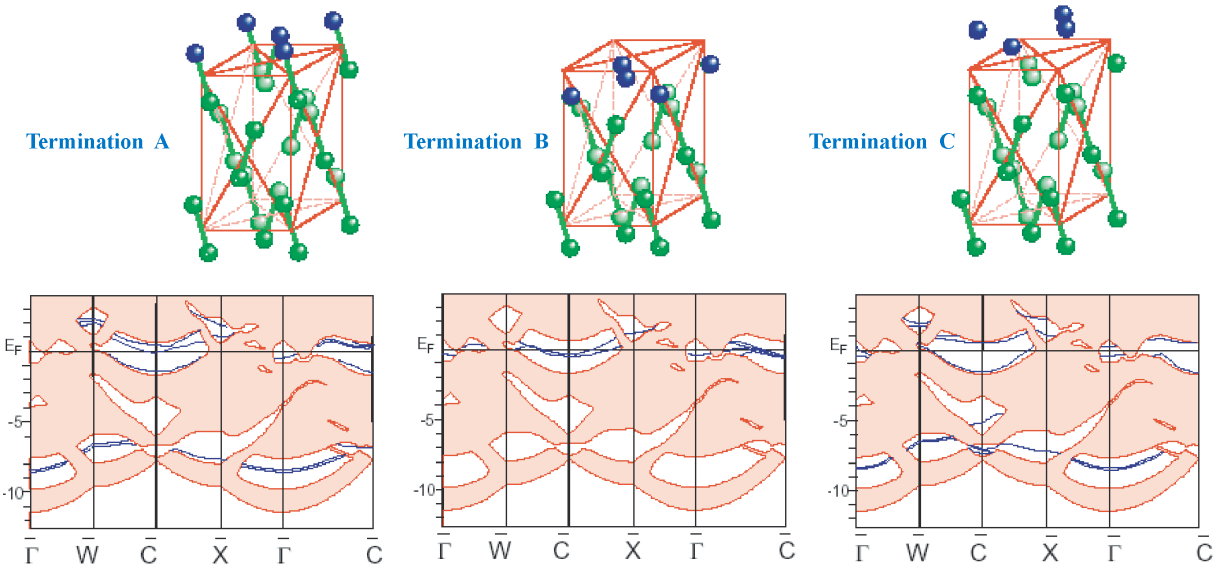



*Fig. 9*

*Three possible terminations of* $\alpha - Ga$ *together with results from DFT calculations [7].*

Two truncated bulk structures are possible for the $\alpha - Ga$ (010) surface, one with the dimers intact (Termination A) and one with the dimers broken or cut (Termination B), creating the surface with dangling bonds. In addition to these a third termination (Termination C) has been predicted by Bernasconi et al [7] described as a (1x1) reconstruction which can be thought of as two layers of GaIII, covering the (010) surface of $\alpha - Ga$. For all three terminations every odd-integer spot towards [100] direction is missing at the LEED pattern in normal incidence, because of the glide plane symmetry of bulk $\alpha - Ga$ which is preserved in the surface structure. Calculations show that the topmost layer appears identical in STM measurements for all three cases, therefore this method is not suited to distinguish between the terminations [6]. Recent x-ray [8] and quantitative LEED I-V investigations of the $\alpha - Ga$ surface show that the structure is the Termination B. In *Fig.9* the three possible terminations of the $\alpha - Ga$ (010) surface are shown together with results from DFT calculations [7].

***Preparation of the sample***

The preparation of the $\alpha - Ga$ (010) surface is not straight forward and depends critically on several factors. One needs to take into account the sputtering energy and current, chamber pressure from the sputter gas, sample temperature, speed of the cooling to liquid helium temperature in LT STM measurements and the residual background pressure during and after

preparation. The surface was usually cleaned by 30 minutes sputtering with Ne gas with an energy of 0.7 – 1.3 keV at temperatures in the interval from 273 K up to room temperature, followed by healing cycles of 30 - 60 minutes before and after sputtering in the same temperature interval. The speed of cooling to liquid helium temperature was varied from 5 minutes up to 45 minutes.

Although an ideal surface preparation was not achieved, the dependence of the surface appearance on the preparation conditions shall be exemplified. The He atom scattering and LEED results were taken prior to the STM measurements and suggest a better surface quality, possibly due to different UHV conditions or a sample polishing procedure taken place after the He scattering experiment (see HAS experiment chapter). It follows an illustration of the surface appearance after different preparation procedures and imaged with low temperature STM:

1. In the first example of the preparation procedure the Ga(010) sample was annealed for approximately 1 hour at room temperature, then sputtered with Ne gas at 1.3 keV for 30 minutes at room temperature and then again healed for 20 minutes at room temperature. After preparation the sample was quickly cooled to liquid helium temperature (about 5 minutes). The result of such a preparation is shown in *Fig.10*.

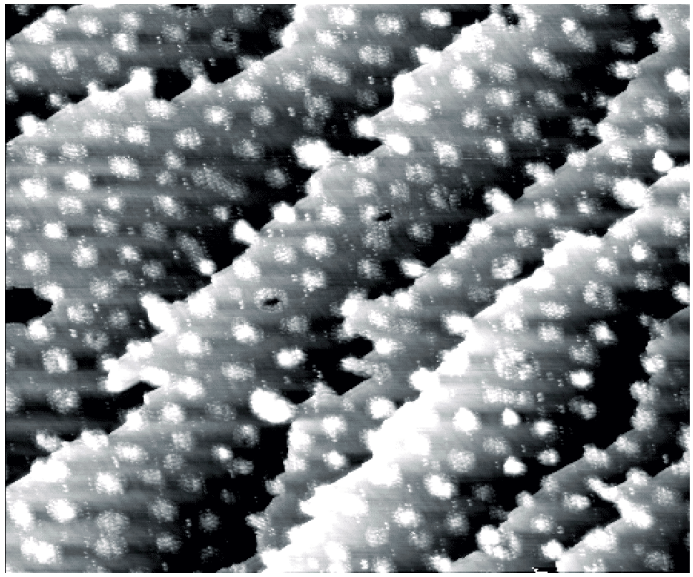


*Fig.10*

*Example 1: (420 x 420) nm Ga(010) image (1nA, -220 mV, 5K). One can see flat terraces covered with small islands separated by steps.*

The surface is covered with amorphous islands of approximately (15 x 15) nm size. A powerspectrum taken on such islands does not show ordering. Three different sources shall be discussed here: (1) These islands are adsorbate islands which form because the low temperature phase of Ga is easily contaminated, so the islands consist of adsorbates from the residual gas pressure. (2) During rapid cooling from room temperature to liquid He temperature, and during occurring phase transition, a mass transport takes place and because of the low temperature and limited time interval not all of the Ga atoms were in time to find their new place on the surface. (3) During sputtering and annealing cycles at room temperature the Ga bulk started to melt (the surface of Ga melts after the bulk) and these islands are molten Ga from the bulk which went onto the sample surface [9]. Together with the following examples it will become clear which one of the proposed explanations is most likely. The area in between the islands can be resolved atomically (*Fig.12*) and consists of two types of stripe-like domains (see topography section).

2. In example 2 the surface was prepared by first annealing for 30 minutes around 273 K then sputtered with Ne gas at 0.7 keV for 30 minutes at the same temperature and finally annealed for 10 minutes around 285 K. After the preparation, the sample was rapidly (in 5 minutes) cooled to liquid helium temperature. Here the surface became much more rough. The amorphous islands grew in size, formed stripes running in the [010] direction and were covering almost 50% of the surface. In *Fig.11* one can see the result of such a preparation.

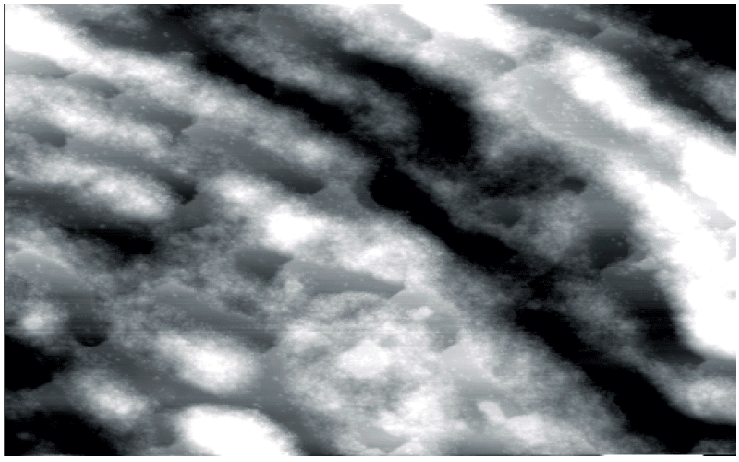


*Fig.11*

*Example 2: (420 x 250) nm image of the Ga surface at 5K.*

On the terraces the surface is again well ordered and can be reproducibly atomically resolved showing the same as in example 1 the two stripe-like domain structure.

Comparing the result of example 1 (at 300 K) and example 2 (at 273 K) it becomes clear that the amorphous islands and stripes cannot be caused by the melting of the Ga bulk because example 2 was prepared at temperatures far away from the Ga melting temperature. So the two remaining explanations for the presence of islands and stripes are fast contamination of the low temperature Ga phase and rapid cooling of the sample to liquid helium temperature.

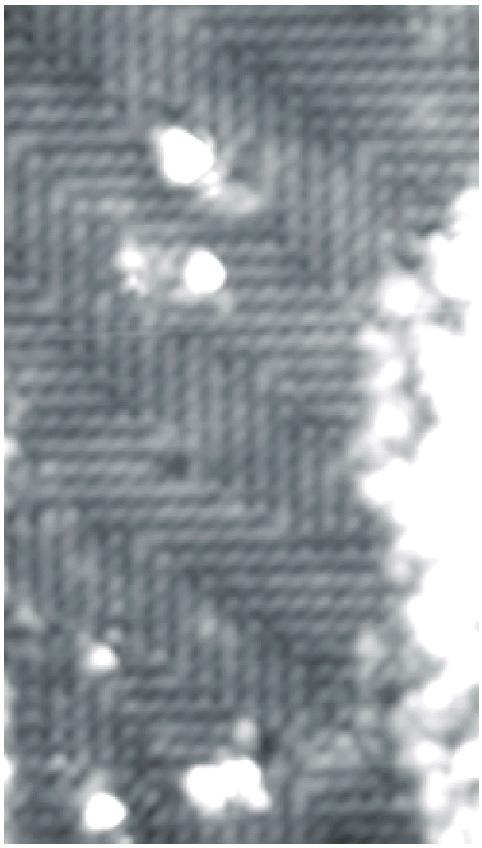


*Fig.12*
*Routinely obtained atomically resolved (20x40) nm image showing two stripe-like domains (5 K).*

3. In example 3 the Ga sample was first annealed for 45 minutes at 273 K, then sputtered with Ne gas at 1 keV for 30 minutes at the same temperature and finally again annealed for 30 minutes at 273 K. After the preparation the sample was slowly cooled to liquid He temperature. The cooling of the sample took about 45 minutes which is much slower than in the preceding examples. After the preparation again amorphous stripes have formed on the surface, this time narrower than in example 2. Consequently the terraces are broader. To conclude it appears that the cooling time has no major influence on the surface quality.

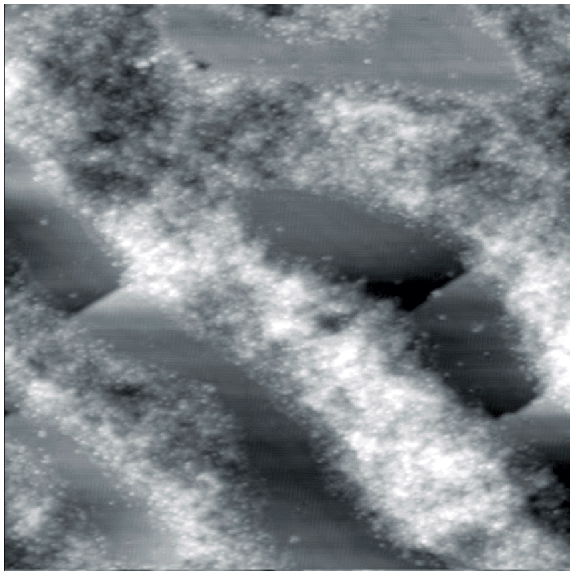
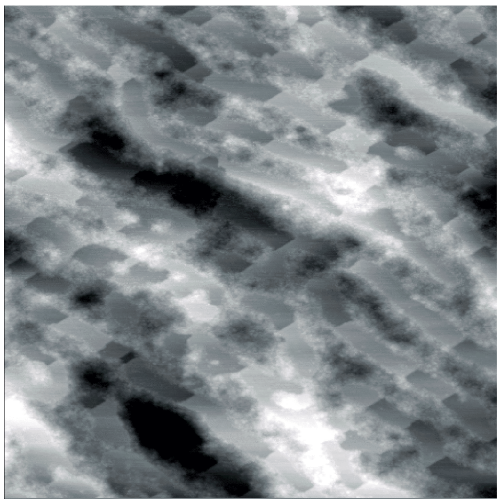


*Fig.13*
*Example 3: (125 x 125) nm image of the Ga surface (5 K).*

It is also possible that the stripes are the result of the surface roughening during the sputtering e.g. a strong dependence on the sputtering energy and current.

4. In example 4 the result of the preparation process with a lower sputtering energy of 0.7 keV is shown (*Fig.14*). The ordered terraces and stripes of the amorphous material are getting more narrow, but the atomic or molecular resolved images again show two stripe-like domains after this preparation (*Fig.15*).



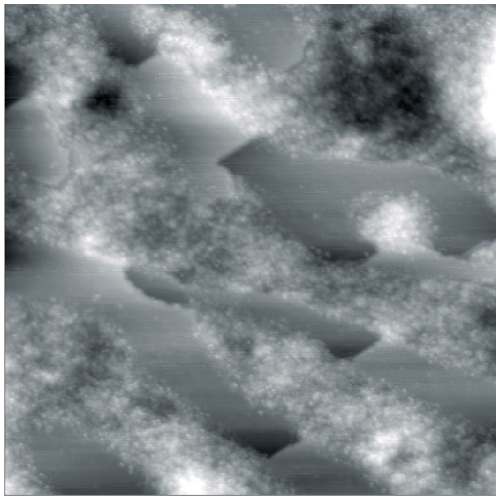


*Fig.14*

*Example 4: The result of the preparation process with a lower sputtering energy (0.7 keV). Left: (420x420) nm image. Right: (126x126) nm image. Images are taken at 5K.*

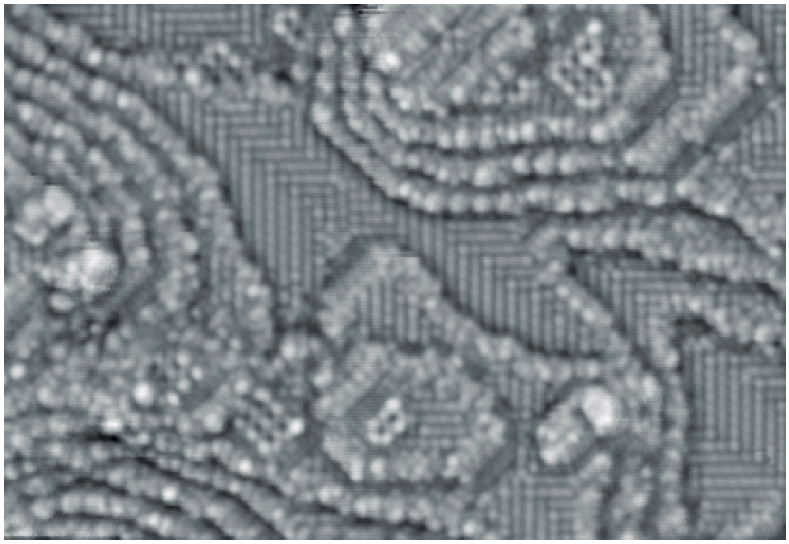


*Fig.15*

*The atomic or molecular resolution of two stripe-like domains is still present after the preparation with a low sputtering energy even in a more uncommon area. This (60x40) nm image is high-pass filtered which made possible to view all terraces in the same time.*

In conclusion, an ideal surface preparation was not achieved. About 40 preparations showed essentially varying amounts of ordered surface areas. Thereby the disordered areas can form islands or stripe-like structures. By exchanging frequently the sputtering gas and working at best possible UHV conditions (background pressure < $3x10^{-10}$ mbar) a contamination from residual gas can be excluded. Therefore the disordered areas most likely consist of Ga atoms, dimers or small clusters. An improvement of the surface quality by annealing is here not possible since (1) the preparation was already done close to the melting point and (2) a surface diffusion as indicated by step diffusion is not present at the used temperatures (see section RT STM measurements). Results from the room temperature measurements show a similar surface appearance. Therefore the disordered areas do not originate from the phase

transition. The most important result is that the same surface appearance of the ordered terraces in all preparations which therefore is considered as the true surface appearance.

***Topography***

Another crucial difficulty in the STM measurements on the $\alpha - Ga$ (010) surface was the condition of the tip. In the experiment a PtIr tip was used, although due to contact of the tip with the surface the chemical and structural constitution of the tip apex is not known. As in the case of metal surfaces the tip formation by gently touching the surface to achieve a stable and sharp tip is not possible on the Ga surface. In case of a very rough surface it was not even possible to take STM images at all. But in the present case it was possible to form the tip on a stainless steel part of the sample holder. The stability of the tip turned out to be closely related to the state of the Ga surface, e.g. roughness and cleanliness of the surface. In the four examples described before, the state of the tip is relatively stable in comparison with the performance of the same tip on the pure metal surface.

In *Fig.16* a typically obtained terrace of $\alpha - Ga$ (010) surface is shown together with the zoomed-in atomically (or molecularly) resolved image. In all these scans one can clearly see two stripe-like domain structures. These domains run in the [010] direction (*Fig.17*). The domain itself consists of alternating `bump` and `zigzag` rows. The angle between these rows in the neighbor domains is exactly 90°.

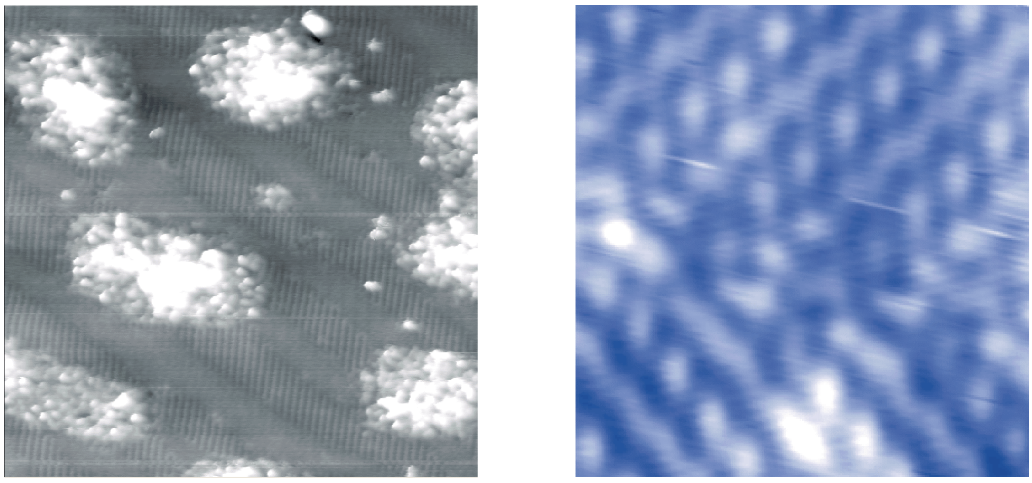


*Fig.16*

*Left: Typically obtained terrace of $\alpha - Ga$ (010) surface at 5K; (63x63) nm image.*
*Right: Alternate `bump` and `zigzag` rows forming the domain; (8x8) nm image.*

The comparison of `bump` and `zigzag` rows in neighboring domains show that they form an ordered anti-phase (*Fig17, left image*). The `bump` and `zigzag` rows of both domains run under the angles of +45° and -45° from the glide plane direction (*Fig.17, right image*). The wall between the domains consists of a single `bump` row and runs perpendicular to the glide plane direction. By zooming into the domain structure one can see that the `bumps` themselves in the both domains point in the direction of the glide plane. From this one can conclude that one domain cannot be obtained from another by a simple 90° rotation. After such a turn the `bumps` in the domains will point in the direction perpendicular to each other. One domain can be obtained from another by a 90° rotation and an additional reflection at a mirror plane in the [110] direction. In this sense the domains show chirality. The most commonly observed width of the domain stripes amounts to 18 unit cells. The stripes are highly ordered and are running parallel. Such a high degree of order can be found also on reconstructed metal surfaces. There the driving force is the tensile stress between the unit cells, which is released at the domain boundaries.

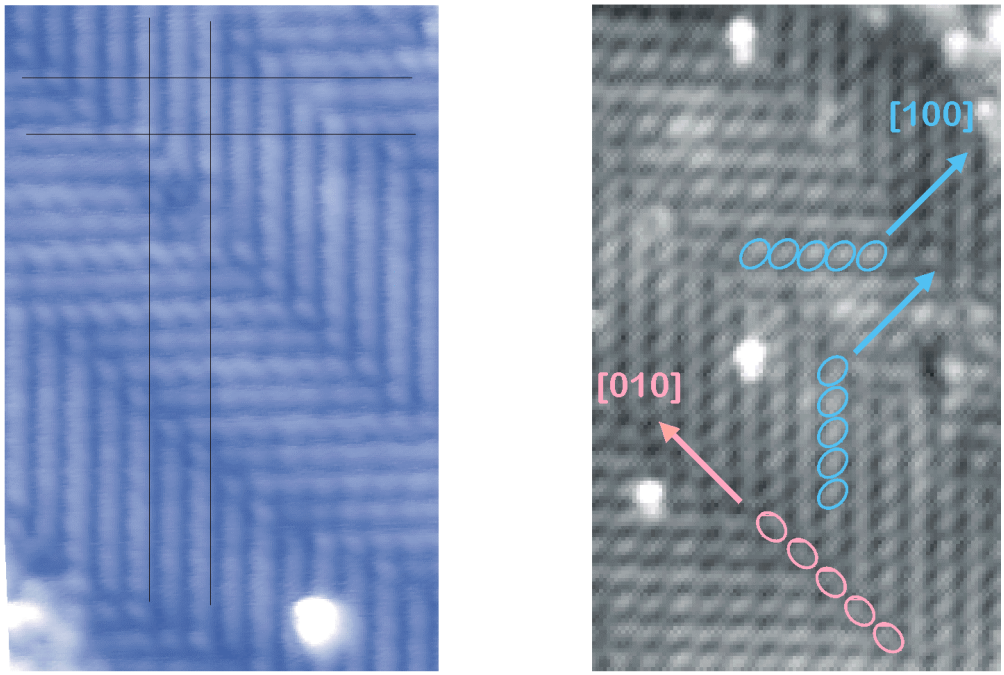



*Fig.17*

*Left: (12x20) nm image shows that the `bump` and `zigzag` rows in the neighbor domains order anti-phase.*
*Right: The `bumps` themselves in both domains point in the direction of the glide plane [100], `bumps` are marked with blue ellipses. The wall between the domains consists of a single `bump` row and runs in the [010] direction, `bumps` are marked with pink ellipses.*

In *Fig.18* one can see an image of the $\alpha - Ga$ surface containing terraces and steps. The steps always point in the direction of the glide plane. If not pinned on defects, domain walls run perpendicular to the step edges. There is no certain rule how the domains meet each other at the step edges. Phase, anti-phase and other intermediate variants have been observed.

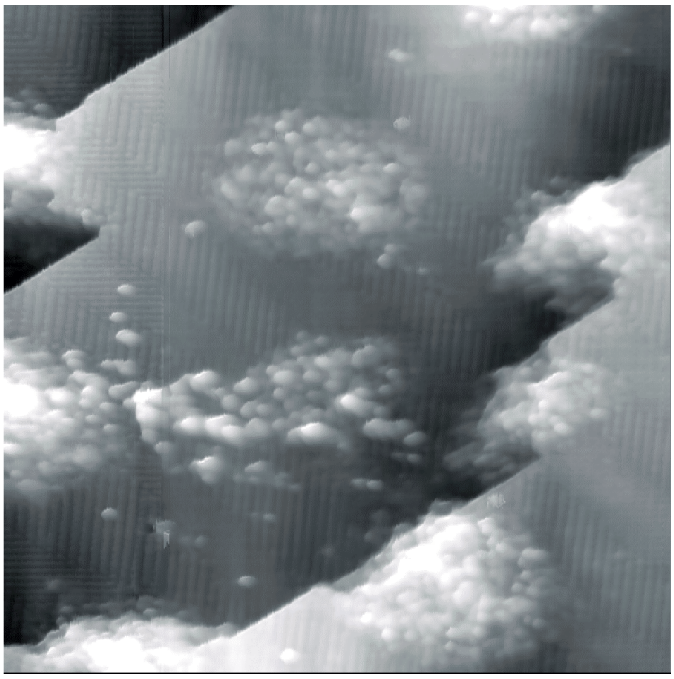


*Fig.18*
*$\alpha - Ga$ surface scan containing terraces and steps. The steps always point in the direction of the glide plane. (63x63) nm image*

In *Fig.19* one can see two examples showing the situation at the step. The left one shows anti-phase situation, the right one shows the in-phase situation. Both images consist of two parts put together: Each of these parts is plane subtracted to make the terrace completely visible.

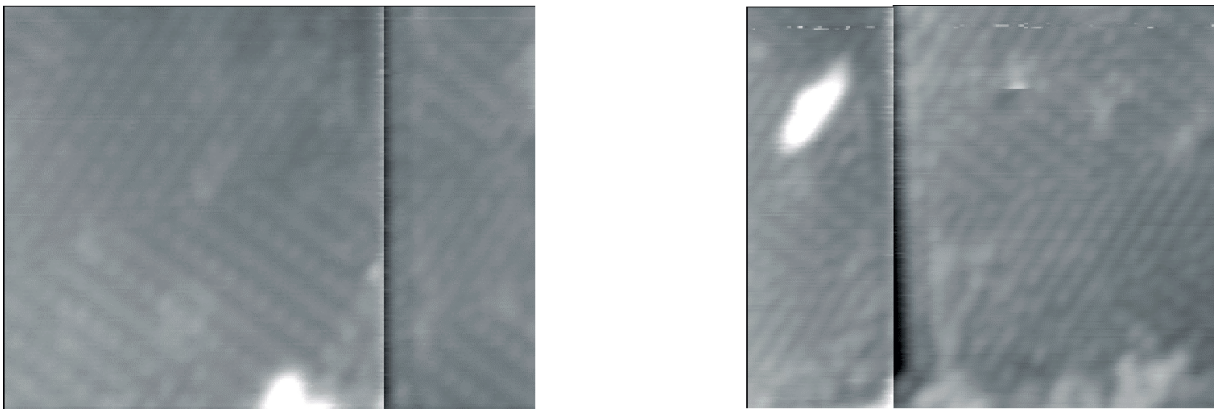


*Fig.19*

*The left image shows the anti-phase situation of the domains at the step edge, the right one shows the in- phase situation. (16x10) nm and (16x12) nm images correspondingly.*

The height of the steps is always 0.38 nm (*Fig.20*). No steps with a height of 0.19 nm were found in the low temperature phase of $\alpha - Ga$. This means that only one termination is possible on the surface: Either A or B or C, but not two or three terminations.

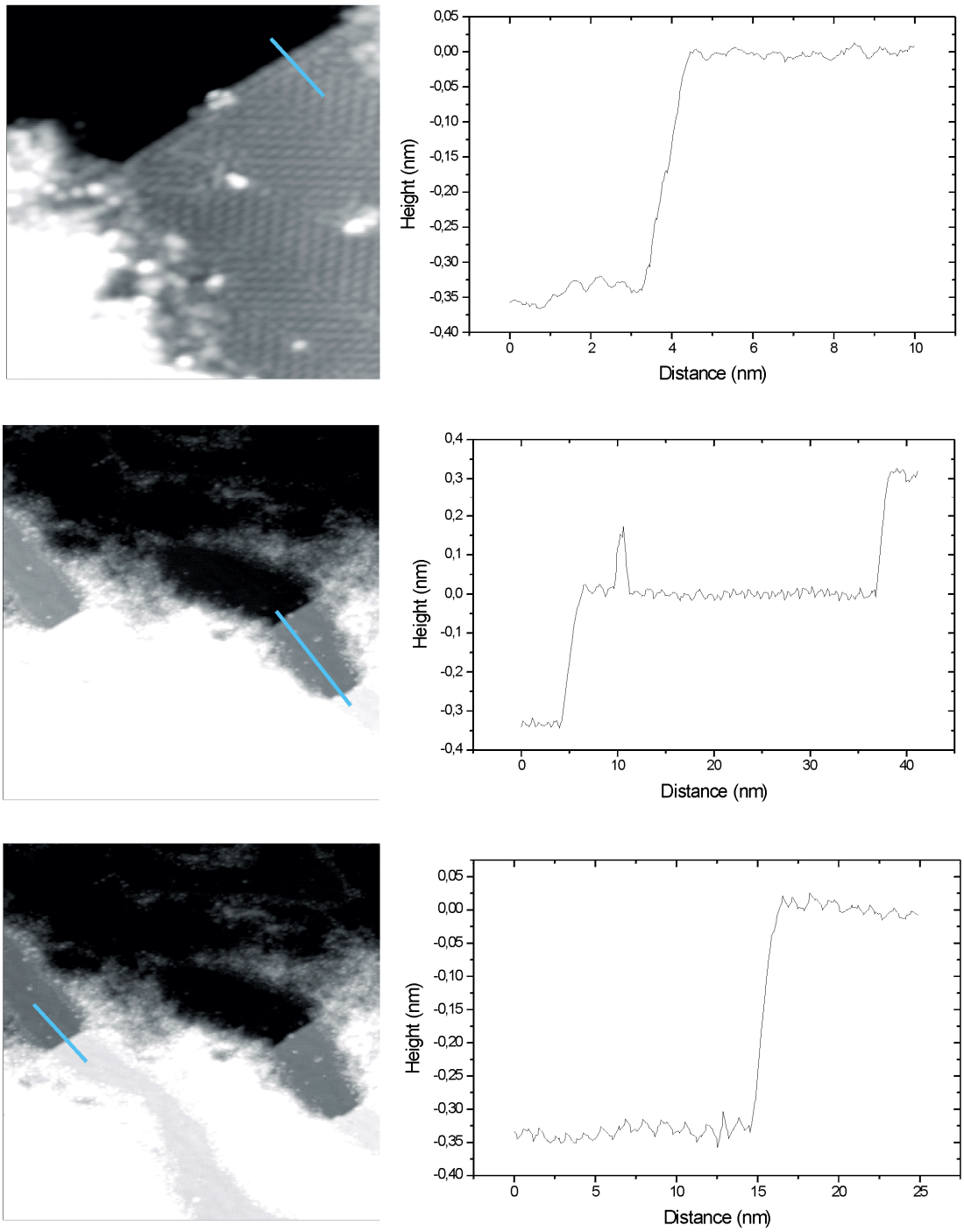



*Fig.20*

*The height of the steps is always 0.38 nm which corresponds to the Ga dimer layer distance in the bulk. The images show results of different surface preparations.*

***Structure model***

The surface structure of the room temperature phase is known from experiment and theory. Before the STM investigation in this work only one experiment [3] was done to clarify the low temperature phase structure which shall be reviewed here. The structural model shown here is a result exclusively of the analysis of LEED measurements. The long range periodicity of 18 unit cells (fractional point splitting) found in the SPA-LEED studies was not taken into account, e.g. the split of the $\left(\pm 1/2, \pm 1/2\right)$ spot was treated as a single spot.

The $\left(2\sqrt{2}x\sqrt{2}\right)R45°$ unit cell has 8 atoms per layer. Since the symmetry inside the unit cell is lost in this reconstruction, each atom in the unit cell was allowed to move independently in the x, y, and z direction. Therefore a LEED analysis allowing 3D displacements only in the topmost layer has 25 independent fit parameters (24 structural parameters and the real part of the inner potential). The structural analysis was carried out for several variants: For the first layer (24 structural parameters), for the first two layers (48 structural parameters), and for the first four layers (96 structural parameters). In each of these cases several different models were used as a starting point during the fitting procedure.

The result of the fit procedure of the I-V LEED curves to simulated curves for the low temperature structure is shown in *Fig.21*. This phase exhibits the same cut-dimer termination B as the room temperature structure but the atoms within the unit cell shift to new positions. The topmost atoms are black, the atoms in the layer below are dark grey, atoms in the third layer are light grey, and atoms in the fourth layer are white.

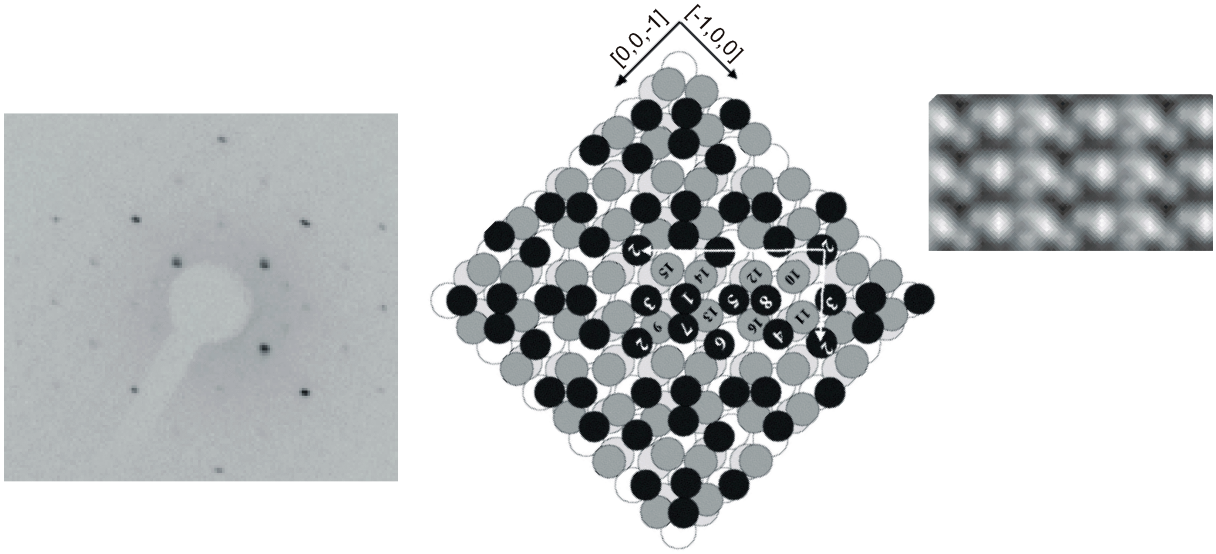



*Fig.21*

*Low temperature structure from the fitting procedure (middle) together with the corresponding LEED pattern (left) [3] and an STM image simulation for this model (right).*

In the low temperature structure the surface atoms shift to dimerize within the top two layers, resulting in a network of mostly covalent bonds, which form both parallel and perpendicular to the surface plane. The bond lengths of some of these dimers are about 10% shorter than the bond lengths found in the $\alpha - Ga$ bulk and are thus shorter than any $Ga - Ga$ bonds reported so far.

A comparison of this structure model with the STM measurements cannot be done directly with a structural model (see Section STM theory) but the sphere model already does not coincide with the STM measurements. A direct comparison with tight binding calculations cofirms this (see also section Calculations). Therefore a different structural model is proposed as an intuitive model made on the basis of the low temperature STM topography measurements. In *Fig.22* one can see two variants of the present structure model: One with 8 atoms per unit cell (middle) and another with 4 atoms per unit cell (right). Both of these models show more order than the model proposed in [3] in accordance with the measurements.

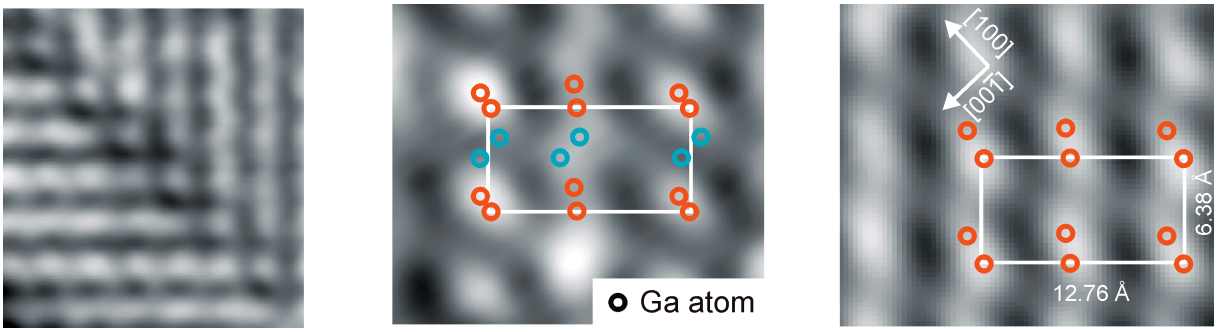



*Fig.22*

*Left: The surface (8x8) nm area from which both images for structural modeling are taken Middle and right: Unit cells for structural models with 8 and 4 atoms correspondingly. U=220 mV; tip has changed between the images.*

So one can conclude that both of these models are incompatible. This is due to neglegtance of the fractional spot splitting (long range periodicity found by SPA-LEED) in the structure model based exclusively on LEED. Additionally the existence of the boundaries between the domains was not taken into account, although these boundaries take about 10% of the whole surface area. The model proposed here was thoroughly improved with the help of calculations shown in the last section of this chapter.