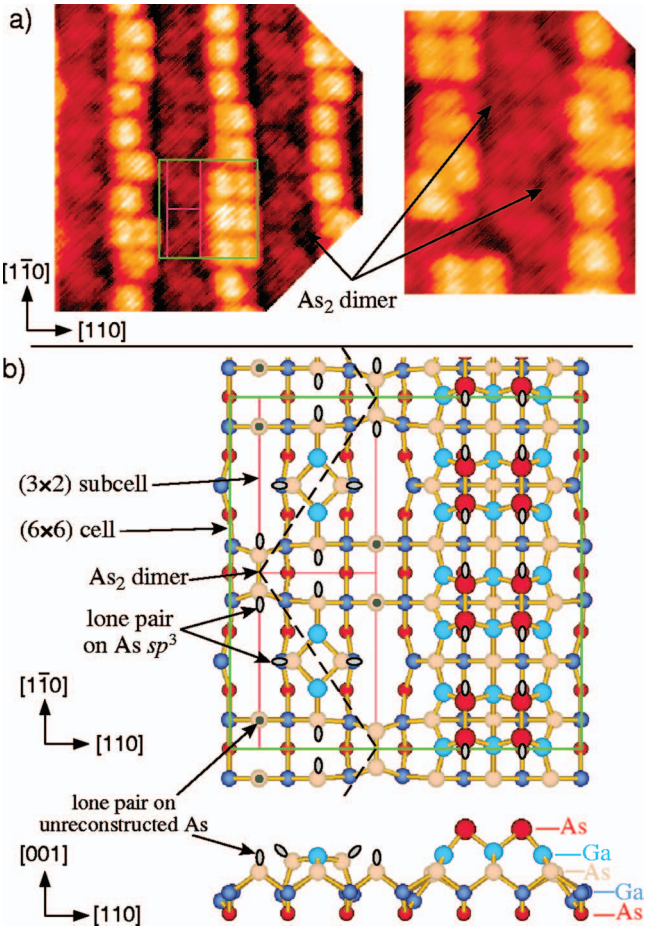

FIG. 4. (Color) (a) Filled states STM image of a (6×6) reconstructed area: the underlying As atoms are zigzag patterned. (b) Atomic structure of the (6×6) cell: the underlayer As plane is organized in (3×2) subcells linked by one As dimer shifting from side to side at each connection between (3×2) subcells.

hybrid lone pair perpendicular to the surface.[18] A statistical analysis on a 200×210 Å^2 STM image of a (3×1) area shows that 45% of this surface is covered by these (1×1) cells, 39% by (3×2) cells, and 16% by dimer row pieces and one ML holes. Furthermore, from the same STM image, we count 970 surface Ga sp^2 atoms involved in the (3×2) cells as well as those located at the holes and upper dimer rows ledges.[15] However, if this surface were fully $\beta 2(2\times4)$ reconstructed there would be 1330 Ga sp^2 located at the upper dimer rows ledges. On this (3×1) surface there is a significant decrease by 27% of the number of sp^2 reactive Ga sites compared to the regular $\beta 2(2\times4)$ growth surface.

Figure 4(a) shows two atomic resolution STM images of the ($n\times6$) area. A close view of the dark stripes reveals that underlying As atoms are zigzag patterned resulting in a ×6 period along [1$\bar{1}$0]. A similar (6×6) reconstruction has already been observed for the Ga-rich surface and often mixed with the $\zeta(4\times2)$.[16,17] This means that the (6×6) is the bridge between As-rich and Ga-rich surfaces. A careful analysis of the As underlayer plane between the As-dimer rows allows us to determine the As position and bonds. As shown in Fig. 4(b), the As and Ga atoms are organized there in two (3×2) subcells aligned along [1$\bar{1}$0] and linked together by one As dimer. Neighboring (3×2) cells on the (3×1) areas depicted in Fig. 3(a) do not have this As dimer. The linking As dimers, between the (3×2) subcells of the (6×6) cell, shift from side to side at each connection between subcells, leading to the observed zigzag pattern. Finally, we also note on the upper dimer rows that some dimers are missing, this both when using the As cracker or the As cell. There is no correlation between defective dimers and the zigzag position in the neighboring rows.

This occurrence of (3×2) and (6×6) reconstructed cells as well as large amount of non dimerized As atoms in (3×1) growth conditions also leads to revisiting a very compelling model used to predict the most stable reconstructions. In the lowest energy state, the electron counting rule (ECR)

predicts that the dangling bond of As atoms are occupied whereas the Ga one must be fully empty,[18] leading to a semiconducting band structure for the surface. All the previously known reconstructions proposed for GaAs(001) comply with this rule. A straightforward calculation gives that neither the (3×2) nor the (6×6) fulfill the ECR, having the same excess of one sixth electron per (1×1) unit mesh. For the non dimerized surface As atoms with one *sp* lone pair, one half electron remains. Clearly all these atomic structures observed on the (3×1) surface do not comply with the ECR, as has also been found for some structures on other GaAs surface orientations.[19,20] Another tricky point to be discussed is the presence of the unreconstructed As atoms. Until now they were considered to be unstable as their energy is higher than the As_2 dimers. But on the (3×1) surface presented here, they are mixed with two other reconstructed area, which probably lower the energy of the whole surface.

Now we want to point out the impact of the Ga sp^2 decrease observed on this (3×1) surface. As usually admitted, the background impurity during growth of 2DES originates in the incorporation of group IV C atoms substituting as acceptors for group V As atoms. This substitution means that C atoms are bound to Ga and this process may be possible during growth only by creating a first bond with a surface Ga sp^2 atom. Thus the decrease by 27% of Ga sp^2 on the (3×1) surface must induce a similar C content reduction compared to $\beta2(2\times4)$ growth. Our high mobility structures,[3] were in fact grown in these conditions. The present data on the amount of Ga sp^2 atoms therefore suggest that, without this effect, the electron mobility of our best sample (6.0×10^6 cm^{-2} V^{-1} s^{-1}),[4] grown in empirically optimized (3×1) conditions, would have been reduced to a mobility $\approx4.4\times10^6$ cm^{-2} V^{-1} s^{-1} instead.

In conclusion, during weakly As pressure MBE growth on GaAs(001), we have put into evidence by STM that the (3×1) growth surface consists of (3×2) cells intermixed with unreconstructed As atoms, and coexistent with (6×6) cells localized close to the step edges. Most of the As atoms on this surface are not dimerized. In spite of the importance of the (3×1) surface, which corresponds to optimized growth for high mobility heterojunctions, neither of these cells has been included in recent calculations of the reconstructions formation energy versus As chemical potential.[12] A simple explanation is offered why (3×2) cells lead to a (3×1) RHEED. We reveal from the decrease in the amount of Ga sp^2 surface atoms, why (3×1) growth is able to reduce the carbon contamination of the GaAs channel. We also point out that the (3×2), (6×6), and unreconstructed As atoms all violate the ECR, which up to now has seemed to be a very strictly obeyed rule on GaAs(001).

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