

A sample chamber for in situ high-energy X-ray studies of crystal growth at deeply buried interfaces in harsh environments



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ABSTRACT

We introduce a high pressure high temperature chamber for in situ synchrotron X-ray studies. The chamber design allows for in situ studies of thin film growth from solution at deeply buried interfaces in harsh environments. The temperature can be controlled between room temperature and 1073 K while the pressure can be set as high as 50 bar using a variety of gases including N₂ and NH₃. The formation of GaN on the surface of a Ga₁₃Na₇ melt at 1073 K and 50 bar of N₂ is presented as a performance test.

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1. Introduction

Interfaces are encountered on a daily basis. Examples are the formation of an interface between immiscible fluids, like oil and water; artificially bonded wafers, like microelectromechanical systems (MEMS); a solid in contact with its melt, like water on ice; a metal in contact with a semiconductor, like a Schottky contact; growth of single crystals from a liquid source, like gallium nitride (GaN) liquid phase epitaxy (LPE) growth. The ‘buried’ interfaces between two bulk systems, as described above, are often causing interesting phenomena. Examples are enhanced liquid density [1], liquid order [2] or liquid layering [1,3,4]. These phenomena are important factors with respect to the mass transport towards the growing interface and therefore growth speed and crystalline quality. Surface X-ray diffraction is capable of resolving a complete 3D structure of the interfaces described above. However, the structure at the interface is difficult to investigate with conventional X-ray energies ($E \approx 10$ keV) due to the attenuation by the material to be penetrated.

The last two decades, however, the creation of proper instrumentation [5,6] at high brilliance high-energy X-ray sources allowed scientists to start exploring these more realistic systems and more complex interfacial phenomena [7–10].

Many interfaces in crystal growth are formed in harsh conditions often combining high pressure, high temperature and dangerous gases or liquids to form the required material. A suitable sample environment is therefore key to investigate the buried interfaces formed during crystal growth in such environments.

This paper presents a reusable batch reactor specifically designed for in situ studies of growing, heated and pressurized buried interfaces in corrosive environments by means of high-energy X-ray reflectivity (XRR) and crystal truncation rod (CTR) measurements. The use will initially be limited to GaN growth using the Na-flux technique. However, this is only one of the experiments that can be envisioned.

To the best of our knowledge this chamber is unique in that it is the first large volume cell designed with a carbon fiber window that is capable of surface diffraction experiments at elevated pressure and temperature using corrosive gases and liquids. Previous pressure cells for XRR were not made for temperatures over 360 K nor corrosive materials [9] and references therein). Pressure cells for CTR measurements are even more scarce [11], and to the best of our knowledge not available for the combination we present here.

2. Interface diffraction from deeply buried interfaces

Performing diffraction from deeply buried interfaces means that one of the materials forming the interface has to be penetrated. This implies the use of high energy X-rays, because the

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X-ray attenuation coefficient (μ) rapidly decreases with increasing X-ray energy: $\mu(E) \approx E^{-3}$.

An additional benefit of X-rays is that for increasing X-ray energy the scattering angle of a specific signal will decrease. This means that for high energy surface X-ray diffraction (SXRD) signals will be found relatively close to the (000) reflection which reduces the demands for X-ray windows in chambers.

A disadvantage of (high energy) X-rays is that they are not intrinsically surface sensitive and the bulk signal can drown the surface signal. By selecting surface sensitive reflections and additionally setting slits to suppress parasitic scattering and increase the signal to noise ratio this problem is largely overcome. Additionally one can increase the signal to noise ratio further by choosing small incident angles for CTR measurements, typically equal to or lower than the critical angle of reflectivity ensuring total reflection of the incident beam. The small resulting incident angle can lead to complications. Setting an incident angle lower than or equal to the critical angle has a consequence for the required surface quality. The use of high energy X-rays means that the critical angle of reflectivity is very small, typically around 0.03° at 70 keV. Even with a focussed X-ray beam, a small incident angle means illumination of a big surface (e.g. a vertically focussed beam of $8 \mu\text{m}$ at 0.03° incidence angle will illuminate approximately 15 mm of the sample surface). For this reason the sample surface has to be polished to an extremely smooth (surface roughness) and flat (wavyness, curvature) finish. A detailed description on SXRD is given elsewhere [12,13].

The chamber we describe in this paper is designed primarily for transmission SXRD at high energies. However, the available exit angle for scattered X-rays is chosen so that bulk powder diffraction and bulk liquid scattering, as presented in this paper, are optional

alternative techniques. Additionally the chamber can be used with lower photon energies. Compared to 70 keV photons where the transmission through the chamber equals 85%, the transmission at 20 keV is still 68%. Note however that the incident and exit angles available might become an issue when utilizing X-rays of lower energy.

3. Experimental requirements and chamber design

3.1. The beamline

The chamber is developed for use on the high energy micro diffraction (HEMD) stage [5,6] at the high energy beamline (ID15) of the European Synchrotron Radiation Facility (ESRF). The HEMD setup is presented in Fig. 1.

To improve data acquisition the HEMD setup has been equipped with a 2D Maxipix detector with Cadmium Telluride (CdTe) direct detection sensor [14]. Such a detector allows for data collection in the so-called stationary mode [15]. Both the scattering signal and the background can be determined from a single image and there is no need for rocking the crystal. This speeds up data collection tremendously. Combining the use of a pixel detector, the possibility of XRR and CTR measurements, and the use of high energies ($E \geq 70 \text{ keV}$) gives fast access to complete 3D structures of deeply buried interfaces.

3.2. Chamber requirements

The semiconductor Gallium Nitride (GaN) can be grown using several methods. One of the main techniques to grow

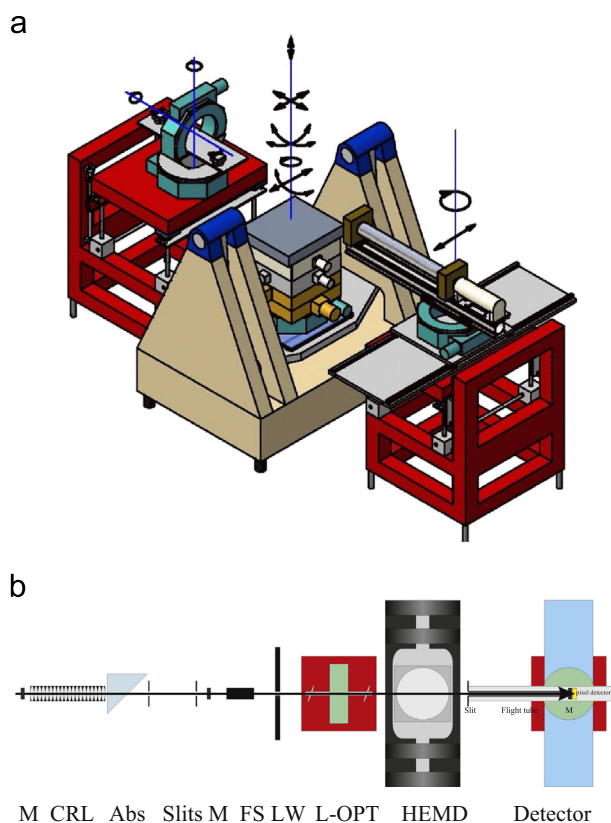


Fig. 1. (a) Schematic of the high energy micro diffraction (HEMD) setup at beamline ID15 of the ESRF showing from left to right the optics for liquid interface/surface studies (L-OPT in (b)), the HEMD and the detector table (Detector in (b)). (b) Top view of beamline setup with M, monitor diode; CRL, compound refractive lenses; Abs, PMMA Absorber; FS, fast shutter; LW, lead wall; L-OPT, optics for liquid interface/surface studies; HEMD, high energy micro diffractometer.

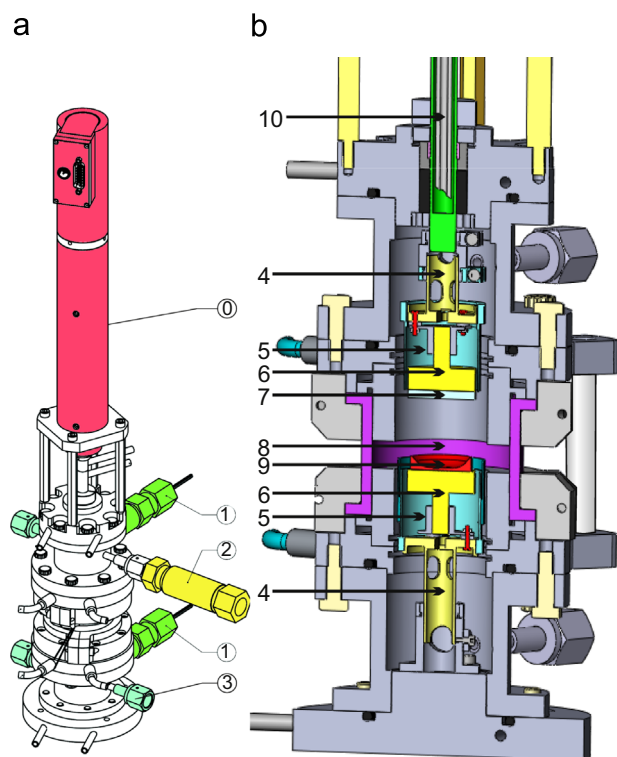


Fig. 2. (a) Schematic showing the actuator (0) for moving the substrate, two high pressure feed troughs (1) (max pressure 250 bar), one safety valve (2) (max pressure 50 bar), 2 gas inlets and 1 gas outlet connector (3). (b) Section view of the furnace's interior showing: heater support (4), heat shield (5), heater (6), substrate (7), carbon fiber window (8), crucible (9), water cooled connection towards actuator (10). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

high quality GaN crystals used at the moment is growth from super-critical ammonia with low quality crystalline GaN as nutrient, so-called ammonothermal growth. This technique requires pressures and temperatures above 100 bar and 650 K respectively. Another technique is the growth using nitrogen gas instead of ammonia which demands pressures up to 2000 bar and temperatures as high as 2000 K. In both cases the pressure forms a problem since a feasible setup with a 360° accessible X-ray window for in situ X-ray diffraction is not easily achievable without risking unsafe working environments. However, there is a third growth technique in which the pressure requirements are drastically reduced. GaN growth can be performed at significantly lower pressures ($P \leq 50$ bar in the case of N_2 use, or $P \leq 5$ bar in the case of NH_3 use) and temperatures up to 1073 K when adding sodium to the liquid gallium [16,17]. Using this last technique, the so-called Na-flux LPE method, a growth chamber for in situ X-ray diffraction is feasible.

Up to now most experiments to form GaN using the Na-flux method are performed in stainless steel tubes which are sealed by welding. After the growth is finished the tubes are cut open to remove the newly formed material and the highly corroded tubes are thrown away.

We set forth to create a reusable chamber (Fig. 2) for in situ optimization of reaction parameters for the GaN Na-flux growth technique.

The chamber is developed keeping in mind that it has to be transported in and out of a glovebox to ensure a safe transfer of sodium and liquid gallium into and out of the chamber. For this reason the chamber dimensions were restricted to that of the antechamber of the glovebox intended for use which resulted in maximum dimensions of the chamber equal to 268 mm height (substrate heater fully up) and 200 mm radius.

What follows is a list of the different requirements and the solutions chosen for the chamber.

Pressure and X-ray window: Given that Na-flux LPE GaN growth can be performed effectively at pressures up to 50 bar, the chamber is designed in such a way that the limiting factor is given by the maximum pressure, P_{max} , that can be applied to the X-ray window of the cell.

Often X-ray windows are made of beryllium (Be) or Kapton to ensure high transparency. Since liquid gallium is used in the chamber a Be window is unsuitable because gallium reduces beryllium to a powder. Also Kapton is not a good candidate because it will be decomposed by ammonia gas and cannot withstand high tensile forces without deforming.

For the above reasons carbon fiber was chosen as a material for the X-ray window. Carbon fiber is transparent for X-rays of relatively high energy, it is mouldable in virtually any shape and can withstand high tensile stress without structural failure. It does give some small angle and wide angle scattering but this can be subtracted from the signals of interest. Since carbon fiber sheets are held together with an epoxy resin, the resin has to be inert in the conditions applied to the window. We used three methods to achieve this. Firstly, by coating the inside of the window with boron nitride paint the window does not suffer from contact with hot ammonia gas while it remains transparent for X-rays. Secondly, gallium does not deteriorate the quality of the window. And lastly, the carbon fiber epoxy is much more resilient against ammonia attack if the window is not getting too hot. Since the window is directly cooled by the water cooled flanges it is attached to, only the small exposed region is heated considerably. By using two high volume ventilators the exposed part of the X-ray window can be kept well below 373 K even if the chamber is working at 1073 K and 50 bar for a long time.

The chamber has been successfully tested using a hydraulic press up to a pressure of 150 bar. This test was performed without attaching the actuator and without internal components and it assures the safe use at the routine pressure of 50 bar. The safe use is additionally assured by 4 metal bolts (one of them is visible on the right in Fig. 2b) which slightly compress the carbon fiber window to reduce the axial load on the glue holding the window (6500 kg at 150 bar). A disadvantage of the bolts is the blocking of X-ray windows over a range of 6° per bolt. Depending on the symmetry of the crystal under investigation the choice for 3 or 4 bolts circumvents this problem partly.

The radial load on the exposed part of the window (10 mm height, 52 mm inner diameter) at 150 bar is approximately 2500 kg. Combining these numbers with a hot and corrosive environment prompted for a large overcapacity in the accepted maximum tensile load on the carbon fiber window. Initial calculations showed that a window thickness of 0.5 mm should be enough to contain 150 bar of pressure at room temperature. By choosing a thickness of 2 mm a safe environment in a hot and corrosive environment should be achievable in terms of the window. The manufacturing of a 2 mm thick carbon fiber tube with rims on top and bottom posed a problem, however. The rim on top and bottom are present to reduce the axial stress on the glue and to provide a good place to clamp the window. Thin rims are however difficult to fabricate, especially when they should reduce axial force. By increasing the thickness of the window from 2 to 4 mm, which consequently increased the amount of material available to form the rims, this problem could be solved. Additional information on the fabrication of the window (type of glue, type of epoxy, carbon weave pattern, et cetera) was kept secret by the manufacturer [18].

All following safety tests were performed with the full chamber assembled. First a temperature test using 1 bar argon at 1123 K for 2 h showed that heaters, thermocouples, cable protection, pressure seals and X-ray window were unaffected. An additional pressure test was performed with a mix of 60% nitrogen and 40% ammonia at 5 bar and

1023 K without sodium and gallium to test the compatibility of the chamber with corrosive atmospheres.

Thereafter, the carbon fiber window was tested for radiation damage by irradiating 1 mm² of the window for 1 week with 10¹² 38 keV photons/s. This treatment introduced a slight discoloration of the inner epoxy layer which disappeared on wiping with a tissue. Subsequent scans of the carbon fiber comparing irradiated and non-irradiated parts show that the window behaves as an amorphous material without a change in absorption and diffraction on the heavily irradiated part. Compared to the more common beryllium or sapphire X-ray windows the carbon fiber window is reducing the price while strength and chemical stability are at least equal. Additionally, should the carbon fiber break, it will rip open, reducing damage to other parts while beryllium or sapphire will fail catastrophically.

Temperature: Basic working temperatures for effective Na-flux LPE GaN growth are reported up to 1073 K. For this reason the chamber is designed to work at a maximum temperature of 1123 K at the maximum pressure. Increasing the temperature further will overheat the carbon fiber window. However, if the pressure is reduced to approximately 25 bar the temperature can be increased to the maximum working temperature of the heaters, 1273 K (heatwave labs model 101275–27). Furthermore both heaters can be controlled independently to allow the use of a temperature gradient. Tests show that the applied gradient can be as high as 600 K over 1 cm.

Corrosion protection: The chamber is made from inconel 600 steel (Ni ≥ 72%, Cr 14–17%, Fe 6–10%) to prevent any corrosion by ammonia, evaporated sodium, liquid gallium or any reaction product (e.g. liquid sodium hydroxide or hydrogen gas). Park et al. used inconel as crucible material for GaN LPE growth [19] which resulted in traces of Cr and Fe in the grown GaN. Since we do not have a direct contact between inconel and metal flux the amount of impurities in GaN originating from inconel should be significantly lower than reported by Park et al.

All cables and feed throughs are coated by Teflon to prevent attack by hot ammonia gas. The temperature of the cables does not exceed 373 K which ensures chemical stability of the Teflon. However, the amount of fluoro-compounds present in the chamber is a cause of concern if one wants to perform other types of experiments.

3.3. The chamber

The carbon fiber X-ray window is marked pink in Fig. 2b. It is glued to both the inner (dark gray) and outer (light gray) metal parts. Additionally the outer metal parts are designed to press inwards, squeezing the window against the inner metal parts to further prevent leaking. All other seals in the chamber use kalrez O-rings (black) that are close to a water cooling channel to prevent degradation of the rubber due to overheating.

Loading the cell with substrate and metals can be done by unbolting several screws (light yellow). A sample change can therefore be done without disassembling the window connections. The crucible (9) can be loaded with the required materials while on the top heater a substrate can be mounted (7) which has a diameter up to 1 in. The substrate can be glued or clamped on an inconel plate that is attached to the physical heater. The inconel plate protects the heater from being corroded by gallium, sodium and sodium hydroxide and is easily exchanged.

There are two electrical feed throughs (Spectrite WFS 1/4"NTP with exchanged wire coating, marked (1) in Fig. 2a), one on the top and one on the bottom designed to withstand a pressure of 250 bar. The feed throughs are using a teflon plug to seal in the pressure. Additionally, there are four multi-connectors of which one is reserved for a safety valve, marked (2), which opens at

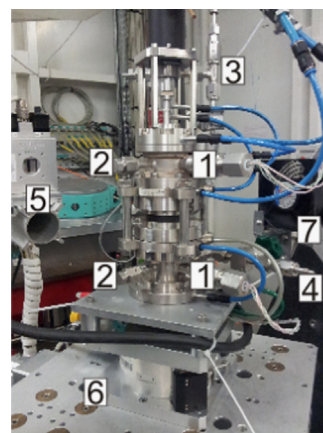


Fig. 3. The cell undergoing safety tests for pressure, temperature and corrosion at the ESRF high energy beamline. Shown are 1: Electrical feed throughs, 2: gas connectors, 3: gas inlet, 4: gas outlet, 5: detector arm, 6: HEMD diffractometer tower, 7: high volume fan.

50 bar. The others, marked (3), can be used for gas lines and a pressure gauge. On the top, marked (0), there is a heavy duty actuator (PI M-238.5PL) capable of moving the substrate reproducibly while the cell is under pressure. This specific actuator was chosen because of its maximum load capacity of 400 N. The design of the chamber then allowed for a water cooled tube (marked (10) in Fig. 2b) with outer diameter of 10 mm which at 50 bar generates a pushing force just under 400 N. Four consecutive kalrez gaskets (Dupont KF-3074), compressed by a metal plate on top of the chamber, allow reproducible movements of the tube on a micrometer scale while gases remain contained. The whole actuator and its support structure can be dismantled for easy manipulation and transportation while preparing for experiments. A picture of the whole cell in operation is shown in Fig. 3.

The whole furnace can be cleaned easily, if needed, after an experiment. The furnace, except for the crucible containing leftover sodium, can be immersed in demineralized water to remove any sodium hydroxide residue that could form on the furnace walls. Baking at 373 K in an autoclave will ensure a dry environment for a following experiment.

4. Experiment: Na-flux gallium nitride growth at 1073 K

Production of GaN is possible from the gas phase but yields are low due to large defect densities and crack formation. At the moment high quality GaN wafers grown in supercritical ammonia are commercially available with diameters up to 1 in. The production is however very demanding. The demands for production of GaN using Na-flux growth are potentially much easier to attain while the quality of the grown material is much better than achievable with gas phase growth. For these previous reasons LPE GaN is a likely candidate to compete with expensive high pressure GaN growth techniques for parts of the market where extreme high quality bulk crystals are not needed (e.g. LEDs, lasers). The quality of the bulk GaN crystal is largely dictated by the growing interface. The development of this interface is largely unknown in the case of GaN. At high pressure it is difficult to make an accessible optical path for interface characterization while gas phase reactors are often too bulky to manipulate in their entire form. For these reasons in situ characterization has been limited. For gas phase growth, some information on the amount of material grown and very little on its overall quality can be extracted with the in situ measurement of reflected light from a laser parallel to the surface normal of the substrate

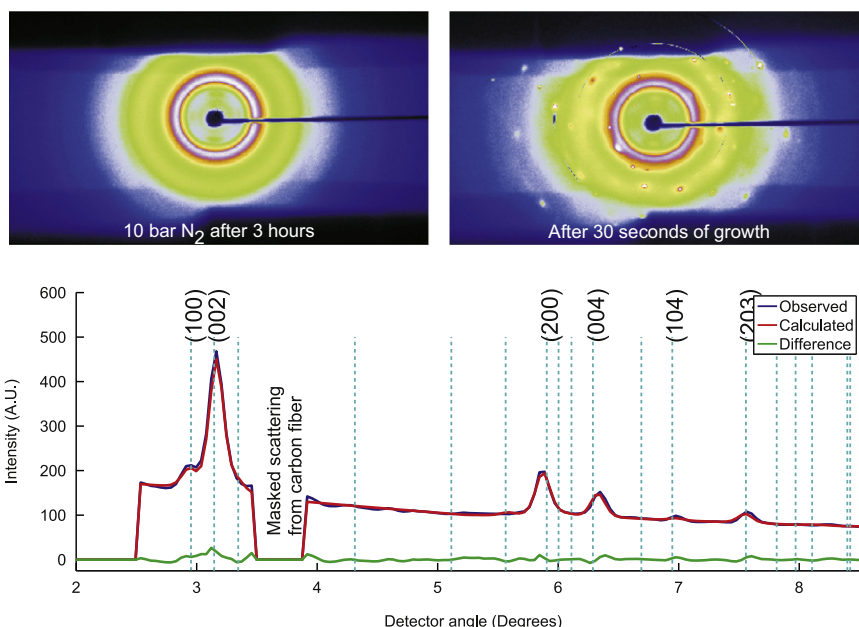


Fig. 4. Top left: Diffraction pattern taken just below the interface between 10 bar N₂ and Ga₁₃Na₇ mix. The intense circle is displaying the first liquid diffraction peak of the GaNa mix. Top right: Diffraction pattern on the interface between 50 bar N₂ and Ga₁₃Na₇ mix showing Bragg spots coming from polycrystalline GaN. Bottom: A standard le Bail fit on the middle image shows intensity on several GaN Bragg positions. The sample was not rotated during the exposure explaining the absence of other Bragg peaks.

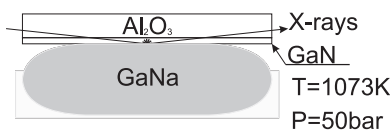


Fig. 5. Schematic of the envisioned high energy surface X-ray diffraction experiment. X-rays will pass through the side of the crystal and exit on the other.

[20, Chapter 3.4.3]. With conditions of 50 bar, 1073 K, liquid sodium and liquid gallium, the in situ characterization of GaN Na-flux growth is possible with our chamber. Additionally our chamber allows easy investigation of growth parameters like temperature, pressure and gas composition which normally requires growth of multiple samples and extensive, often destructive, characterization afterwards.

The experiment: The experiment was performed at ESRF beam-line ID15B using an X-ray energy of 87.3 keV. Solid Ga₁₃Na₇ was used to fill the crucible. In order to perform a controlled and well defined experiment the temperature was first increased in 1 bar of Argon gas. When increasing the temperature to 1073 K it was observed that the metal mix became liquid at a temperature close to 835 K in agreement with literature [21]. After reaching 1073 K the pressure was increased from 1 bar Ar to 10 bar N₂ which was left to equilibrate for 3 h. Growth of GaN at this point is possible according to [17], but very unfavorable. Even on the interface between N₂ gas and GaNa mix we did not observe any change in the scattered intensity during the equilibration time as is visible in top left in Fig. 4.

After increasing the pressure to 50 bar, the first image (top right in Fig. 4) immediately showed Bragg intensity indicating growth of crystalline material on the interface between gas and liquid. The Bragg spots became more intense but did not move in consecutive images which indicates growing polycrystalline material at the edge of the crucible, as expected from literature [22]. A le Bail fit (bottom Fig. 4) shows that the Bragg peaks observed are from hexagonal GaN which indicates that GaN can be grown with the furnace.

Additional use of a 1 in diameter GaN seed crystal (e.g. an MOCVD GaN buffer layer on 1 in sapphire, or an ammonothermally

grown 1 in wafer) which is placed on the top heater in the chamber can act as a smooth surface on which to perform surface diffraction. A well collimated 70 keV X-ray micro-beam can then impinge the crystal from one side (see Fig. 5) and penetrate unrefracted down to the buried interface [5]. The reflected beam which carries information from the buried interface leaves the crystal on the other side after a full transmission and may be detected in a standard way. A small correction should be applied for the change in absorption path length through the whole crystal however. A simple measurement of the total attenuation factor of the direct beam by the crystal, multiplied by the path length at specific angles of incident and exit will suffice. Furthermore, when performing off-specular CTR measurements the crystal rotates which implies an additional change in absorption path length throughout one scan unless circular crystals are used.

The chamber is primarily designed for interface diffraction at the ID15A end station. However, the images collected at the ID15B end station, which are presented here, show the feasibility of the foreseen experiments in this chamber in one image. Numerous Bragg peaks are reachable and not masked by the chamber. The parasitic scattering visible in the images is mainly originating from the carbon fiber window and is not causing problems for experiments at the ID15A end station unless collimation of the exiting beam is not discriminating between the origins of the scattering (front carbon fiber, sample, rear carbon fiber), because the slits are too far from the sample, too close to the detector or not closed enough. Recently the solid liquid interface between GaN and Ga at high pressure and high temperature has been successfully investigated using the HEMD device at the ID15A beamline in combination with the chamber presented in this paper. Those results will be presented elsewhere.

The deterioration of the chamber has been evaluated after several weeks of continued use. We have not found any damage to the chamber due to the harsh experimental conditions except for the two inconel plates holding the sample and crucible. These easily exchanged plates, intended to protect the heaters, should be replaced after approximately 6 months of continuous operation and can be cleaned in between experiments by slightly sanding them down to remove rough parts of the plate.

5. Conclusion

A new experimental setup, enabling high energy surface X-ray diffraction and high energy X-ray reflectivity from deeply buried, pressurized interfaces at elevated temperatures in harsh environments has been described. To demonstrate the potential of the new chamber, we have shown that GaN can be formed in the chamber using the Na-flux method. We have shown that growth occurs on the crucible holding the liquid metal mix. Further experiments and analyses are expected to provide new molecular scale information on the structure and order of the GaN–GaNa solid liquid interface during GaN growth.

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