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Experiment Report Form

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- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** In-situ x-ray study of GaN liquid phase epitaxy: phase 1	**Experiment number**: MA-1928
Beamline: ID15A	**Date of experiment**: from: 30-10-2013 to:05-11-2013	**Date of report**: 28-02-2014
Shifts: 18	**Local contact(s)**: V. Honkimaki	*Received at ESRF:*

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Report:

The experimental aim of the proposal was the in-situ study of ordering and roughness of the gallium-nitride/gallium-sodium solid-liquid interface in equilibrium growth conditions. The results will be summarized below.

Due to the difficulties creating GaN/sapphire heterostructures with low surface roughness we were not able to prepare our GaN substrates on time which caused us to start our experiment using a blank sapphire substrate which was equipped with a macor ring in which solid $Ga_{13}Na_7$ was placed using the glove box of the ESRF chemistry lab (fig 1).

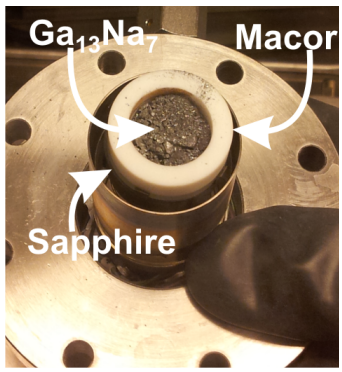

Fig 1: Initial experimental geometry showing GaNa solid powder in a macor ring positioned on top of a sapphire wafer.

During the beamtime we used the liquid monochromator which increased the beamsize from about 6x6 μm^2 to about 6x15 μm^2 with a rotation depending on the applied incident angle, see also figure 7 in [1]. The reflectivity of the blank substrate was measured on both the positive and negative side and gave good results even though there was a powder lying on top of the substrate. From a fit the RMS roughness of the bare sapphire was found to be 2.45 Å. In a previous in-house experiment we found that the equilibrium for GaN growth using $Ga_{13}Na_7$ on bare sapphire is close to 15 bar and 600 °C. We therefore started with an applied 12 bar and increased the temperature stepwise to see the melting of $Ga_{13}Na_7$ at 570 °C by observing a powder ring at 2theta = 0.8° at 69.8 keV. After equilibration of the temperature at 600 °C we observed an unexplainable gap between sapphire and GaNa mix. Reflectivity did not show anything interesting on the sapphire substrate which prompted us to change the sample.

Our second sample was a new blank sapphire wafer with macor ring which we filled with solid gallium pellets. The roughness of this second wafers was again fitted using reflectivity data to 2.45Å. After heating the furnace above the melting point of gallium we found that we were not able to obtain reflectivity data from the positive side of the sapphire crystal indicating that the now liquid gallium was blocking the signal. The reflectivity data on the negative side of the sapphire crystal did not show a critical edge which made us assume that the gallium was not wetting the sapphire yet. To get a proper contact between the gallium and the sapphire we increased the temperature which should break up the oxide layer of the gallium. This did however not work. The subsequent increase in pressure to push the gallium on to the sapphire also did not yield the requested result and ended up with scans showing inhomogeneous density in the liquid gallium leading us to believe that there were individual spheres of liquid gallium that did not want to join together. At 800 °C and 57 bar we saw that the sapphire surface became rough rendering reflectivity or CTR data

impossible. As a last check we increased the beamsize and checked for GaN powder formation on the liquid gallium which we did not observe.
After opening the furnace we observed that the gallium pellets were covered in a thick gray crust. The powder from the crust was analysed at ID15B during in-house beamtime. The result shows the formation of a thick layer of gallium oxide. The origin of the amount of oxygen needed to form the thick crust remains up til now unknown.

Following the MA-1928 experiment we used a slot of in-house beamtime in experiment IH-SI-854 which finished February the 25th. The results obtained there are summarized below.
During the MA-1928 experiment we were not convinced of the wetting of our gallium-sodium mixture with the sapphire seed crystal. This led us to a collaboration with the Polish Institute of High Pressure Physics (Warsaw) which has over 40 years of experience on GaN growth in extreme conditions. Their experience is that gallium will not wet the surface of substrates in a proper way before a "back etching" step in which one disolves the remaining impurities on the crystal surface and breaks the oxide layer around the liquid gallium. Our collaborators futher supplied bulk single crystal GaN wafers with extremely low surface roughness, see figure 2.

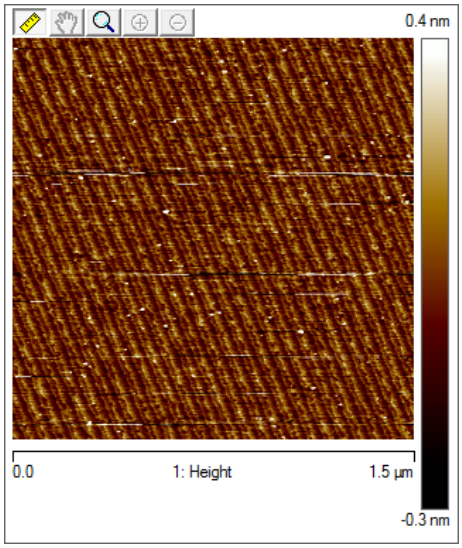

Fig 2: an AFM height image of the initial GaN surface.

With these substrates we are able to investigate the solid-liquid interface between GaN and liquid gallium in great detail. At first, before heating, the result of a first roughness calculation of the initial surface by scanning the (00) crystal truncation rod (CTR) originating from the (002) GaN bragg peak. The CTR signal is tilted due to the miscut of the GaN crystal[2] and therefore does not cross the direct beam. The roughness of the resulting data can be fitted using the program ROD[3]. For the initial surface (fig 2) we report an RMS roughness of 2 Å (fig 3 blue line). Additional CTR's were collected which still need to be analyzed to allow for proper conclusions on the organization of the starting surface.

To continue the experiment we chose to heat the interface in 100% argon atmosphere. At this point any equilibrium is prevented until the nitrogen has saturated the gallium liquid. Following the reflected intensity at the surface sensitive (0 0 1.7) Bragg position we confirmed the roughening of the GaN surface after reaching 570 degrees centigrade. After reaching 700 °C the reflected intensity remained constant upon which we repeated the measurement of the (00) rod (green dots, fig 3) as well as other CTR's.
The roughness at this point is evidently much higher as compared to the starting situation (green dots in fig 3); an exact value is not yet available.
To approach the equilibrium growth condition needed for our experimental aim we changed the argon for nitrogen and applied a comparable pressure of 1.7 bar. This was left to equilibrate for 2 hours upon which we measured the (00) rod again (Black marks in fig 3). The resulting curve shows no significant difference compared with the curve before the gas change. An increase in pressure to 6 bar (not shown in fig 3) also did not show any change in the intensity of the reflected signal. Increasing

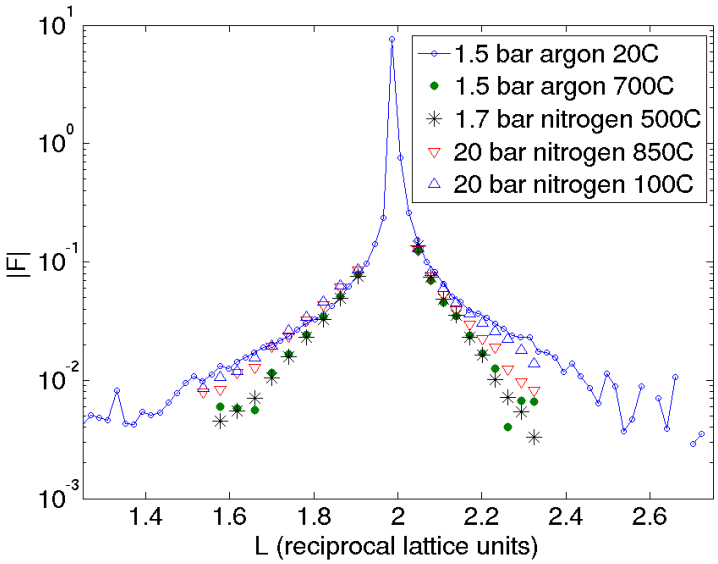

Fig 3: integrated intensities from the (00) rod around L=2. The blue graph is the initial surface. Consecutive scans avoid the Bragg peak at L=2. The green dots mark the surface after being heated to 700 degrees centigrade in 1.5 bar of argon. The black curve shows that a change to low pressure nitrogen is not changing the surface roughness. The following red and blue triangles show that the surface roughness recovers in high pressure nitrogen at high temperature and over time and approaches the initial value of 2 Angstrom.

the pressure to 20 bar however did change the reflected intensity at L=1.7 after several minutes. Further investigation of the (00) rod shows that the roughness is reduced (red triangles fig 3).
After a slow reduction of the temperature over several hours, thereby minimizing the formation of new GaN from solution, we found that the surface roughness of the now wetted solid liquid interface in equilibrium approached the initial surface roughness of the unwetted interface. Part of the measured roughness likely originates from the quasi-liquid Ga layer at the interface, but this requires further analysis.
This result shows that with the help of our second experiment we are able to reach the aim of our proposal MA-1928, an equilibrium growth condition on the solid liquid interface with a roughness that low enough to allow for a detailed in situ structure determination..

[1] V. Honkimaki et al. Journal of Synchrotron Radiation, **13,** (2006) 426–431
[2] E. Vlieg, X-ray diffraction from surfaces and interfaces, Vol. 1: Concept and Methods, Wiley-VCH, 2012, Ch. 3.4.2, pp. 375–425.
[3] E. Vlieg, Journal of Applied Crystallography, **33**, 2. (2000), 401-405