

Preparation of a smooth GaN–Gallium solid–liquid interface

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ABSTRACT

We discuss the preparation of an atomically flat solid–liquid interface between solid gallium nitride and liquid gallium using in situ surface X-ray diffraction to probe the interface roughness. For the creation of this interface it is necessary to start the experiment with liquid gallium which first etches into the solid at a temperature of 823 K in a nitrogen free ambient. After this rigorous cleaning procedure there is perfect wetting between solid and liquid. The roughness created due to the fast etching of the solid has to be repaired at a nitrogen pressure of 10–20 bar and a temperature around 1150 K. The (2,1) crystal truncation rod data are excellently described by a surface model having 0 ± 0.1 Å roughness, which indicates a successful repair. The lateral length scale on which the roughness is determined has a lower limit of 750 ± 50 Å.

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1. Introduction

The role of interfaces is encountered on a daily basis. Examples are the interface formed by immiscible fluids, the forced interface between artificially bonded wafers and, the topic of this paper, the interface of a crystal in contact with a liquid growth medium.

The abrupt change of the atomic surrounding at interfaces is often at the origin of phenomena such as enhanced liquid density [1], liquid layering [1–3] and liquid order [4]. These factors play an important role in mass transport towards an interface during growth and therefore in growth rate and crystalline quality. An atomic-scale understanding of crystal growth from solution is a big challenge for contemporary science, however. The systematic study of solid–liquid interfaces using surface science techniques is severely hampered by experimental difficulties. First of all, the used techniques should directly address the buried interface which means that any probe that is used requires a high penetration power. The availability of proper instrumentation [5,6] using high brilliance high-energy X-ray sources solves this problem and allows for the exploration of more realistic systems and more complex interfacial phenomena [7–13]. Second, the sample preparation is non-trivial. Traditional surface science is done in

ultra-high vacuum, enabling the use of sputtering and annealing in order to obtain well-defined and clean surfaces. Although in principle this route would be possible for solid–liquid interfaces, in practice very often the interesting phenomena that take place at solid–liquid interfaces do not happen in vacuum. On the contrary, they take place at ambient conditions or even elevated temperatures and/or pressures. At these conditions, surfaces are not considered to be clean nor well-defined. This makes for example the contacting and subsequent wetting of the solid by the liquid a non-trivial task. Pouring a liquid on top of a solid and then perform measurements is therefore not the best way to start an experiment.

This paper describes a procedure to create a well-defined interface between GaN and Ga at conditions which are relevant as a starting point for the high nitrogen pressure solution growth (HNPSG) method. Due to the low uptake of Na in solid GaN [14] these results could also improve sodium-flux liquid phase epitaxy growth as the proper formation of an interface likely behaves similar between solid GaN and Na-poor liquid Ga close to the interface.

The procedure consists of preparing the initial materials in a glove box, in which they are placed inside a high-pressure sealed furnace. The furnace is then brought to a synchrotron beamline, where high energy X-rays are used to acquire surface sensitive diffraction signals from which the interfacial roughness is

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determined. This in situ information is used to create a smooth interface. We determined the optimum temperature and pressure treatment to achieve this by exploring two options for roughness reduction: annealing of the surface after the formation of the interface and slow growth close to thermodynamic equilibrium.

Probing the surface roughness in situ adds an additional benefit since it avoids shut-off effects that may change the morphology of the interface under investigation [15]. The preparation of a smooth interface paves the way for future systematic growth studies.

2. The GaN–Ga interface and surface diffraction

The effect of surface roughness on the measurability of surface X-ray diffraction (SXRD) data forces investigators to make big efforts to avoid rough crystal surfaces. Crystals are often annealed [11], grown, etched [12], cleaved [16], polished or a combination of the above to minimize surface roughness and thus maximize the surface signal. Depending on the system some techniques are preferable above others. With respect to GaN crystals, cleaving is not commonly applied since source crystals are not very big. Fortunately, polished GaN wafers are readily available and with a proper polishing technique crystals with a surface roughness below 2 Å are reproducibly obtained as starting material.

Continued growth on GaN crystals, whether they are polished or not, is not easy, however. Even with careful cleaning procedures, the GaN surfaces have to be pretreated to create a good and properly clean interface. The only known way to create a good interface between GaN and bulk liquid Ga is by back etching into the solid [17,18] at relatively high temperature where Ga starts wetting GaN [19]. An unwanted byproduct of the back etching is an increase in the roughness of the interface due to the decomposition of the wafer surface [20], which again poses a serious challenge when performing surface diffraction experiments.

Roughness evaluation: Roughness evaluation using SXRD is described in detail elsewhere [21,22]. In principle, a description of the complete 3D atomic interface structure including relaxations, (quasi)-liquid layers and substrate roughness is needed for a proper evaluation. However, several considerations make the evaluation less demanding. Firstly, surface relaxations often change the shape of a Bragg peak in an asymmetrical way. The measurement of a full rod covering several Bragg peaks therefore makes distinguishing relaxations from roughness straightforward. Secondly, at high enough in-plane momentum transfer, the quasi-liquid scattering contribution to the crystal truncation rods (CTRs) is basically zero [3] meaning that the evaluation can be performed without considering (quasi)-liquid layers. Therefore, we have chosen to use the (2,1) CTR to evaluate the surface roughness. The roughness we measured is averaged over several seconds, i.e., the measurement time of a single data point.

The length scale over which X-rays probe the surface roughness is derived from the width of the diffraction profile [22,23]. Roughness removes intensity from the narrow Bragg contribution of the diffraction profile and distributes this over a broader profile with a width and shape that depends on the lateral correlation of the roughness. In many cases, as in the present one, the roughness is uncorrelated and only the Bragg contribution remains. The experimental width of this profile then corresponds to the effective length scale over which the roughness is probed. The length scale is defined as:

$$S = \frac{2}{\Delta Q_{\text{fwhm}}}, \quad (1)$$

when the profile is Lorentzian shaped. In this equation S is the length scale and ΔQ_{fwhm} is the width of the diffraction profile. For a

Gaussian shape Eq. (1) changes to:

$$S = \frac{4\sqrt{\ln 2}}{\Delta Q_{\text{fwhm}}} \approx \frac{3.33}{\Delta Q}. \quad (2)$$

If the surface roughness indicates 0 Å, it can be concluded that no steps within a length S are present on the surface. This roughness analysis, based on many experimentally determined structure factors, works only under stable conditions of the interface during the measurements, i.e. when the solid–liquid interface is at equilibrium. First of all, it takes a certain amount of time, on the order of hours, to obtain the data and during the measurements certain reference signals are measured regularly to check for any changes. Second, since the scattered X-rays do not carry any information about the lateral position of steps, the experimental technique does not allow us to identify any step movements.

The full alignment of a crystal to measure off-specular rods is however, time consuming, especially if experimental conditions like temperature and pressure have to be changed frequently. The combination of using the specular rod to observe changes, selectively followed by scans of an in-plane rod is therefore the best practice. However, even the full alignment and measurement of the specular rod take a substantial amount of time if low l -values have to be measured properly. Measurements at high l -values are less influenced by small changes in crystal alignment which makes long term observation of one surface sensitive spot on the specular rod during parameter changes a possibility.

To reduce time demands even more, the availability of the phase diagram is useful. The decomposition of bulk GaN in contact with liquid Ga and N₂ gas (Fig. 1) has been investigated by Karpinski et al. [24] for pressures above 100 bar while another report

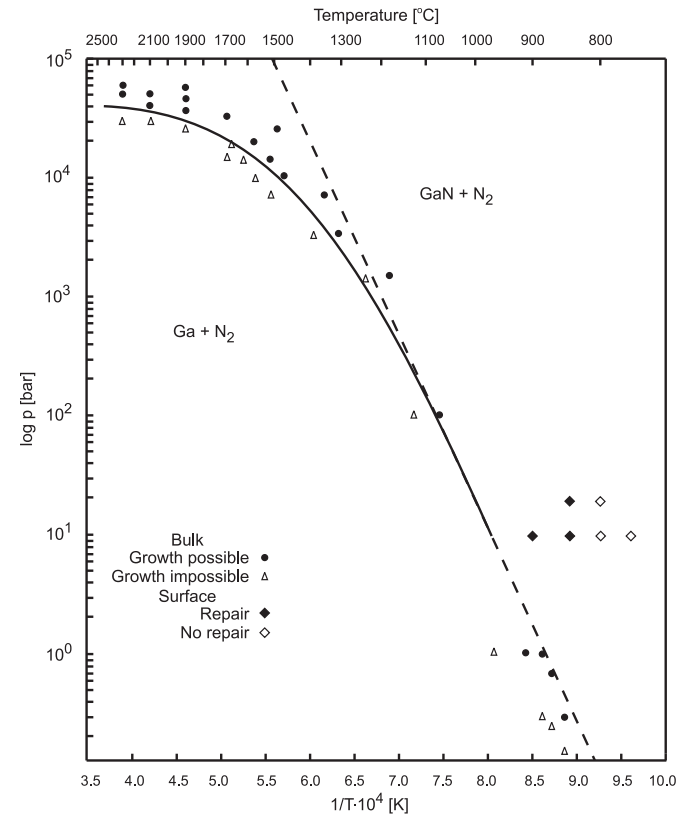


Fig. 1. The phase diagram for the decomposition and surface repair of GaN in contact with liquid gallium and nitrogen gas. ● and △ for decomposition of bulk GaN crystals, high pressure data taken from [24], low pressure data from [25]. The dashed line is calculated for an ideal gas. Our measurements for the repair of the crystal surface are marked ◆ and ◇ indicating whether surface repair is possible or not.

[25] describes the phase diagram for pressures below 1 bar. The latter reports a slight offset from the ideal gas law due to the catalytic nature of Ga on the GaN decomposition. Repair is expected to occur in the vicinity of the phase transition. If the temperature is too low, there is no N_2 activity and growth is kinetically inhibited.

3. Experimental

Ammonothermally grown, epi-ready (001) oriented n-type GaN wafers with a size of 1×1 cm and a miscut of $0 \pm 0.2^\circ$ were bought [26] and repolished using a mechano-chemical polishing device [27]. This resulted in a surface roughness below 2 Å and the surface showed equi-spaced steps on AFM measurements. The wafer was cleaned and placed in a high pressure, high temperature furnace [13] which itself was cleaned using isopropanol and pre-baked in an autoclave for 2 days at 353 K and 1 mbar to reduce its water content and avoid unwanted oxide formation at the sample during the experiment. The wafer was held in an inconel slot to avoid lateral movements in the furnace (see Fig. 2). On top of the wafer a Macor tube, inner diameter 3 mm, outer diameter 6 mm, was placed which itself was stabilized from the top with an inconel mantle resting on 4 legs. This geometry limits the amount of Ga that needs to be penetrated, and thus allows access of the solid–liquid interface using hard X-rays. The choice for 4 supporting blocks on the stabilizer was made based on the six-fold symmetry of the GaN crystal. With 4 supports at least 4 out of 6 reflections can be reached. This design choice was repeated throughout the rest of the furnace. The Macor and inconel pieces were cleaned with isopropanol and ultra pure water in an ultrasonic bath and subsequently baked at 573 K and 1 mbar for one day.

Due to the stability of gallium oxide the gallium used in the experiment has to be cleaned additionally and inserted into the chamber as a liquid. This is a much better route than melting solid gallium. In other experiments we found that the very thin oxide layer formed on freshly etched solid gallium pellets prevents a proper contact between liquid and solid even after heating to 1173 K. The fact that the oxide layer is not broken upon liquefaction is probably caused by the increased density and therefore

volume decrease of liquid Ga compared to its solid form.

The cleaning procedure of the gallium is as follows. Gallium, 7 N pure, obtained from Alfa Aesar [28], was liquefied inside a water and oxygen free (≤ 1 ppm) glovebox, the gallium oxide was removed by transferring the liquid gallium from one glass container into a second one using a glass Pasteur pipet to extract gallium from the middle of the liquid in the container. The benefit of the transfer is that gallium oxide sticks to glass while gallium itself does not. Hereafter a new glass Pasteur pipet was used to take gallium from the second container, again by extracting it from the middle of the liquid, and transfer it as quickly as possible into the Macor tube resting on the GaN wafer. The tube was filled to the top to maximize the weight pushing down on the wafer. Hereafter, the furnace, now containing a GaN wafer and liquid gallium, was closed and filled with argon gas to a pressure of 1.1 bar inside the glovebox. This was done to reduce the chance for oxygen to enter the chamber during transport to the beamline. The 10 milliliter liquid gallium which remained in the second container did not solidify within a 3 month period while being vibrated and supercooled by 10° . That supercooling by 10° is possible over such a long period for such a large amount of material indicates its high purity [29].

The furnace holding the crystal and liquid gallium was subsequently placed on the high energy micro-diffractometer (HEMD) [5,6] at the ID15A beamline of the European synchrotron radiation facility (ESRF) in Grenoble, France. An X-ray wavelength of 0.1784 Å (≈ 69.5 keV) was used throughout the experiment. The beamsize at the sample was 5×5 μm and images were collected using a Maxipix detector with CdTe sensor [30]. The sample was aligned in a standard way to allow for surface diffraction measurements on the specular rod around the (0,0,2) Bragg peak [23].

For the ease of alignment and time constraints, the choice was made to use the rod around $l=2$ to follow the interfacial change during the experiment. Thereafter, the interface was properly formed by increasing the temperature stepwise under flowing argon at 1.5 bar until roughening occurred. By using an environment without N_2 , this roughening due to the decomposition of GaN occurs at a low temperature. Subsequently, argon was changed for stepwise increased pressurized nitrogen at variable temperature to repair the surface. All these steps were observed using the (0,0,1.65) reflection and selected scans of the full CTR around $l=2$. After the return of the signal to its initial state, the surface roughness of the solid–liquid interface was determined by measuring the (2,1) CTR.

After the experiment, the sample was cleaned and the remaining liquid gallium was removed using hydrochloric acid (HCl) followed by a rinse in ultra pure water and blow drying in dry nitrogen. AFM images were taken ex situ to access the surface morphology and the possible influence of the shut-off effect.

4. Results and discussion

Creating the interface: Comparing the alignment of the (0,0,2) Bragg peak with the surface normal showed that the wafer had a miscut of 0.046° , which corresponds to an average terrace width of approximately 3200 Å. The rod around $l=2$ could be measured between $l=1.3$ and $l=2.7$ (blue line in Fig. 3). A fit to the data using only the bulk GaN crystal structure without reconstructions and surface relaxations yields an RMS surface roughness of approximately 2 Å.

The back-etching of the crystal surface was monitored in Ar atmosphere on the (0,0,1.65) reflection which showed a drop in intensity after reaching a temperature of 823 K. Compared to the temperature mentioned in [20] our finding of the onset of surface decomposition is 170° lower. This is probably due to our much

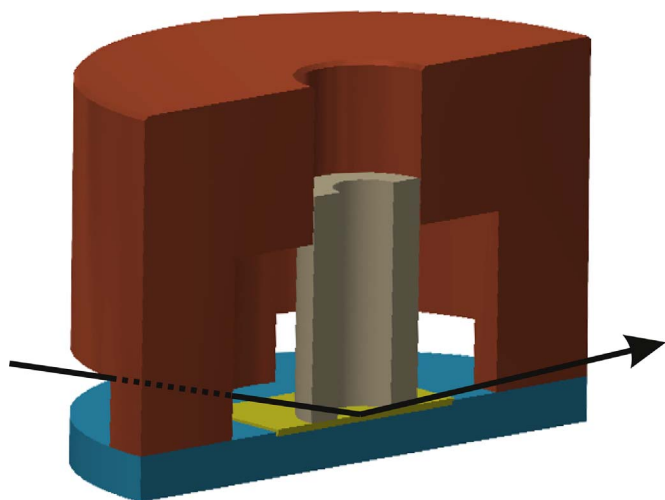


Fig. 2. Cut through of the parts holding the wafer. In blue: inconel base plate; yellow: GaN crystal; gray: Macor tube; red: inconel stabilizer for the Macor tube. The arrow indicates the trajectory of X-rays during the measurement of a single point on the (0,0) rod. It can be seen that for specific orientations of the crystal only the Macor tube and liquid gallium inside the Macor tube have to be penetrated. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

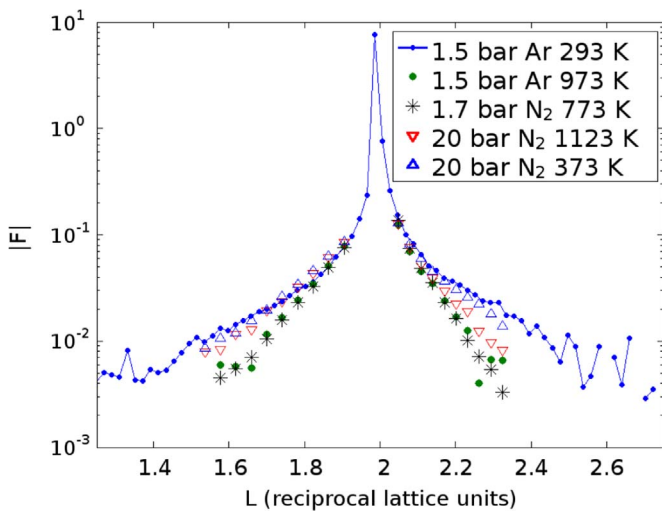


Fig. 3. Measurements of the (0,0) rod around $l=2$ showing the initial surface (blue line) followed by an increased roughness due to back etching (green solid dots). The roughness did not decrease in low pressure nitrogen (black stars), however at a pressure of 20 bar nitrogen and 1123 K the roughness decreased (red downwards facing triangles) and almost returned to the level of the initial surface at 373 K (blue upward facing triangles). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

more sensitive observation technique. The change in intensity is attributed to the instability of the GaN crystal at elevated temperatures. Before the decrease in intensity a proper interface between solid and bulk liquid did not exist. Therefore, the roughening of the GaN crystal can initially only be described by the escape of nitrogen from the crystal lattice. Due to the escape of nitrogen from the crystal surface, liquid gallium is created which is directly attached to the crystal. Depending on the temperature this can be in the form of droplets or a fully wetted film [19]. In any case, the connection between the droplets or thin film and the bulk liquid above then leads to a fully wetted solid–liquid interface.

Since annealing of the interface can cause a high mobility of the surface atoms which can move to a thermodynamically more favorable place, this could decrease the surface roughness. However, increasing the temperature to 973 K resulted in a drastic increase in surface roughness to approximately 6 Å (green dots in Fig. 3). Increasing the temperature to 1073 K decreased the intensity even more. Apparently under these conditions the surface decomposes not only at the step edges, but also on the terraces. Thus a high-temperature anneal without N_2 cannot generate a smooth surface. The fact that back-etching occurs means that a full contact between GaN and Ga is present and that growth and surface repair is possible. At this point the estimation of the interfacial roughness using the specular rod is probably inaccurate since the contact with the gallium liquid on top might influence the actual value. This is confirmed by the more asymmetric form of the specular rod after roughening the initial surface.

Repair of the interface: As was done for the surface roughening, the intensity of the (0,0,1.65) reflection was used to follow the increase in signal due to surface repair. The flowing argon was first replaced with flowing nitrogen at 1.7 bar and a temperature of 773 K was set, but under these conditions no effect was observed (black stars in Fig. 3). However, a change to a pressure of 20 bar and a temperature of 1123 K caused a rapid increase in the measurable signal (red triangles in Fig. 3). Cooling down to 373 K resulted in intensities on the whole rod comparable to its initial state (blue triangles in Fig. 3). In a separate experiment the “repair” was performed at a pressure of 10 bar and 1173 K which resulted in a

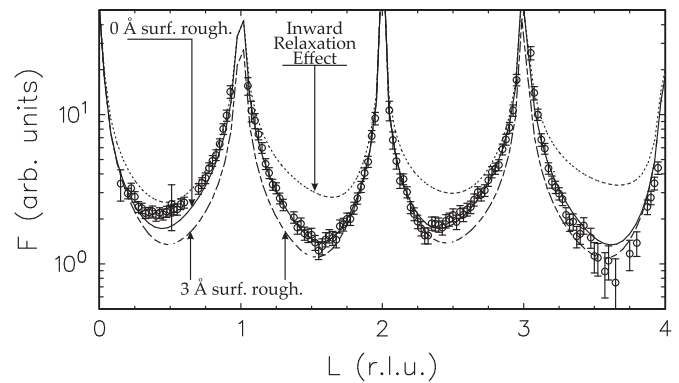


Fig. 4. The (2,1) rod of the GaN–Ga solid–liquid interface. The large in-plane momentum transfer of the (2,1) rod leads to a low sensitivity for in-plane preferential order of the interface. The reflected intensity is therefore a good measure for the surface roughness. Measured data is shown by circles plus error bars, the solid curve is the fit of the interference sum with free parameters for the in-plane Debye–Waller factor of only the top-most bulk solid Ga. The deviations visible in the fit at low l -values are caused by an absence of liquid Ga, while the deviations at high l -values are caused by an absence of properly integratable data due to a very low intensity of scattered signal. The simulated influence of 3 Å roughness as well as very large inwards surface relaxation are indicated.

slower, more controlled, increase in signal over time. These results have been added in the phase diagram of Fig. 1.

One of the disadvantages of performing the repair at the high temperatures required while using either 10 or 20 bars of nitrogen is the increase in the width of the bulk GaN Bragg peaks. The FWHM of the (0,0,2) Bragg peak changed from 0.0056° before to 0.02° after repair, indicating a decrease in crystalline quality. A repair at higher pressure and lower temperature might solve this issue. However, the pressures required to repair the surface at temperatures significantly lower than those used in this paper are not available with the setup used in this experiment.

Due to the connection between the solid and bulk liquid the surface roughness of the “repaired” interface is no longer determined by the GaN surface only. The interference of the liquid on top will play an important role in the reflected intensity, even relatively close to a Bragg peak. The determination of the surface roughness was therefore performed on the (2,1) CTR of the solid–liquid interface. The data and fit are depicted in Fig. 4. The fit assumes a variable Debye–Waller factor of only the top-most Ga of unrelaxed Ga-terminated bulk (001) GaN and reveals a surface roughness of 0 ± 0.1 Å. The surface roughness extracted from the fit of the (2,1) rod is measured with an incident angle of 0.2° which leads to a footprint of approximately 1.4 mm. Within this footprint the surface roughness is measured according to the lateral length scale defined in Eq. (2). The full width half maximum of a surface sensitive peak at $(h, k, l) = (2, 1, 2.8)$ is equal to 3 ± 0.2 pixels or $165 \pm 11 \mu\text{m}$ (see Fig. 5). With a detector-sample distance of 1.3 m, the surface roughness is then determined to be 0 ± 0.1 Å over a lateral length scale of 750 ± 50 Å.

Shutoff effects: After the experiment, the temperature was reduced while keeping the nitrogen pressure at 20 bars. The GaN crystal was cleaned in HCl and images of the crystal surface were made using a Cypher AFM from Asylum Research. The surface morphology of the sample ex situ is quite different from what was expected based on the X-ray results and most likely caused by a shut-off effect. There are islands as well as crystallites present on the surface. The large and flat regions on the surface resulting in a roughness of 0 Å are not visible. The islands as shown in Fig. 6 (a) can be explained by bubbles of gas present between GaN and liquid Ga during the experiment. The bubbles are likely stabilized by additional GaN decomposition during the experiment and the possible presence of gallium oxide during the insertion of the

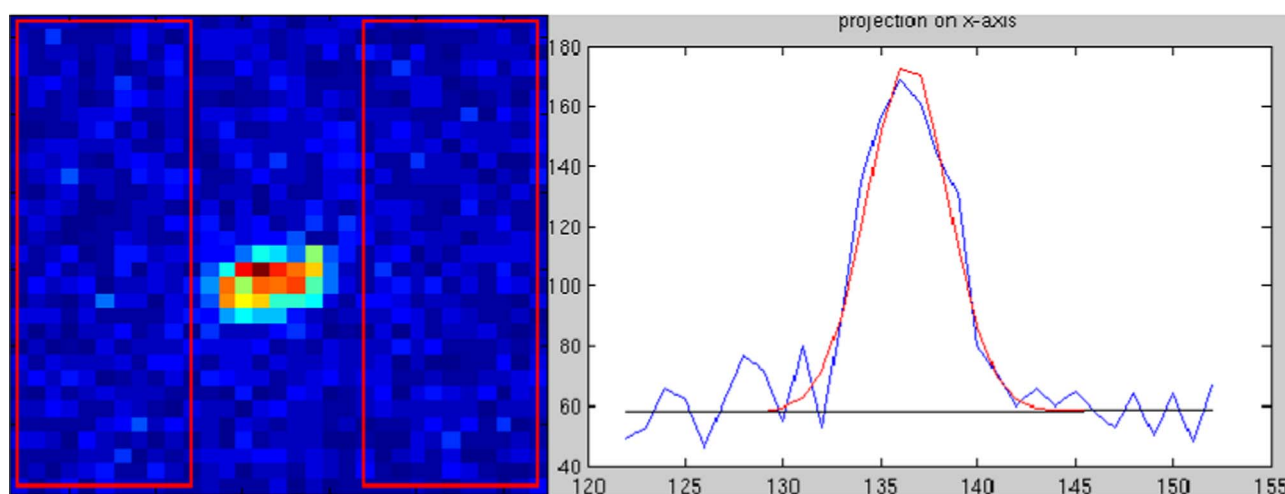


Fig. 5. Left: Part of a typical X-ray detector image showing the (2,1,2,8) CTR diffraction peak. Pixels on the detector are $55 \times 55 \mu\text{m}$. Right: 1D integrated projection of the image on the left. The background (black line) is determined using the integrated intensity in the two rectangles in the left image and is used as a base for the Gaussian fit (red curve) on the peak between the two rectangles. The fit of the CTR diffraction peak has a full width half maximum of 3 pixels which corresponds to a surface roughness length scale of $750 \pm 50 \text{ \AA}$. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

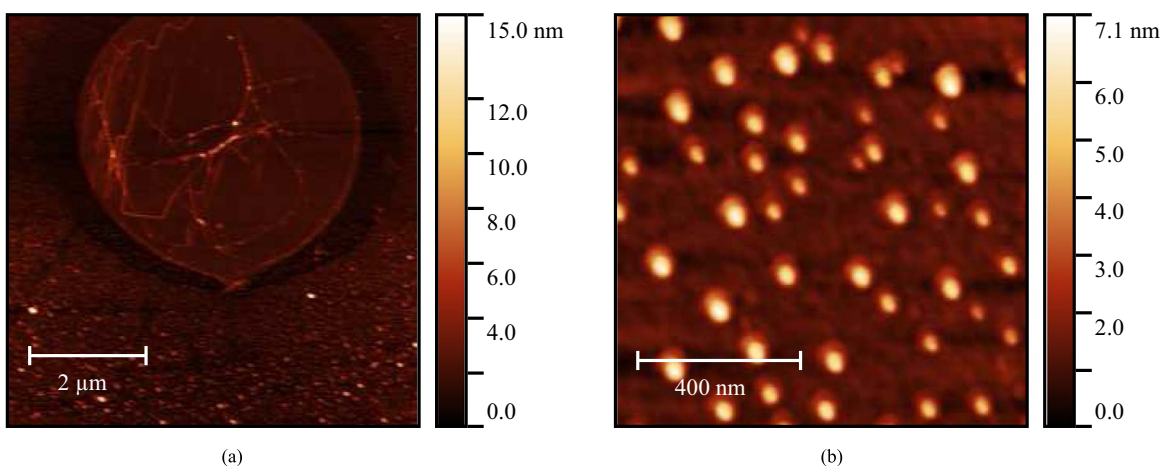


Fig. 6. AFM images of the ex situ GaN crystal surface. (a) An island surrounded by crystallites. The island is likely caused by a bubble of gas or incomplete wetting between solid and liquid due to remaining gallium oxide. (b) A zoomed in view of the crystallites. A shut-off effect is seen as their origin as their presence during the experiment would result in an increase of the surface roughness and corresponding decrease of the length scale on which a smooth surface can be characterized.

liquid into the furnace. The crystallites seen in Fig. 6 are caused by a shut-off effect. If the crystallites would be present during the X-ray diffraction experiment, the surface roughness, and especially the length scale on which the roughness is measured, would reflect this. The drop in temperature, while keeping the nitrogen pressure at 20 bars, is likely causing an increase in the supersaturation of the liquid which forces growth of new material leading to a rough interface. However, according to the in situ analysis the interface is perfectly flat at high temperatures. Other in situ techniques, like in situ microscopy [31–34] or a careful study to minimize shut-off effects might avoid the roughness we see using AFM. It would be highly desirable to use such microscopy techniques for further studies of GaN solution growth and it would advance the current understanding substantially, in particular by complementing atomic-scale studies as presented here. However, for our sample and experimental conditions data from such techniques is not available.

5. Conclusion

We have shown how to prepare an atomically smooth solid–liquid interface between solid GaN and liquid gallium. Such

smooth interfaces are a prerequisite for detailed atomically resolved GaN growth studies using SXRD. We found that it is imperative to liquefy the gallium prior to the start of the experiment. However, even the direct use of liquid gallium does not form the interface. The formation has to be forced by back-etching the GaN surface. Initially the roughness is most likely created due to the escape of nitrogen out of the solid, leading to a buildup of liquid gallium on top of the GaN which can act as a contact for the bulk liquid above.

After the formation of the interface the roughness cannot be repaired by a traditional annealing method. The repair requires elevated nitrogen pressures at a higher temperature than needed for the initial roughening.

The final roughness is found to be $0 \pm 0.1 \text{ \AA}$. The use of in situ X-ray diffraction was essential to determine the conditions to generate this smooth interface. This interface is perfectly suitable for detailed growth or structural studies using XRD.

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