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Reactions

Ceramic liner technology for ammonoacidic synthesis

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ABSTRACT

The ammonoacidic crystal growth is a comprehensive method for the synthesis of novel compounds like nitrides or amindes but also for the growth of bulk single crystals like gallium or aluminum nitride for power electronics and photonics. In this report we describe a novel liner technology for growth autoclaves, showing high potential for several research purposes. Thereby the applicability of several ceramic materials as liner materials was investigated for the first time. Moreover, the effectivity of the new apparatus was verified in experimental studies. The described concept based on a silicon nitride crucible is characterized by low costs and diverse possible applications. For example its use is of advantage in fundamental research to explore new nitride materials. Furthermore, it shows high potential for X-ray imaging to investigate basic principles in growth of gallium nitride.

1. Introduction

The ammonothermal synthesis as a technique of high industrial potential already allows the commercial growth of gallium and aluminum nitride [1–6] with high quality, inter alia low dislocation density and low strain level for the use in optoelectronics and high power electronics. Moreover, the ammonothermal route is of high scientific interest in fundamental chemical research, providing new synthesis routes which yield new compounds. Multinary nitrides like $Ca_2Si_5N_8$ or $Ba_2Si_5N_8$ are applicable in nonlinear optics [7]. Doped nitrides like $Ca_2Si_5N_8$:Eu^{2+} or $Ca_2Si_5N_8$:Ce^{3+} are of interest for the fabrication of LEDs due to their efficient luminescence [8,9]. The growth or ferromagnetic semiconductor materials, like metal nitrides of the form Me_xN_y (with Me = Mn, Fe, Ni and N = Nitrogen) are of interest for spintronics [10].

The ammonothermal growth takes place in high pressure/high temperature autoclaves made of a nickel base alloy. Depending on the alloy, pressure and temperature range is limited because the complete autoclave is placed in a heater to achieve high internal process temperatures. Although the maximum pressure is not only determined by the high-temperature strength, dimensioning is also an influencing factor. Common materials for ammonothermal autoclaves are alloys from the Inconel© group (composition Ni-Cr/Fe-Al/Ti) [11–13], alternative materials like alloy 41 allow the realization of higher process temperatures [14] (see Table 1).

In order to increase the growth rate of the nitride, so-called mineralizers are commonly used as additives to improve the solubility of the nitride in supercritical ammonia. Two different groups of mineralizers can be distinguished: ammonobasic and ammonoacidic mineralizers. Ammonobasic mineralizers (e.g. lithium amide $LiNH_2$, sodium amide $NaNH_2$ and potassium amide KNH_2) introduce amide ions NH_2^- causing an ammonobasic solution which contains the corresponding alkali metal ions Li^+, Na^+ or K^+. Ammonobasic solutions are connected to moderate corrosion but also to low growth rates with the use of a liner [5].

Ammonacidic mineralizers (ammonium halides, e. g. ammonium chloride NH_4Cl, or ammonium fluoride NH_4F) introduce NH_4^+ ions causing an ammonoacidic solution that contains the corresponding halide ions Cl^- or F^-. Ammonoacidic environments are highly corrosive to the autoclave material, on the other hand, they enable higher growth rates than ammonobasic ones. As mineralizer also influences temperature dependence of solvent properties of the fluid, ammonoacidic conditions lead to a positive solubility coefficient and a forward solubility in the temperature range accessible in alloy 718 autoclaves [11]. The temperature profile of an ammonoacidic growth reactor is characterized by higher temperature in the dissolution region compared to the crystallization zone [3,12].

The corrosion of the autoclave material due to the supercritical ammonothermal fluid is a limiting factor for both growth routes,

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Table 1
Process parameters of ammonothermal growth reactors, used in different research groups [11,14].

Alloy	Specification	Ammonothermal reactors: process parameter window
Alloy 41	René© 41 UNS 07041/2.4973	$T_{max}^{alloy\,41} = 850\,°C$ $p_{max}^{alloy\,41} = 150\,MPa$
Alloy 718	Inconel© 718 UNS N07718/2.4668	$T_{max}^{alloy\,718} = 600\,°C$ $p_{max}^{alloy\,718} = 300\,MPa$

including growth rates and crystal quality [5,15]. Several groups are working on an improved reactor design to minimize autoclave corrosion for improved crystal purity. Recently, Pimputkar et al. [2] presented an ammonobasic growth setup with a silver liner. This capsule was non-hermetically sealed and allowed pressure balancing between inner and outer crucible volume. This set up enable enormous progress in crystal quality and growth rate.

State of the art reactors for ammonoacidic crystal growth are mostly equipped with a shrunken platinum crucible. However, this technique is limited because passivation of the sealing is not possible. High corrosive character of the fluid leads to the solution of large amounts of reactor metals, even if described small areas are not lined [15]. First, this leads to the incorporation of metal ions in grown crystals. Second, corrosive attack leads to high maintenance effort of sealing parts. Long term exposure could finally also cause fatal damages of the autoclave [16]. An alternative technique recently developed circumvents this sealing related issue by using a noble metal capsule, which is hermitically closed by welding [17]. That means, it is closed after filling with precursors, mineralizer, ammonia and seed. The closed capsule is positioned in a reactor with an internal heating system. This liner concept allows higher temperature and pressure range compared to the conventional ammonothermal growth reactors.

2. Materials and methods

2.1. Ceramics as liner materials

Due to latest scientific progress in the ammonoacidic crystal growth [11,18–20], we also focused on the implementation of a liner technology for this growth route. Ceramics are a promising alternative to the noble metal based concepts described above, due to their high corrosion resistance in many applications even in contact with acidic and supercritical fluids [21–26]. Furthermore, material costs are comparatively low. An appropriate liner technology should meet the following requirements:

i. For minimized impurity source, the material should show high chemical resistance under ammonoacidic conditions and low concentration of additives or binder. Moreover, nitride ceramics are preferred.
ii. Sufficient mechanical stability should allow a stable handling at high pressures.
iii. Beside growth experiments, the liner technology should allow a variety of alternative application options.
iv. To provide impermeability of the liner material as far as possible low porosity is required.
v. Low material and processing costs of ceramic material are essential to realize efficient up scaling.

To meet these requirements, two approaches were investigated. First, the suitability of ceramic films to passivate the reactor surface was tested. In the second part, a concept based on a pressure balanced ceramic crucible was developed.

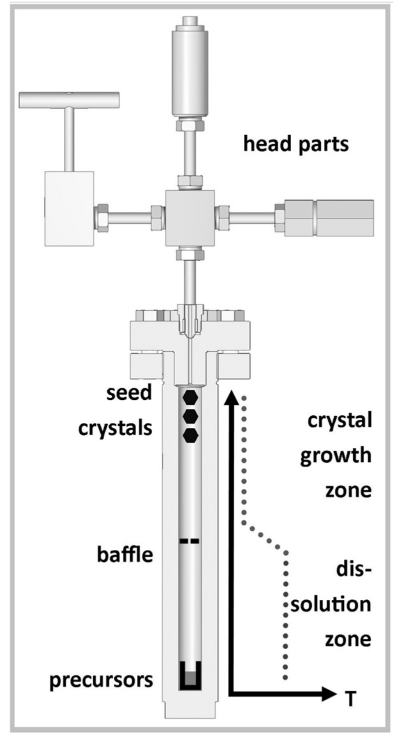

Fig. 1. Typical autoclave for the ammonothermal crystal growth including internal setup. Temperature gradient is realized by an external heater.

2.2. Screening tests

Chemical and physical stability of different material samples with a simple geometry was evaluated by carring out resistance experiments in an unlined custom made ammonothermal reactor made of alloy 718 as shown in Fig. 1. Head parts like fittings, tubes or rupture disk are commercially available and made of stainless steel (e.g. 1.4571 or 1.4435) and manufactured by SITEC-Sieber Engineering AG, Switzerland. The samples were tested in ammonia (Linde, 99.999%), where ammonium chloride (Sigma-Aldrich, 99.998% based on trace metals basis) was added with a concentration of $c_{mol}(NH_4Cl) \approx 6\%$. The mineralizer was placed in a small crucible at the bottom of the autoclave. Ceramic corrosion samples were positioned using a small rack inside the vessel. The complete inner setup was also made of alloy 718. After the autoclave was closed, it was connected to the pilot plant, evacuated and purged with nitrogen three times to eliminate oxygen. Finally, the autoclave was charged with ammonia to reach the desired filling rate. Heating the complete autoclave using custom made heating sleeves (Winkler GmbH) to $T \approx 450\,°C$ delivered a vapor pressure of the supercritical fluid of approximately $p \approx 300\,MPa$ (pressure transmitter P2VA1, HBM). To obtain information regarding the general chemical resistance, an exposure time of two days was chosen. After this reaction time, the autoclave was cooled down to room temperature, ammonia was discharged and finally the vessel was purged with nitrogen and evacuated for three times again to remove ammonia. Then the autoclave was opened and samples were cleaned with distilled water in an ultrasonic cleaner to eliminate loose particles and ammonia containing residuals.

3. Physical and chemical stability of ceramic coatings under ammonoacidic conditions

3.1. Experimental procedure

After corrosion test were carried out as described in Section 2.2, the coating samples were investigated metallographically. That