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Surface Morphology of MBE-grown GaN on GaAs(001) as Function of the N/Ga-ratio

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Molecular beam epitaxy growth utilising an RF-plasma nitrogen source was used to study surface reconstruction and surface morphology of GaN on GaAs (001) at 580 °C. While both the nitrogen flow and plasma excitation power were constant, the grown layers were characterised as a function of Ga-flux. In the initial growth stage a (3x3) surface reconstruction was observed. This surface periodicity only lasted up to a maximum thickness of 2.5 ML, followed by a transition to the unreconstructed surface. Samples grown under N-rich, Ga-rich and stoichiometric conditions were characterised by high-resolution scanning electron microscopy and atomic force microscopy. We found that the smoothest surfaces were provided by the N/Ga-ratio giving the thickest layer at the (3x3)=>(1x1) transition. The defect formation at the GaN/GaAs interface also depended on the N/Ga-flux ratio.

1 Introduction

Gallium nitride is one of the most promising materials for optical applications in the blue range of the visible spectra due to its direct energy band gap of 3.39 eV at room temperature. The optical emission range of the GaN-based alloys can cover the whole visible range from near infrared to ultraviolet. Therefore much attention has been paid to these systems during the recent years. Heteroepitaxial layers, in the form of the thermodynamically stable hexagonal wurtzite crystal structure have mainly been grown by metal-organic vapor phase epitaxy (MOVPE) [1] [2]. The GaN can also be grown in the cubic (zinc blende) crystal structure [3], which is the usual form of other III-V compound semiconductors. However, the cubic nitrides are less stable than the hexagonal ones. The lack of a suitable lattice-matched substrate for high-temperature growth results in reduced GaN crystal quality. The most commonly used substrate is sapphire, where the lattice-mismatch is as large as 14%, and hexagonal GaN is obtained. The growth of the metastable cubic phase is unfavourable under equilibrium growth conditions such as MOVPE. The molecular beam epitaxy (MBE) technique provides the required nonequilibrium conditions at low growth temperatures. One advantage of MBE-growth on GaAs is the surface control given by reflection high-energy electron diffraction (RHEED) [3] and the know-how of cubic substrates. The cubic GaAs and Si substrates have a large lattice-mismatch.

The detailed conditions for MBE growth of layers with good structural quality are still not well known [4] [5]. A near-stoichiometric growth [5], or even slightly Ga-rich conditions [6] have been found to be important since the surface reconstruction of GaN on GaAs (001) depended on the N/Ga-ratio [7] [8] [9] [10]. When switching from N-rich to Ga-rich conditions, the surface ordering changed from (1x1) to c(2x2) via a (2x2)-reconstruction [8] [9] [10].

Due to the difference in lattice constant between GaAs and GaN, and the reactivity of the active nitrogen, the initial uncovered GaAs surface is expected to be sensitive to the initial deposition processs. When the ordered GaAs-surface was exposed to a nitrogen plasma, a reconstruction change occurred during the initial nitridation step [8] [11] [12] [13]. A transition from the initial GaAs (2x4) structure to a nitrogen induced (3x3)-pattern took place almost immediately [13], as observed by RHEED. This reconstruction has been confirmed by scanning tunnelling microscopy (STM) [11] and was interpreted as a replacement of As with N, giving a single phase of N dimers [11] [13] with regular arrays of missing N atomic rows both in $[\bar{1}10]$ and [110] directions [11] [12]. A further nitridation (exceeding 5 seconds) resulted in diffraction spots [11], which was explained by the formation of a complete GaN-layer covering the surface.

In this work we studied the surface morphology of thick GaN on GaAs(001) due to variation of V/III-flux ratio (by changing the Ga-flux) and keeping both the RF-power and the substrate temperature constant. The transition in surface reconstruction of thin layers (MLs) was used as an effective tool to predict optimum growth conditions. The surfaces were characterised by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

2 Experimental

The layers were grown with a turbopumped, solid Ga-source Varian GEN II Modular system on indium-free mounted semiinsulating GaAs substrates. The active nitrogen was provided by a liquid nitrogen cooled Oxford Applied Research CARS25 RF-activated plasma source. The nitrogen source was purified N_2 that was boiled off from liquid nitrogen. The growth temperature was kept constant at 580 °C for each layers, and substrates were semiinsulating GaAs(001). The Ga-flux was calibrated by GaAs RHEED-oscillations, converted to the cubic GaN(001) growth rate. The N/Ga-flux ratio was varied by changing the well controlled Ga-flux. An RF-power of 200 W and nitrogen flow of 0.3 sccm were used. The nitrogen plasma was ignited and adjusted with closed nitrogen shutter.

High-resolution secondary electron (SE) images were taken by a JEOL JSM-6301F scanning electron microscope for the characterisation of the surface morphology. The quantification of the surface roughness was made by atomic force microscopy.

3 Results and discussion

In Figure 1 the relation between the GaN thickness for the (2x4) and (3x3) surface reconstructions and their transitions, (2x4=>3x3) and (3x3=>1x1) are shown as a function of the GaN-growth rate (in the unit of relaxed cubic GaN). After the annihilation of the (3x3)-reconstruction, an unreconstructed (1x1)-pattern with dim and broad lines was observed. The GaN-thickness at this transition varied with the Ga-flux (growth rate) at a constant nitrogen supply (200 W RF-power, 0.30 sccm flow). In order to investigate the surface morphology after the termination of the 1x1-layer, three samples were grown with different growth rates (N/Ga-ratios, by varying the Ga-flux), 0.025, 0.1 and 0.6 ML/s, representing nitrogen-rich, near-stoichiometric and Ga-rich conditions, respectively. The near-stoichiometric conditions were predicted to occur at growth rates close to the peak region of the surface reconstruction transition diagram, illustrated in Figure 1. Detailed description of the RHEED investigation can be found elsewhere [14].

The samples grown at N-rich condition showed a typical formation of trenches as illustrated by the SEM image in Figure 2a. At strongly N-rich conditions the layers included a high density of trenches, as seen in Figure 2b, and the GaN could be removed by simple peel-off from the substrate. Both the trenches in the layer and the remaining hollows in the substrate surface showed same density. As a contrast, the GaN surface between the trenches was smooth. The substrate surface displayed not only the hollows but also nano-crystallites, shown in Figure 2c, appearing as bright features around the hollows. The backside of the peeled-off GaN layer had homogeneously distributed crystallites, originating from the substrate, seen in Figure 2d. These features had random hexagonal shape, and were bordered by low-index crystallographic planes with smooth surface. While the backside of the GaN layer was smooth between the crystallites, the corresponding substrate region showed polycrystalline structure, as shown by the high-resolution SEM images of Figure 2c and Figure 2d. We assume, that these features emerge from a nitrogen-radical damaged region of the substrate, revealed after the layer peel-off.

By strongly increasing the growth rate by the Ga-flux over the predicted optimum up to 0.6 ML/s, Ga-rich layers were deposited. The excess Ga accumulated in the form of droplets, shown as bright rounded features in the high-resolution SEM image in Figure 3a. The droplets were always formed on top of trenches and most of them were covered. There was an average droplet size of ~1.5 µm, while the trenches had different sizes, between ~1 µm and ~2 µm. The regions between the features were smooth. Etching in hydrochloric acid (50°C, 5 min) removed the droplets, as shown in Figure 3b, confirming the presence of Ga. Moreover, nanocrystallites became observable on the walls and edges of those trenches, where Ga-droplets have been removed. Thus the Ga-droplet covered areas had worse surface morphology compared to the smooth region between the features.

From the RHEED study, the growth rate of 0.1 ML/s in Figure 1 was predicted to be at near-stoichiometric conditions. The resulting surface morphology on a 400 nm thick layer is shown by the high-resolution SEM image in Figure 4a. The surface was smooth with neither droplets nor trenches on the surface. The estimated surface roughness was ~20 nm, as determined by nanocrystalline grains. After peeling off part of a layer, the columnar structure of small grains is clearly seen in the high-resolution cross-section image in Figure 4b. The surface part of the substrate shows no indication of hollows or the presence of polycrystalline structure. For the exact determination of the surface roughness, AFM characterisation has been made on a 1 μm^2 area, illustrated in Figure 5. The AFM investigation confirmed the good surface roughness of ~20 nm or better, in agreement with the high-resolution SEM.

Previous investigations suggested that the hollow formation at the interfaces was due to arsenic desorption caused by high growth temperatures [5]. In our investigations we used a low substrate temperature, and except for the Ga-flux, we kept all other parameters fixed. We observed by high-resolution SEM that a smooth GaN/GaAs interface can be formed without a formation of hollows and polycrystalline structure, while the GaN surface morphology is determined by the size of nanocrystalline grains, without formation of trenches and Ga-droplets. The optimum Ga-flux can easily be obtained from reconstruction transition diagrams. The maximum growth rate thus obtained was ~0.3 μm. Our observations correspond to the TEM cross-sectional investigations on similarly grown structures by Ruvimov *et al*. [15].

4 Conclusion

The (3x3) RHEED reconstruction and its transition to (1x1) was studied during the initial GaN MBE growth on a GaAs substrate. All growth parameters were fixed, while the Ga-flux was changed to find optimum growth conditions. It was found that the critical thickness for the (3x3=>1x1) reconstruction change depended on the N/Ga-flux ratio and was correlated to the stoichiometric growth. Using this reconstruction transition diagram, samples grown under Ga-rich, near-stoichiometric and N-rich conditions were studied. High-resolution SEM characterisation revealed extensive defect formation both on the substrate surface and the layer surface for N-rich or Ga-rich conditions, respectively. At optimum growth conditions smooth GaN/GaAs interface and surface roughness of ~20 nm was obtained, as detected by SEM and AFM.

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FIGURES

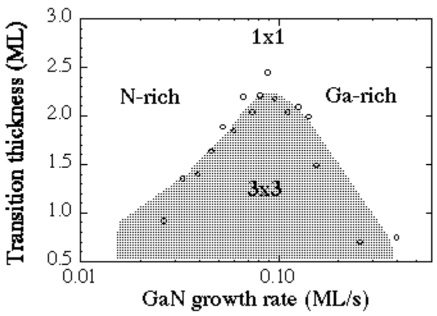

Figure 1. Surface reconstruction and transitions between different ordering with GaN thickness and growth rate as parameters. The growth was initiated on GaAs (001)-2x4. The maximum thickness for the transition indicates the border between nitrogen and gallium rich growth.

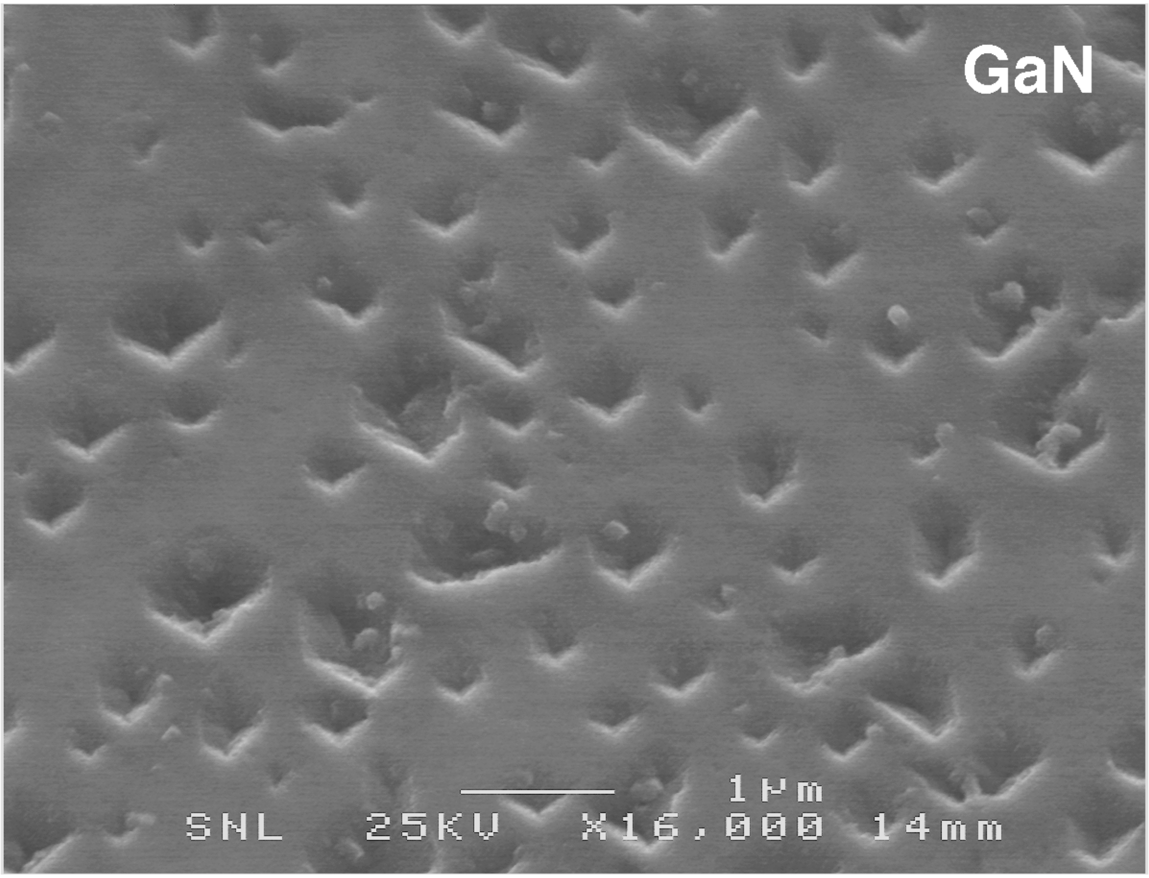

Figure 2a. High-resolution SEM image of a GaN layer grown at N-rich conditions. Trenches can be seen on the surface, however, the area in between is smooth.

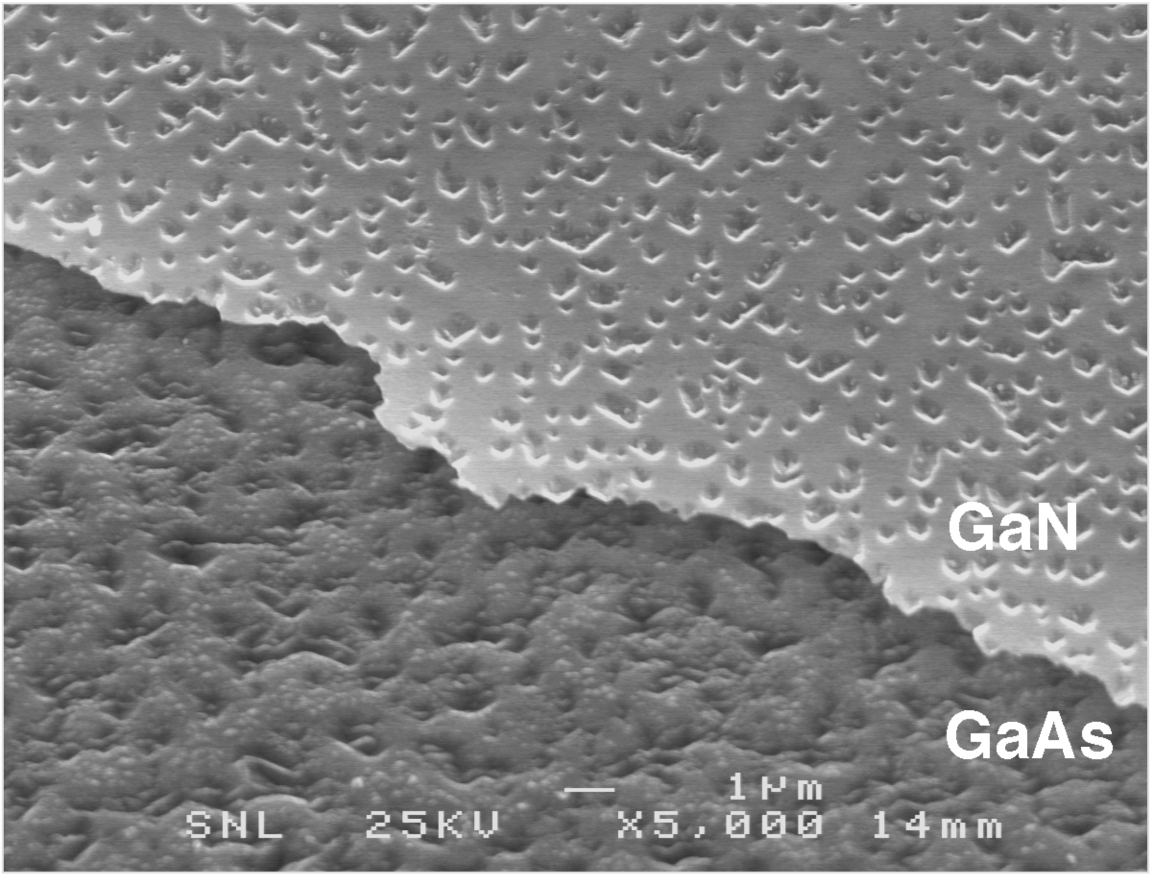

Figure 2b. High-resolution SEM image of a GaN layer grown at N-rich conditions. Both the layer surface and the GaAs substrate are shown, where part of the layer has been peeled off.

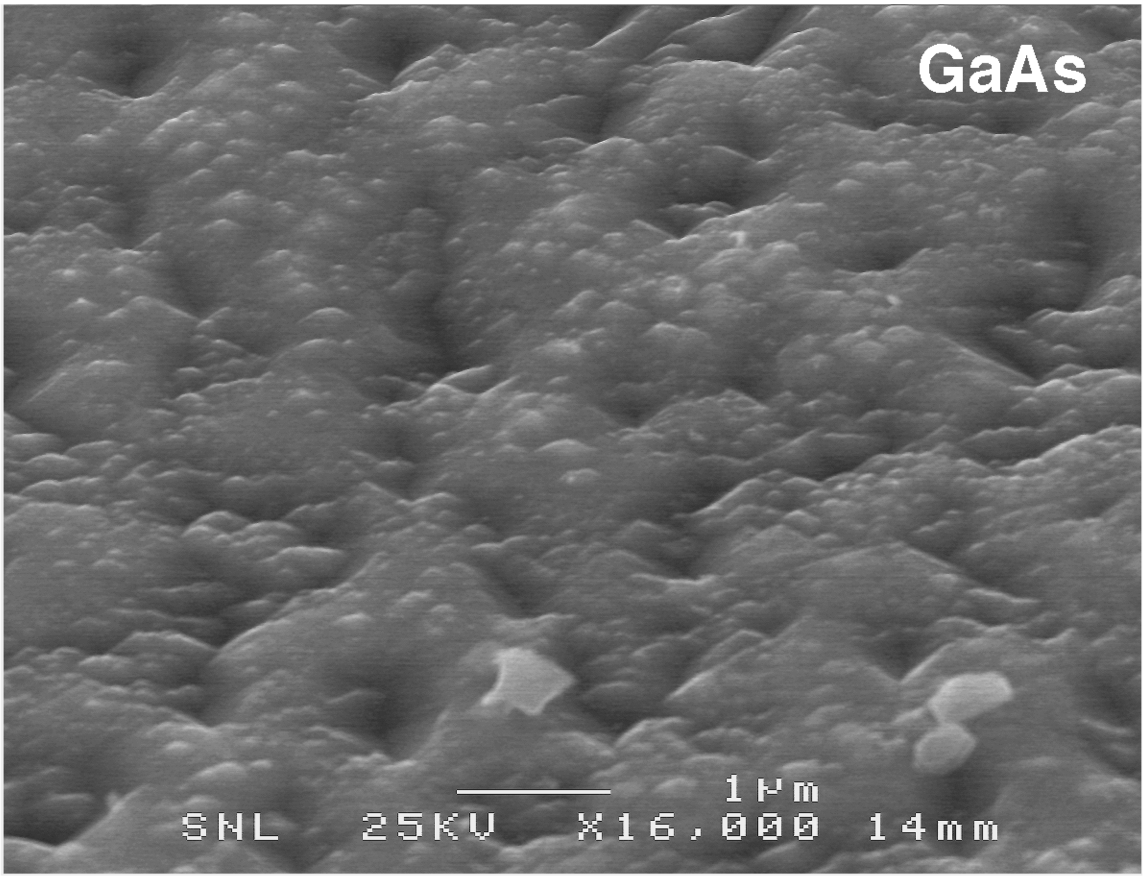

Figure 2c. High-resolution SEM image of a GaN sample grown at N-rich conditions. The surface of the GaAs substrate is shown, revealing polycrystalline structure with hollows, where the GaN layer has been peeled off.

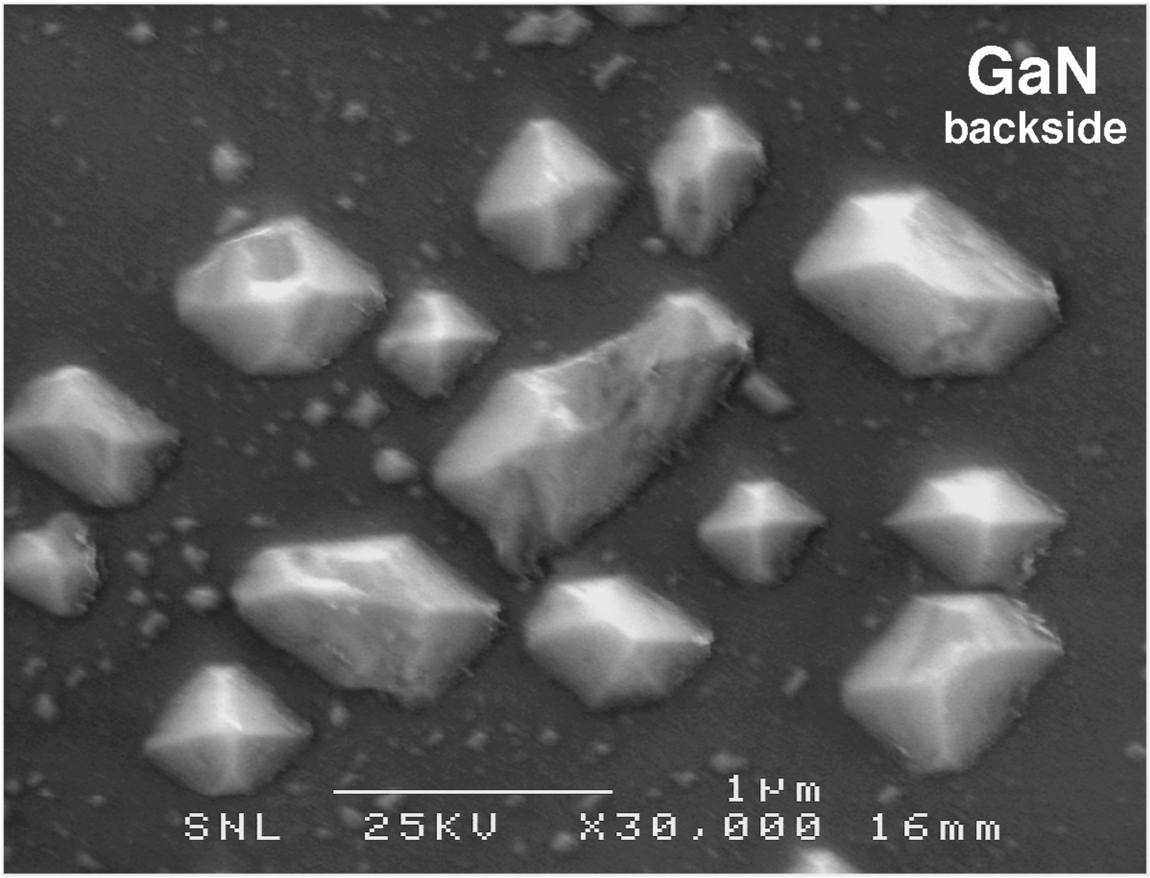

Figure 2d. High-resolution SEM image of a GaN layer grown at N-rich conditions. The smooth backside of the peeled-off GaN layer is shown, revealing homogeneously distributed and randomly shaped hexagonal crystallites, originating from the GaAs substrate.

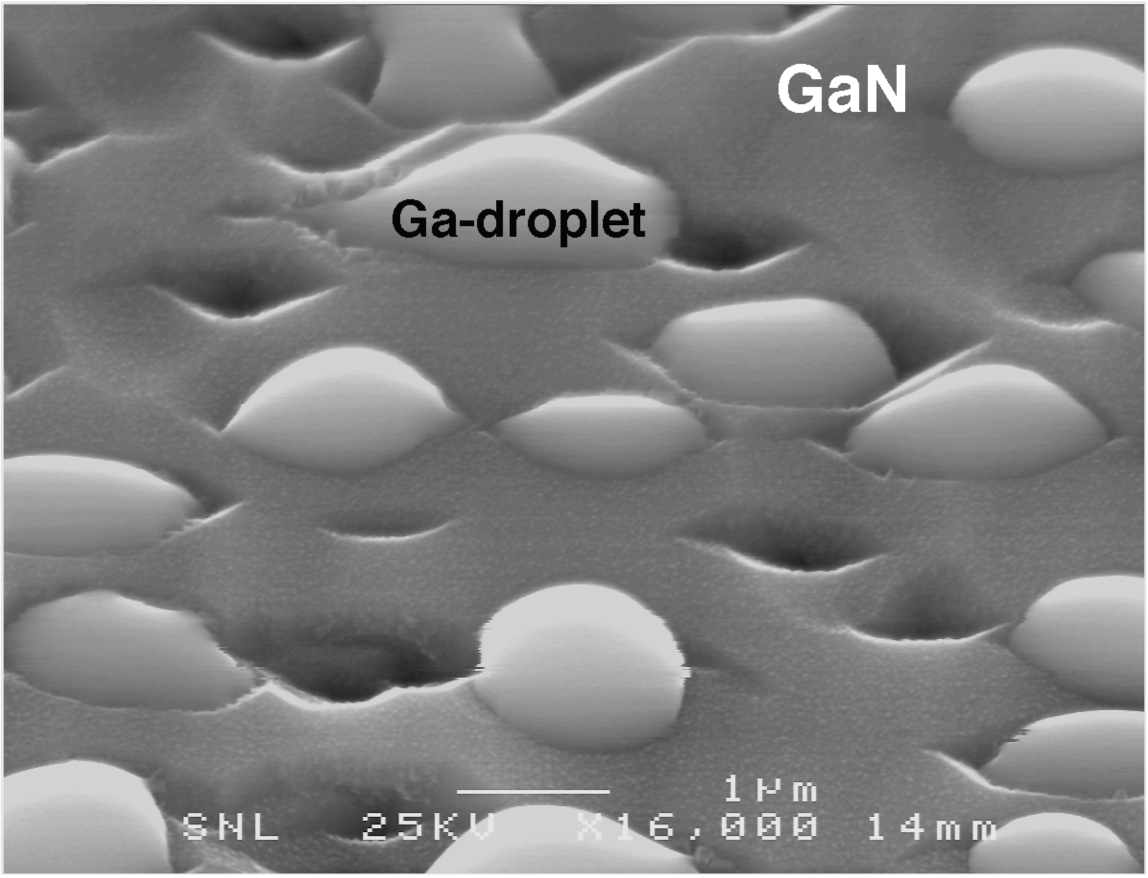

Figure 3a. High-resolution SEM image of a GaN layer grown under Ga-rich conditions. The excess Ga has formed droplets which are trapped in trenches.

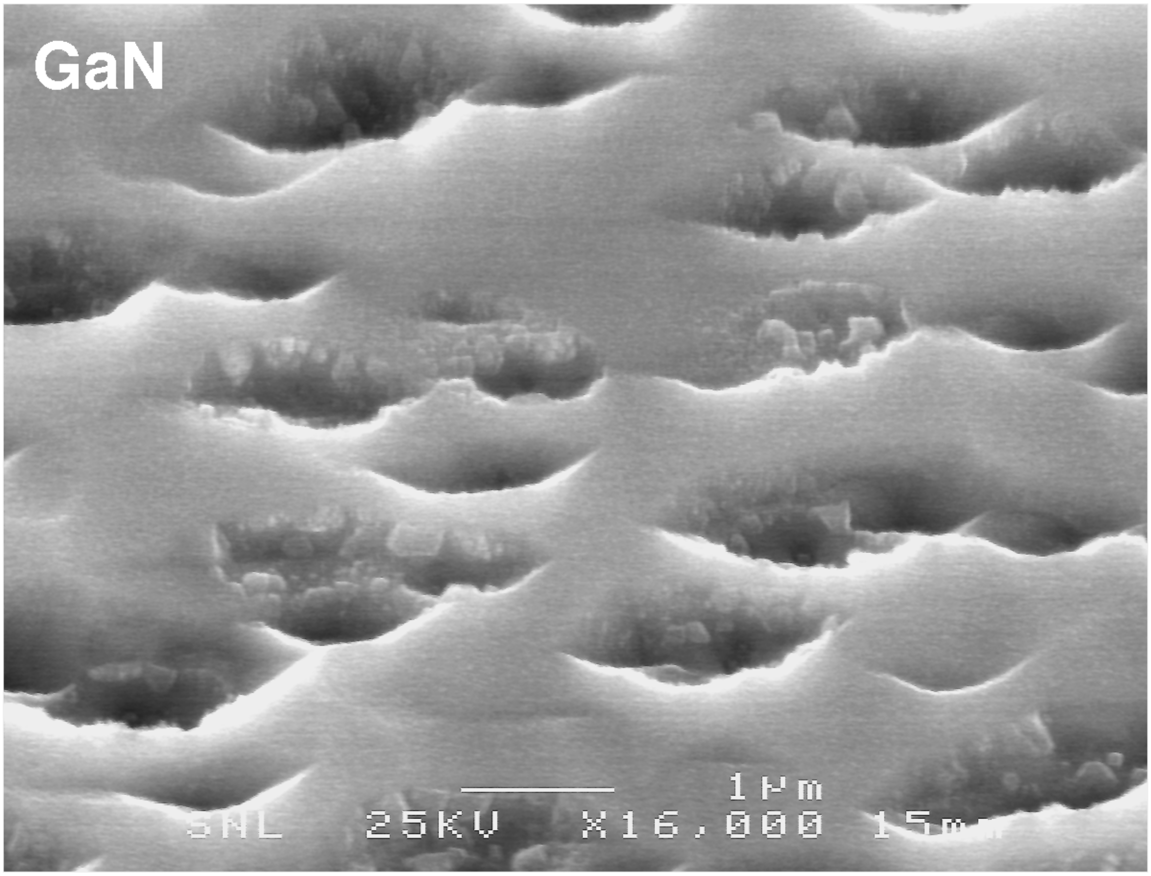

Figure 3b. High-resolution SEM image of a GaN layer grown under Ga-rich conditions. The removal of the Ga-droplets revealed nano-crystallites on the walls and edges of the trenches.

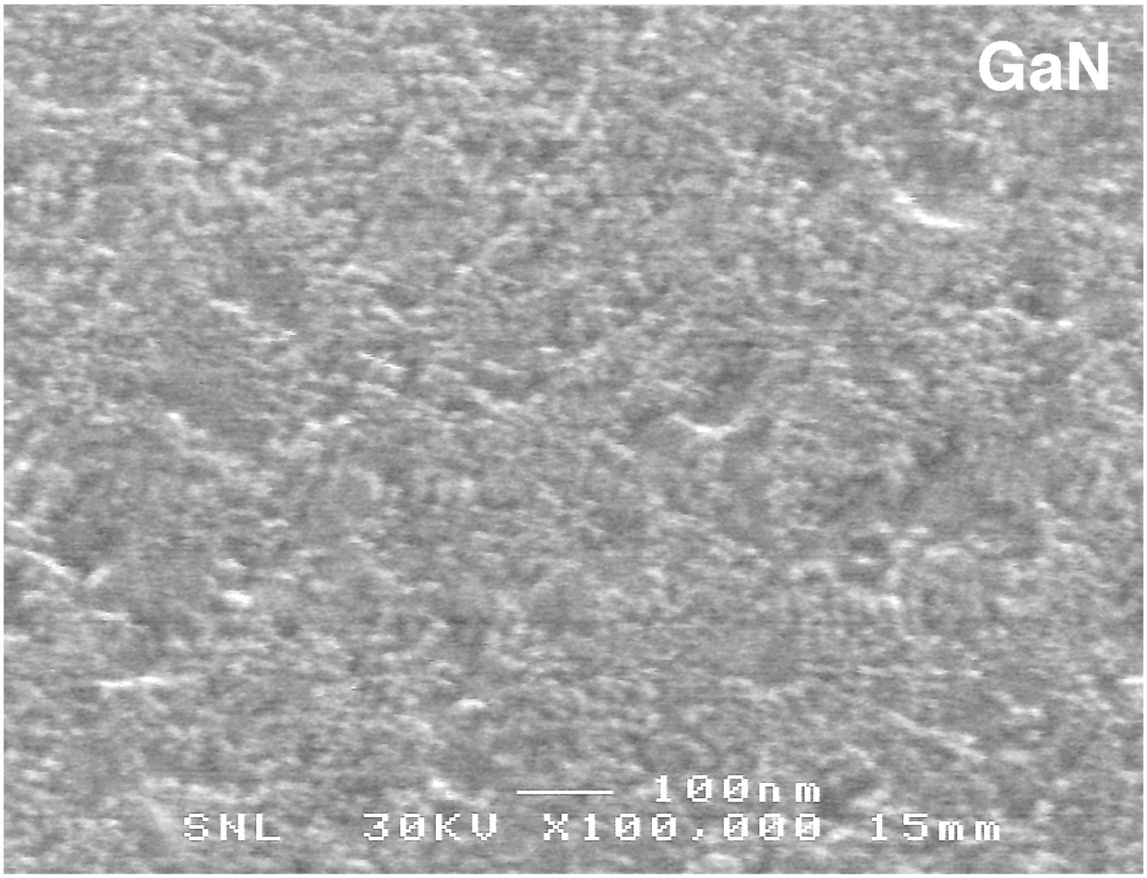

Figure 4a. High-resolution SEM image of a GaN layer grown at near-stoichiometric conditions. The estimated surface roughness is ~20 nm, as determined by the nano-crystalline grains.

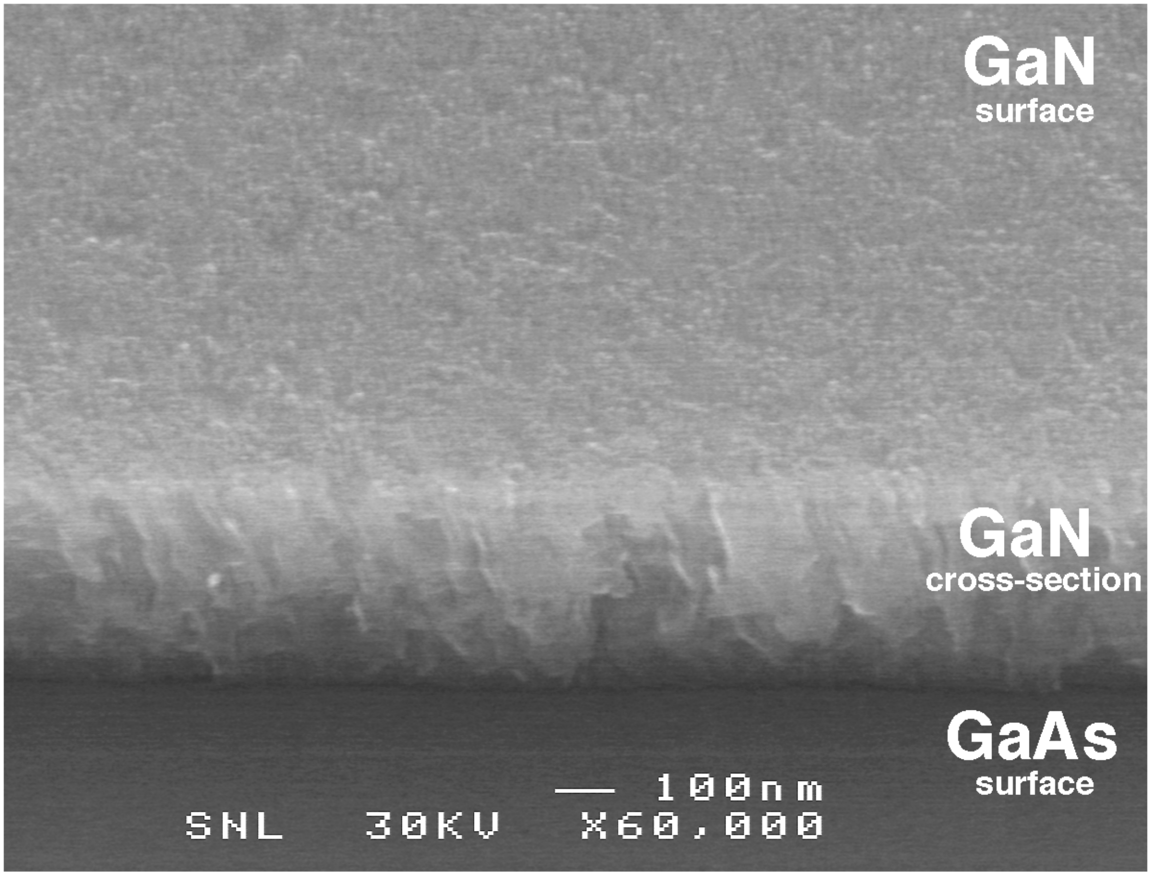

Figure 4b. High-resolution SEM image of a GaN layer grown at near-stoichiometric conditions. It illustrates the columnar structure of small grains in the layer cross-section, while the surface part of the GaAs substrate shows neither indication of hollows, nor presence of polycrystalline structure.

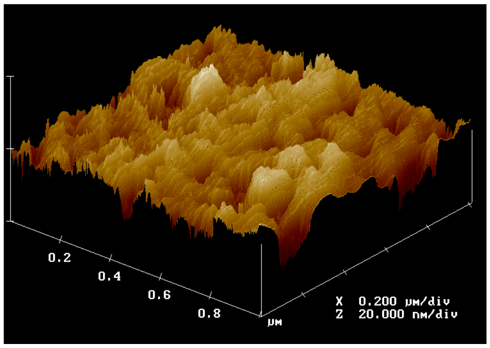

Figure 5. AFM image of a GaN layer grown at near-stoichiometric conditions. The characterised area of 1 μm^2 confirms the good surface roughness of ~20 nm or better, as was estimated by high-resolution SEM.