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Reconstruction of the GaAs(001) surface induced by submonolayer Si deposition

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We have studied the change of the GaAs(001) surface reconstruction due to Si deposition by reflection high-energy electron diffraction and scanning tunneling microscopy (STM). We find that with increasing Si deposition below 15% of a monolayer at substrate temperatures above 600 °C new reconstructions form that are not observed on the initial surface. The initial surface, prepared by molecular-beam epitaxy, is the (2×4) As-stabilized reconstruction. STM reveals straight missing dimer rows with two As dimers per unit cell. With an increasing amount of Si deposited on this surface, the reconstruction shows an increasing disorder due to kinks that develop in the missing dimer rows. The Si deposition leads to an overall decrease of the As coverage. After a Si deposition of 5% of a ML a new Ga stable (3×2) reconstruction starts to develop. With further increasing the Si concentration or the substrate temperature at this Si level, the surface continues to get more Ga stable transforming via a (5×2) to a (4×2) reconstruction.

The surface orientation most widely used in molecular-beam epitaxy (MBE) of GaAs is the (001) surface. Depending on the substrate temperature and the Ga to As ratio during growth various surface reconstructions establish on this surface that can be monitored *in situ* with reflection high-energy electron diffraction (RHEED).[1] Most of these surface reconstructions could also be imaged with scanning tunneling microscopy (STM).[2–4] The MBE growth conditions commonly used lead to a (2×4) surface reconstruction. This reconstruction is composed of two As dimers and two missing dimers or three As dimers and one missing dimer per unit cell in dependence on the As flux and the substrate temperature.[2,5] The effect of Si doping on this reconstruction has first been studied with STM by Pashley and Haberern.[6] The maximum Si concentration used in their experiment is 1.6×10^{13} cm^{-2}. Higher Si concentrations up to a ML of Si and subsequent Si growth on GaAs has so far been studied by RHEED only.[7–9]

In this paper we present the effect of the Si deposition on the surface reconstruction to six times higher Si concentrations than in Ref. 6, i.e., 15% of a ML that we studied with RHEED and STM. We find two new surface reconstructions on the GaAs(001) surface that do not exist on undoped material. These are a (3×2) and a (5×2) reconstruction terminating the surface with Ga. These reconstructions start to develop at a Si coverage of 3×10^{13} cm^{-2}, i.e., 5% of a ML. In the phase diagram of the surface reconstructions[1] they lie between the As-terminated (2×4) and the Ga-terminated (4×2) reconstruction.

The experiment was performed in a combined MBE-STM chamber that allows for a short turn around time between the MBE growth and the STM imaging in a vacuum better than 2×10^{10} Torr. Epi-ready n-type GaAs samples with a 0.5° miscut towards (111)A were used as substrate material. The slight miscut was chosen to facilitate the surface ordering on (001) terraces of limited size. After thermal oxide desorption that was used to calibrate the reading of the thermocouple to 580 °C, a 100-nm-thick GaAs layer, Si doped with 2×10^{18} cm^{-3}, was grown at a growth rate of 0.5 ML/s. The Si calibration was performed by capacitance-voltage (C-V) profiling. The Si was then deposited in pulses of 1 min at a flux of 1×10^{11} cm^{-2} s^{-2} (corresponding to 0.58 ML/h) at a substrate temperature of 580 °C. A time of 1 min between the Si pulses was used to anneal the surface at the same temperature. An As beam flux equivalent to a pressure of 4×10^{-6} Torr measured with an ion gauge at the sample position was used throughout the deposition of the GaAs and the Si. Quenching of the resulting surface reconstruction after the growth was performed by slowly cooling the sample to room temperature and lowering the As background pressure at the same time. During this process the surface was monitored with RHEED. The cooling rate and the As background pressure were optimized in such a way that the RHEED pattern remained unchanged during the whole process. The transfer of the sample into the STM chamber was established at pressures below 2×10^{-10} Torr. During STM imaging the pressure remains below 2×10^{-11} Torr. Positive tip voltages of 3–4 V at tunneling currents of 300–500 pA were used during the STM imaging resulting in filled stated images.

Figure 1 shows the RHEED pattern and a typical STM image of the initial GaAs surface before the Si was deposited. For all figures the left RHEED pattern is taken along the [110] direction. A clear (2×4) RHEED pattern with a pronounced Laue circle indicative for a flat surface is observed. STM confirms this notion and shows a well-ordered (2×4) structure with straight As missing dimer rows. A monolayer high step runs through the image and is due to the miscut of the substrate of 0.5° towards (111)A. High-resolution images reveal the two dimers plus two missing dimers configuration of the unit cell similar to the finding in Ref. 5. After Si deposition of only 1×10^{12} cm^{-2}, the RHEED pattern gets streaky and the intensity of the half-order diffraction feature of the $\times4$ direction decreases. Figure 2 shows the RHEED pattern and a typical STM image at a Si concentration of 3×10^{13} cm^{-2} on the surface. Similar to the work of Pashley and Haberern[6] on bulk doped material we find in the STM images that the ordering of the (2×4) reconstruction is reduced and that kinks form in the missing dimer rows. In their work, the number of kinks was found to be of the order of the Si-doping concentration, a finding that

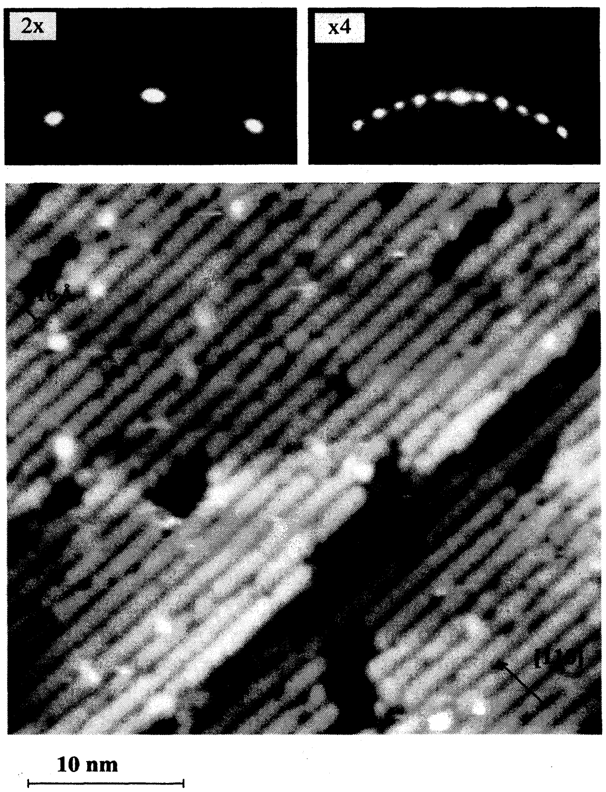

FIG. 1. STM image and RHEED pattern of the (2×4) surface reconstruction of the low-doped GaAs(001) surface. Straight missing dimer rows are formed containing two As dimers and two missing As dimers per unit cell.

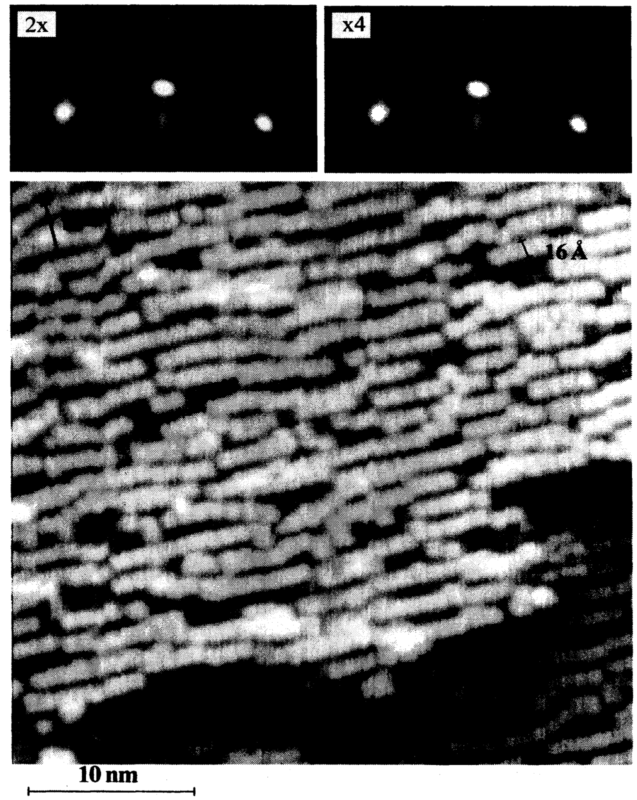

FIG. 2. STM image and RHEED pattern of the (2×4) surface reconstruction of the Si-deposited GaAs(001) surface. The Si deposition (in this case 3×10^{13} cm^{-2}) results in an increasing amount of disorder going along with a decrease of the As coverage.

led to the conclusion that each kink forms an acceptor.[6] The Si, being incorporated on a Ga site, acts as a donor. The high electron concentration thus introduced at the surface changes the surface polarity that governs the surface reconstruction. As a consequence the overall fractional coverage of the surface with As is reduced due to the Si deposition. This trend is continued to higher Si levels, up to 15% of a ML studied in this work. Ultimately a new Ga stable reconstruction is formed.

Increasing the Si deposition to levels above 3×10^{13} cm^{-2}, we find that at temperatures above 615 °C a new (3×2) surface reconstruction forms. This surface reconstruction is not observed on undoped GaAs. The RHEED pattern as well as a typical STM image are shown in Fig. 3. The 90° rotation of the dimer direction ($\times2$ in RHEED) and of the missing dimer rows (in the STM images) with respect to the As-terminated (2×4) reconstruction is evidence for the termination of this reconstruction with Ga. We propose that the threefold periodicity is formed by one Ga dimer row and two missing dimer rows as sketched in the ball and stick model in Fig. 3. The vertical corrugation of this reconstruction measured by STM is smaller than that of the As-terminated reconstruction.[10] This was also found for the (4×2) reconstruction, another Ga-terminated reconstruction.[2] With further increasing the Si concentration or increasing the substrate temperature at the same Si concentration the (3×2) reconstruction changes to a (5×2) reconstruction. At the transition temperature both reconstructions could be observed in RHEED. Quenching this reconstruction to room temperature we find that the (3×2) reconstruction dominates over the (5×2) reconstruction at lower temperatures and/or higher As background pressures. This clearly indicates that the (5×2) reconstruction contains more Ga than the (3×2) reconstruction. Figure 4 shows the RHEED pattern and a typical STM image of these surface reconstructions. Ga dimer rows oriented perpendicular to the step edges form domains of threefold and fivefold periodicities. The fivefold periodicity is formed out of the threefold by shifting two adjacent Ga dimer rows closer to each other by one lattice constant. Between each Ga dimer row pair constructed this way we find two missing dimer rows similar to the threefold periodic structure (see the ball and stick model in Fig. 4). The domain boundaries are formed by domain walls that run along [110] on a terrace and the step edges that are introduced due to the 0.5° miscut of the substrates. The Ga coverage of the two domains is $\frac{1}{3}$ and $\frac{2}{5}$, respectively. Forming domains, the surface is flexible in adjusting the average Ga coverage continuously between these two values by changing the domain size ratio. This will depend on the Si concentration, the As background pressure, and the substrate temperature.

Including the Si concentration as an additional parameter, the phase diagram of the surface reconstruction[1] has to be extended. The result for one value of the As beam flux used

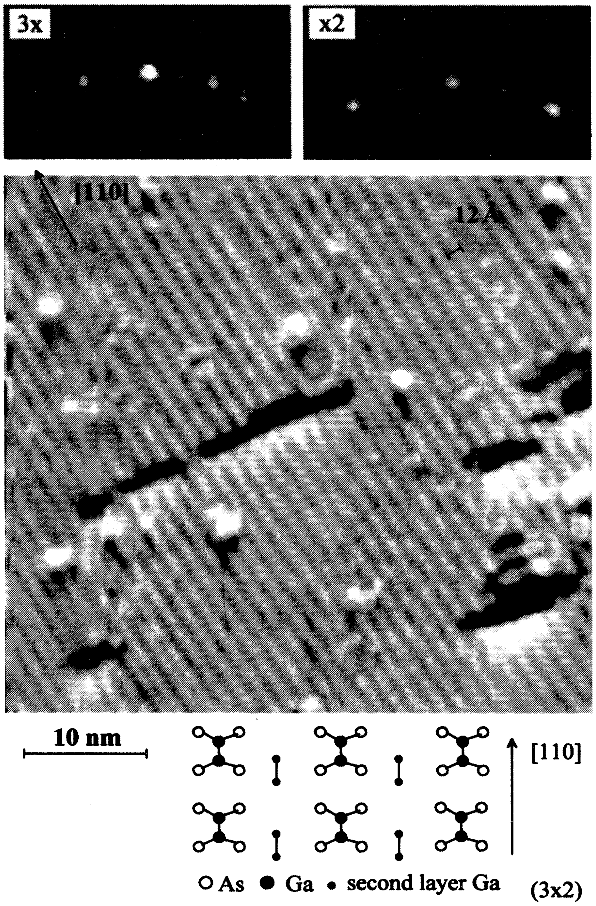

FIG. 3. STM image and RHEED pattern of the Ga-terminated (3×2) surface reconstruction of the Si-deposited GaAs(001) surface. The Si deposition is 6×10^{13} cm^{-2}. The ball and stick model shows the proposed atomic structure for the (3×2) unit cell being formed of first- and second-layer Ga dimer rows oriented along the [110] direction. The white spots on this and the next image are attributed to residual arsenic adsorbed as clusters on the surface during the quenching process.

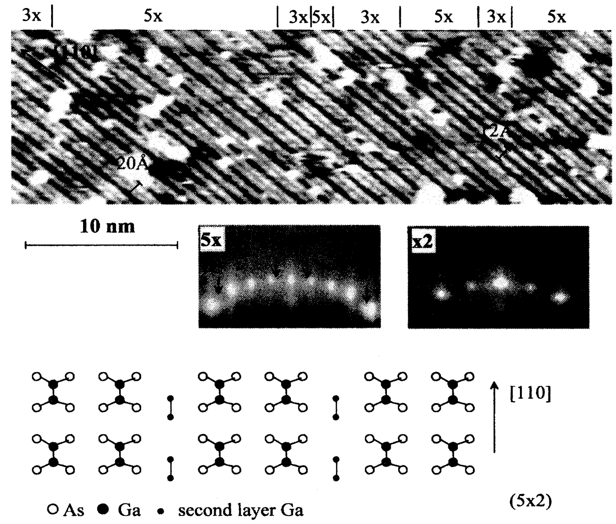

FIG. 4. STM image and RHEED pattern of the (3×2)+(5×2) surface reconstruction of the Si-deposited GaAs(001) surface. The Si deposition is 9×11^{13} cm^{-2}. Satellite spots in the RHEED pattern close to the third-order diffraction spot evidence the existence of domains with fivefold periodicity observed in the STM image. The ball and stick model shows the proposed atomic structure for the (5×2) unit cell being formed of first- and second-layer Ga dimer rows.

in our experiment is shown in Fig. 5. This phase diagram has been constructed from RHEED measurements. The Si was deposited the same way described above, but also at different substrate temperatures while the surface was monitored with RHEED. For temperatures below 590 °C Si was deposited and the substrate was subsequently annealed to higher temperatures. The Si concentration and/or substrate temperature at which the surface reconstructions change mark the boundaries of the surface reconstructions within the diagram. With increasing Si concentration, the temperature at which the (2×4) surface reconstruction changes to a (3×1) decreases. This finding agrees well with that of Ref. 9. We find a distinct transition from the (3×1) to the (3×2) surface reconstruction at Si concentrations above 3×10^{13} cm^{-2}. There is a clear difference in the RHEED pattern between the 3× of the (3×1) and the 3× of the (3×2). The former consists of broad streaks only and shows asymmetry. A similar asymmetric 3× pattern was previously observed also by others.[11] The 3× of the (3×2), however, forms distinct and symmetric spots on a clear Laue circle. At the same Si concentration the half-order spots appear in the perpendicular azimuth. The high intensity of the diffraction spots on the Laue circle in the RHEED pattern is another indication for the surface being Ga terminated. This behavior is typically found also on the Ga-terminated (4×2) reconstruction.

Our present STM study shows that the (3×2) RHEED pattern corresponds to a homogeneous Ga-terminated surface reconstruction. At the same substrate temperature and at the same As background pressure at which the initial surface shows an As-terminated (2×4) reconstruction, the Si-deposited surface favors a Ga-terminated reconstruction. Our

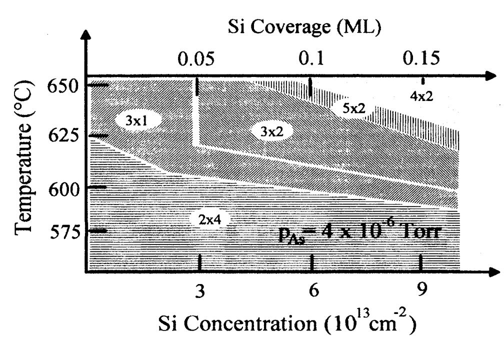

FIG. 5. Phase diagram of the GaAs(001) surface reconstructions spanning the Si deposition and temperature space. At a Si deposition above 3×10^{13} cm^{-2} the Ga-terminated (3×2) reconstruction forms at temperatures above 610 °C. Increasing the Si deposition or the temperature the Ga-terminated (5×2) and eventually the (4×2) reconstruction forms.

present understanding of this process is as follows. The nonpolarity requirement, expressed in the electron counting argument[12] and found to govern the surface reconstructions on undoped material, has to be extended to high Si concentrations. Using the electron counting argument the proposed surface reconstruction model for the (3×2) reconstruction and also for the (5×2) reconstruction can be identified as electron deficient. The (3×2) unit cell is missing one electron and the (5×2) unit cell two electrons. Such electron deficient reconstructions are not stable on the semiconducting GaAs(001) surface. In the case of the Si-deposited surface, however, the Si atoms act as donors that provide the missing electrons, and thus stabilize the otherwise unstable surface reconstructions. Our STM study also shows that the deposited Si does not grow in a layer-by-layer growth mode on top of the surface As layer but that the initial stages of Si growth on GaAs are more complex. Most probable the Si performs an exchange reaction and directly moves into the second layer which is a Ga layer. A diffusion of the Si further into the bulk can also not be excluded. A direct observation of the Si at such low coverages with the STM is difficult and the chemical contrast of Si in a Ga layer not known so far. Besides the nonpolarity requirement, other mechanisms have to be taken into consideration. It is known that the surface reconstruction is sensitive to surface strain which may be applied by surface alloying. Surface strain plays a substantial role, for example, in the (7×7) reconstruction of the clean Si(111) surface. From the RHEED observations of the appearance of a Ge-induced (5×5) structure it has been concluded that a large strain is accommodated in the surface due to the dissolution of Ge atoms.[13] Calculations of structural energies have shown that 0.5% compression (expansion) can induce this transition.[14] Using recently published data on lattice constants for $(GaAs)_{1-x}(Si)_x$ metastable alloys[15] one finds for a Si concentration of $x=0.1$ a compression of 0.4%. Therefore, the structural changes observed in the present work for Si coverages of 0.05–0.15 ML Si on GaAs(001) might be explained also by surface strain effects. The problem of the Si-doped GaAs surface is, however, more complex than the Ge alloyed Si surface since a variable surface stoichiometry has to be taken into account.

In conclusion, we have studied the change of the surface reconstruction phase diagram induced by Si deposition with RHEED and STM. At Si concentrations above 3×10^{13} cm^{-2} a new (3×2) Ga-terminated surface reconstruction can be observed at temperatures above 615 °C that does not exist on the initial GaAs surface. For higher Si concentrations and/or substrate temperatures the reconstruction transforms via a (5×2) to a (4×2) reconstruction subsequently increasing the Ga coverage. Two mechanisms are considered to be important for the explanation of the experimental results. The Si doping provides electrons resulting in surface reconstructions that would be electron deficient and unstable on the undoped material. On the other hand, the incorporated Si concentration leads to changes in surface strain which can also drive a phase transition. The present study also shows that the initial stages of Si growth on GaAs are more complex than a simple layer-by-layer growth.

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[10] Different to the As-terminated reconstructions, filled states cannot only be found in the first layer dimer rows (the Ga dimer bonds) but also in the missing dimer rows (the As dangling bonds in the second layer), thus giving rise to a tunneling channel into this layer. As a result the contrast between dimer and missing dimer rows is reduced. Also, filled and empty state images should look the same at this resolution similar to the As-terminated reconstruction (Ref. 4). Only when the single dangling-bond states can be resolved are the images expected to differ.

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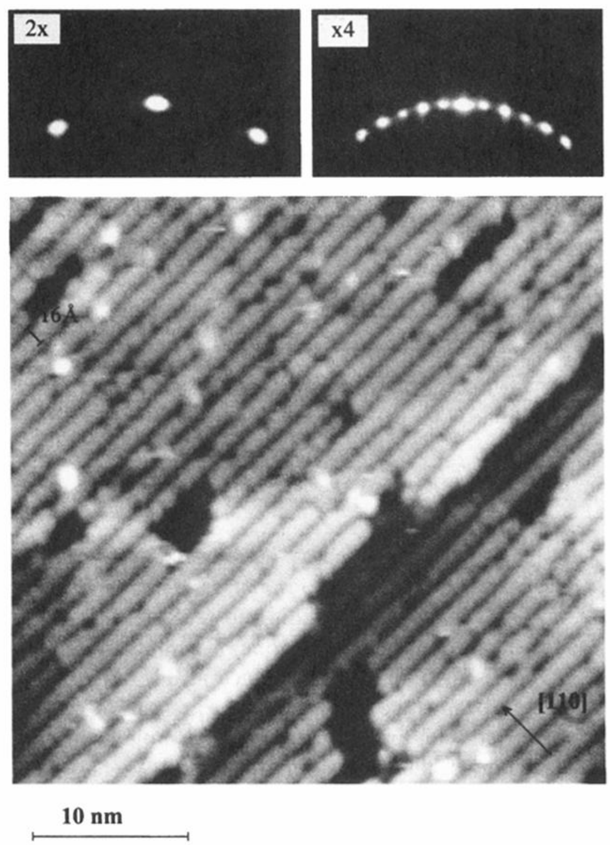
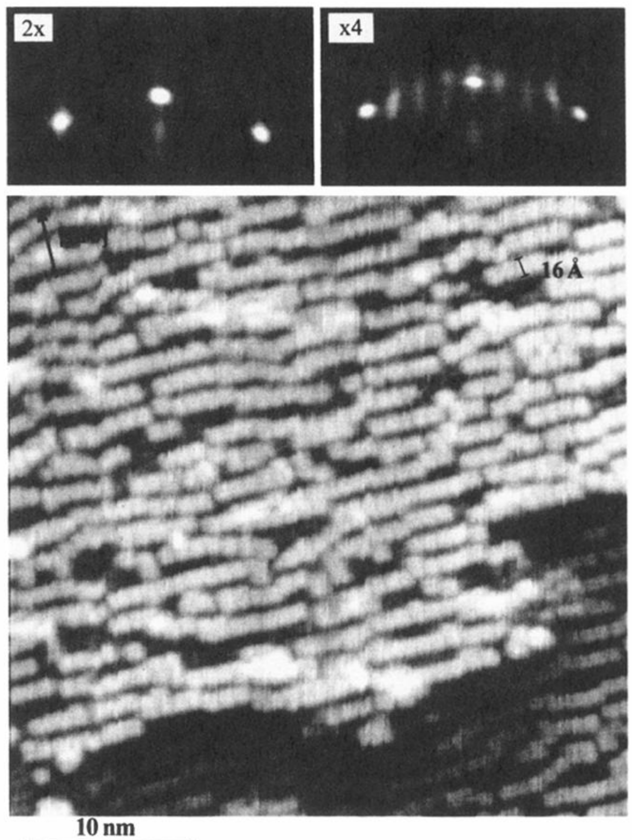


FIG. 1. STM image and RHEED pattern of the (2×4) surface reconstruction of the low-doped GaAs(001) surface. Straight missing dimer rows are formed containing two As dimers and two missing As dimers per unit cell.



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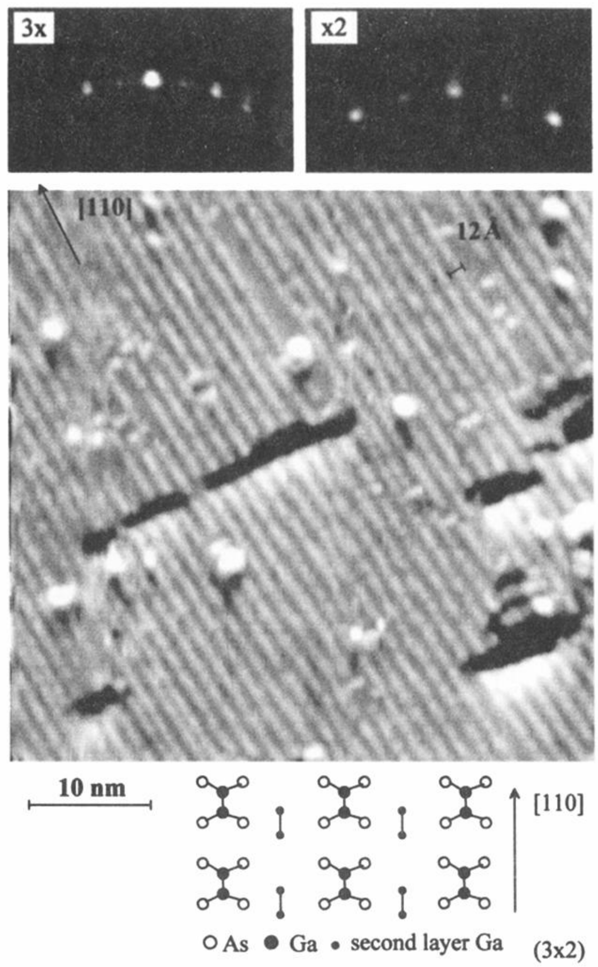

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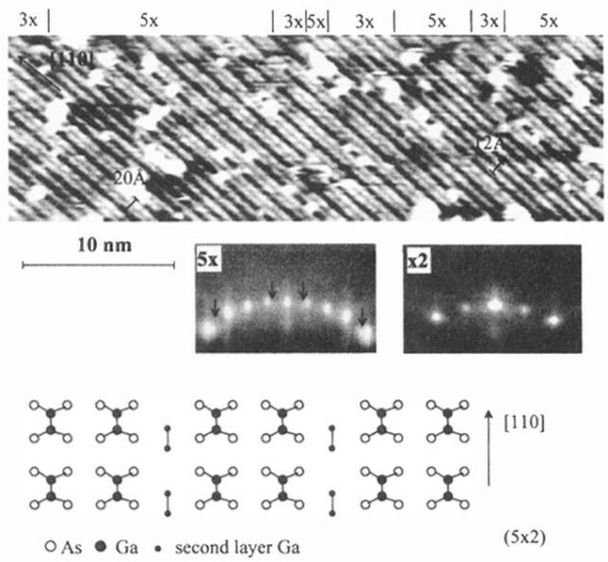

FIG. 4. STM image and RHEED pattern of the $(3\times2)+(5\times2)$ surface reconstruction of the Si-deposited GaAs(001) surface. The Si deposition is 9×11^{13} cm^{-2}. Satellite spots in the RHEED pattern close to the third-order diffraction spot evidence the existence of domains with fivefold periodicity observed in the STM image. The ball and stick model shows the proposed atomic structure for the (5×2) unit cell being formed of first- and second-layer Ga dimer rows.