Journal of Crystal Growth 498 (2018) 214–223

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

In situ X-ray monitoring of transport and chemistry of Ga-containing intermediates under ammonothermal growth conditions of GaN

S. Schimmel[a,*], P. Duchstein[b], T.G. Steigerwald[c,d], A.-C.L. Kimmel[c], E. Schlücker[c], D. Zahn[b], R. Niewa[e], P. Wellmann[a]

[a] Materials Department 6, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Martensstraße 7, 91058 Erlangen, Germany
[b] Computer Chemistry Center, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Nägelsbachstraße 25, 91052 Erlangen, Germany
[c] Institute of Process Machinery and Systems Engineering, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Cauerstraße 4, 91058 Erlangen, Germany
[d] Erlangen Graduate School in Advanced Optical Technologies (SAOT), Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Cauerstraße 4, 91058 Erlangen, Germany
[e] Institute of Inorganic Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

ARTICLE INFO

Communicated by Dr. Jaime Andrade Freitas

Keywords:
A1. Solvents
A1. Mass transfer
A1. Diffusion
A2. Growth from solutions
A2. Ammonothermal crystal growth
B1. Gallium nitride

ABSTRACT

Formation and transport of Ga-containing intermediates are essential for ammonothermal bulk growth of GaN. In this work, in situ X-ray transmission measurements are established as a tool for monitoring face-selective dissolution of GaN crystals as well as the Ga-concentration in the fluid. The accuracy of concentration determination by X-ray transmission measurements is evaluated and the detection limit for dissolved species is estimated. The detection limit is given both as a gallium concentration and as an attenuation coefficient, thus, it can easily be transferred to other materials of interest. Face-selective ammonothermal etching is investigated for both ammonoacidic and ammonobasic mineralizers. Time- and space-resolved monitoring of the concentration of Ga-containing intermediates is demonstrated using NH_4F mineralizer. The results are discussed with respect to the formation of Ga-containing intermediates and mechanisms of mass transport. Based on molecular dynamics simulations, the experimentally observed, unexpectedly low diffusion coefficient for the Ga-transporting species is ascribed at least partially to the diffusion of larger $[Ga_xF_y]^{3x-y}$ aggregates.

1. Introduction

Supercritical ammonia containing solubility-enhancing additives (mineralizers) has shown great potential as a solvent for the synthesis of nitrides [1]. Besides the III-nitrides AlN, GaN [2] and InN [3], multinary nitrides [4–6] and oxonitride perovskites [7,8] have also been obtained through ammonothermal synthesis methods, outlining the great potential of the ammonothermal method as an explorative tool for the synthesis of novel nitride and oxonitride materials [9]. Dissolution of the educts and transport of the dissolved species are particularly relevant to crystal quality and reasonably high crystallization rates in bulk crystal growth but also highly beneficial for the synthesis of microcrystalline products. Despite the fact that gallium nitride is the best-investigated material regarding its ammonothermal crystallization, literature on the nature of intermediates, dissolution kinetics and solubility is incomplete and partially contradicting. While relevant progress has been made in the identification of intermediates presumably representing the gallium-transporting species [10–12] as well as in numerical studies of convective mass transport in ammonothermal bulk crystal growth reactors [13], no experimentally obtained data on the distribution of intermediates within the fluid have been published.

We have developed a technique for in situ monitoring of ammonothermal reactors that is based on X-ray imaging [14,15]. This technique has so far been applied for studies of dissolution kinetics and solubility [14,15]. In this work, measurements obtained primarily during ammonoacidic dissolution experiments will be analyzed with respect to face-selective dissolution rates and concentration changes of intermediates. Face-selective etching rates are analyzed with regard to the chemistry of intermediates. Monitoring concentration inhomogeneities yields insight into transport mechanisms dominating in the employed nearly convection-free, nearly isothermal optical cell. Supplementary information is obtained from ex situ characterization of the surface morphology of the ammonothermally etched samples.

2. Experimental

Ammonothermal dissolution experiments were conducted in an optical cell that allows for monitoring the crystal and the surrounding

* Corresponding author.
E-mail address: saskia.schimmel@fau.de (S. Schimmel).

https://doi.org/10.1016/j.jcrysgro.2018.06.024

Available online 26 June 2018

fluid in situ by X-ray imaging by the use of window materials with low X-ray absorption [14]. The resulting projection image contains information about the dimensions of objects perpendicular to the path of rays. Thickness, density and mass attenuation coefficient of the objects in direction of the path of rays determine the image contrast, therefore, the images also contain information about thickness and material of the objects [16]. Experimental parameters used in individual experiments are given in Table 1. In experiment C1, one window made of sapphire and one made of boron carbide were used whereas in all other experiments the optical cell was equipped with sapphire windows at both sides. Supplementary information on the applicability of various materials as autoclave window materials for in situ X-ray measurements can be found in [17]. A drawing of our optical cell and a picture of a crystal mount can be found in [14]. Fill level refer to the boiling point of ammonia at atmospheric pressure.

It is important to note that unlike autoclaves designed for bulk growth experiments, our optical cell for crystal dissolution is designed so that local temperature gradients as well as convection are minimized. This is achieved by (i) a short reaction chamber which is oriented horizontally in the field of gravity and (ii) thick autoclave walls favoring homogenization of temperature gradients by fast heat transfer within the autoclave walls. The temperature measured at the outside surface of the sapphire windows is only about 1 °C lower than the temperature measured at the inner autoclave wall, indicating that even the sapphire windows do not represent major heat sinks. A local deviation in ammonia temperature of 1 °C at typical process conditions causes a density deviation in the order of 10^{-4} g/ml. This density deviation is two orders of magnitude lower than the density change caused by the highest concentration of dissolved species reported in this work, confirming that convective flow does not dominate mass transport (except during major leakages). In addition, no fluctuations of the internal temperature in the order of several °C within one second, which we have been identified as a typical sign of convection in other setups, have been observed even while heating up the autoclave. Thus, the design of our optical cell for crystal dissolution allows for the establishment of equilibrium conditions, facilitating the study of equilibrium parameters such as solubility. Moreover, the distribution of Ga-containing species within the fluid can be investigated without a dominating influence of convection, potentially yielding insights into diffusive transport.

The experimental setup and procedure for the ammonothermal GaN dissolution experiments with in situ X-ray monitoring are described in more detail in [15] and [14]. In all ammonoacidic experiments, 0.76 mmol mineralizer per ml autoclave volume were used. The mineralizer concentration in the ammonobasic experiments was 0.58 to 0.72 mmol/ml. Varying amounts of ammonia were used. See Table 1 for resulting pressure as well as for the temperatures used (measured at the inner wall of the autoclave using a type K thermocouple). The varying temperatures primarily originate from intentional variation of the preset temperature for investigating solubility at different temperatures (results of the solubility study have been published in [14,15]).

In order to visualize small changes in X-ray absorption, colormap plots were used (e.g. Fig. 5). In case of increasing background signal due to temperature increase at the CCD-based X-ray detector, the background signal for each image was evaluated in the area surrounding the area of view and subtracted prior to further image evaluation. Changes of X-ray absorption were evaluated with a custom-made Matlab script using reference images in a similar way as described in [16]. If necessary, disturbing shifts in the position of the area of view within the image were corrected by manually selecting the area of evaluation accordingly. Instead of plotting separate grayscale images showing local X-ray transmission increase and decrease as in [16], colormap[1] figures (as shown e.g. in Fig. 1) were used also for plotting difference images. The colorbars in the respective figures show 16 bit grayscale values. Supplementary image evaluation was done by analyzing profile lines through the images using Origin (e.g. Fig. 5). If necessary, background subtraction for profile line analysis was done directly in Origin in a semi-automatic procedure (manual control and, if necessary, adjustment of the selection of data points used for background determination). The cause for significant changes of the background signal during some experiments is a temperature increase of the detector at high operating temperatures of the optical cell due to the proximity of the devices.

Table 1
Overview of experiments and applied parameters. The temperature given is the temperature measured at the inner wall of the optical cell. Internally measured heating rates were about 60 ± 10 °C/h.

Experiment	Mineralizer	Maximum temperature [°C]	Maximum pressure [MPa]
A1	NH_4Cl	601 ± 2.5	135.2 ± 0.5
A2		549 ± 2.5	147.2 ± 0.5
A3		545 ± 2.5	231.7 ± 0.7
B1	NH_4F	600 ± 2.5	163.2 ± 0.5
B2		572 ± 2.5	49.7 ± 0.2
B3		404 ± 2.5	2.4 ± 0.1
B4		568 ± 2.5	67.0 ± 0.3
C1	NaN_3	538 ± 2.5	258.9 ± 0.8

For determining the mean effective photon energy in our setup, a calibration experiment using pure nitrogen was performed. Using pure nitrogen ensures that the composition and density of the absorbing medium inside the autoclave is precisely known in the calibration experiment. The relevant devices of our setup are an X-ray tube with tungsten anode and a filtration 2.5 mm Al-equivalent at 70 keV (Poskom PXP-20HF PLUS, operated at 100 keV acceleration voltage), a CCD-based X-ray detector (Dürr DR6.2) and two sapphire windows with a thickness of 10 mm each.

Supplementary characterization of samples was done by scanning electron microscopy (Jeol, JSM-7610F), energy-dispersive X-ray spectroscopy (Oxford, Aztec) and X-ray diffraction (Panalytical, Empyrean). By convention (following [18,19]), the [0 0 0 1] direction is chosen in the direction of the bond running along c-direction from the gallium to the nitrogen atom, with the (0 0 0 1) face being denoted as Ga-face and the (0 0 0 −1) face termed N-face. The polarity of the GaN samples was initially known from the HVPE process and is indicated in the respective images. If necessary, the polarity of specific samples was verified post-run by etching with phosphoric acid following the procedure described in [20] based on [21].

3. Results and discussion

3.1. Face-selective etching of GaN in presence of NH_4F, NH_4Cl and NaN_3 as mineralizers

Differently charged intermediate species are suspected to significantly contribute to the face-selectivity of growth rates [1]. Analogously, face-selective dissolution velocities are thought to contain information on intermediates. In the following, face-selective dissolution observed using ammonoacidic and ammonobasic mineralizers will be analyzed.

In order to visualize areas of predominant dissolution in the in situ X-ray projection images more clearly, subtraction of subsequent images was applied (unintentional movements of the autoclave are corrected if necessary). The procedure and exemplary results are described using

[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.