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# Ammonothermal Crystal Growth of Indium Nitride

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Keywords: Indium nitride; InN; Crystal growth; Ammonothermal synthesis

InN crystals with hexagonal shapes were grown from  $InCl_3$  and  $KNH_2$  in supercritical ammonia at around 280 MPa. For a successful crystal growth a molar ratio of the chloride to the amide of 1:3 was applied, thus providing an essentially ammononeutral milieu. The obtained InN crystals vary in size and aspect ratio depending on the applied furnace temperature: at 663 K hexagonal platelets up to 2 µm in diameter, as well as rods with lengths of 4 µm and diameters of 1 µm were obtained; at 773 K rods grew up to 2.5 µm in length. By combining both temperature programs, with a 10 h annealing step at both temperatures, we were able to increase the crystal size up to 5.2 µm in length and 0.4 µm in diameter.

#### Introduction

Group-III nitrides have attracted a lot of attention during the past years. Their optical and electronic properties are of high interest for optical devices (LEDs, lasers) and electronic applications.<sup>1</sup> Except for thallium(III) nitride, all binary nitrides of group III elements are known.<sup>2</sup> There is only very little experimental evidence for the existence of an explosive Tl<sub>3</sub>N.<sup>3-5</sup> At ambient conditions cubic and hexagonal graphite-like BN are stable, while a thermodynamically metastable wurtzite-type BN can be obtained at pressures of more than 10 GPa.<sup>6-8</sup> *h*-BN has a bandgap of 5.77 eV,<sup>9</sup> AlN of 6.2 eV,<sup>10</sup> and GaN of 3.39 eV.<sup>11</sup> The bandgap for InN was estimated on InN films grown from molecular-beam epitaxy by IR-reflection experiments to 0.7 eV.<sup>12</sup> Other experimentally obtained bandgap values scatter from 0.9 to 1.9 eV and apparently depend on the the morphology (for example layers, nano-rods, nano-particles) and growth technique of the InN.<sup>13,14</sup> The growth technique in this sense determines defect types and densities as well as impurities and their concentrations as major factors affecting the experimental band gaps.

While the synthesis and crystal growth of many technological relevant nitrides has seen significant advances, InN is still notoriously difficult to produce. InN can be obtained as thin films or microstructures by various procedures like molecular-beam epitaxy (MBE),<sup>15</sup> metal-organic chemical vapor deposition (MOCVD),<sup>14</sup> ammonolysis of In<sub>2</sub>O<sub>3</sub> or thermolysis of In(NH<sub>2</sub>)<sub>3</sub>, Na<sub>x</sub>In(NH<sub>2</sub>)<sub>3+x</sub> (x = 1 - 3) and K<sub>x</sub>In(NH<sub>2</sub>)<sub>3+x</sub> (x = 2, 3).<sup>16,17</sup> Additionally, nanocrystalline particles and fibers can be obtained using wet chemical approaches.<sup>18,19</sup> The main problem is the low thermal stability (decomposition ~500 °C)<sup>20</sup> of InN and the low heat of formation of -28.6 ± 9.2 kJ/mol in synthesis. InN is metastable towards the decomposition into the elements above 258 K.<sup>21</sup> In InN layers the formation of In nanoparticles and four atom

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clusters are suspected, which would have huge influence on experimental measured values like electron mobility and saturation velocity.<sup>22,23</sup> Furthermore, in MBE and MOCVD the use of carbon containing precursors or organic solvents leads to carbon impurities and a higher defect concentration in the InN microcrystals or layers. Due to the stabilizing effect of ammonia and nitrogen pressures, the successful synthesis of InN via the ammonothermal route was predicted in 1995 by Dwilinski analogous to the ammonothermal GaN synthesis.<sup>24</sup> GaN can be synthesized using a great variety of mineralizers in the ammonoacidic milieu, as well as in the ammonobasic milieu. In the ammonoacidic milieu, ammonium halides can be used as mineralizers, or it can be started directly from the gallium halides. Syntheses in the ammonobasic milieu can be performed using alkali (Li – Cs) or alkaline-earth metal (Ba, Sr) amides.<sup>2,25,26</sup> Wang and Callahan indicated the formation of microcrystalline InN from metallic indium with KNH<sub>2</sub> as mineralizer at 450 °C under ammonothermal conditions, but gave no details.<sup>27</sup> In an independent experiment, Purdy et al. reported the transport of elemental indium in a temperature gradient under ammonacidic conditions.<sup>28</sup>

Here we report the first growth of InN crystals in the  $\mu$ m range from ammonothermal synthesis employing InCl<sub>3</sub> and KNH<sub>2</sub> as reactants.<sup>29</sup>

#### **Experimental section**

Due to the oxygen sensitivity and hygroscopic properties of the starting materials all handlings were performed in an argon-filled glove box (MBraun, Garching, Germany).

Reactions were carried out in a customized 97 ml autoclave made of nickel-based Alloy 718® with ceramic liners manufactured from boron nitride and silicon nitride.<sup>30,31</sup> The autoclave was heated in an one side closed tubular furnace (HTM Reetz GmbH, Berlin, Germany), which leads

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to a natural temperature gradient. The given temperatures refer to the temperature of the furnace, however, our set up leads to an average temperature about 150 K lower inside the reactor vessel and a temperature gradient of about 100 K between hottest and coldest spot.<sup>32</sup> During the reaction the pressure was monitored using a digital pressure transmitter (P2VA1/5000bar and DA2510, HBM GmbH, Ismaning, Germany).

Ammonia (99.999 % anhydrous, Linde) was purified to a final grade of < 1 ppbV of water, oxygen and carbon dioxide (MicroTorr MC400-720F gas purifier, Rainer Lammertz pure gas products, Hürth, Germany). The amount of ammonia condensed into the autoclave was determined volumetrically using a self-built tensieudiometer after Hüttig.<sup>33</sup>

The following chemicals were purchased and used as delivered: InCl<sub>3</sub> (99.999% metal basis, Sigma Aldrich) and KNH<sub>2</sub> (synthesized from K (Merck) in liquid ammonia at 373 K using an autoclave purchased from Roth with a volume of 100 mL).

The ceramic liner was loaded with  $InCl_3$  (2.3 mmol) and  $KNH_2$  (5.75 – 9.2 mmol) and assembled in the autoclave. The autoclave was evacuated and afterwards filled with ammonia (1.33 mol) to a filling degree of 92.5 %. All experiments were carried out in a ceramic liner.<sup>30</sup> The autoclave was placed in a vertically orientated tubular furnace and heated with a heating rate of 1.4 K·min<sup>-1</sup> from room temperature to 663 K – 723 K. The maximum temperature was maintained for 10 h to 120 h at a maximum pressure of 300 MPa, then left to cool down to room temperature with various cooling rates (see Results and Discussion). Afterwards, the excessive liquid ammonia was vented in a controlled manner via an oil filled bubbler, before the reaction products were collected.

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The products were analyzed by powder X-ray diffraction (PXRD), using a powder diffraction system STADI-P (Stoe & Cie) equipped with a Mythen 1K detector and Mo-K<sub> $\alpha$ 1</sub> radiation ( $\lambda$  = 0.71093 Å).

Scanning electron microscopy (SEM) images were taken using different microscopes: a Zeiss DS982 Gemini, a Zeiss Gemini II (both Carl Zeiss Microscopy GmbH, Jena, Germany) and a FEI Quanta 250 (FEI Company, Hillsboro, OR, USA). The SEM samples were prepared in air without sputtering.

Elemental analysis of H, N, and O was obtained using the hot gas extraction technique (ONH836 determinator, Leco Corporation, St. Joseph, Michigan).

#### **Results and Discussion**

A series of experiments with different molar ratios of KNH<sub>2</sub> and InCl<sub>3</sub> ranging from 2.5 to 4 at a maximum temperature of 723 K and a maximum pressure of 300 MPa was carried out. In the ammonobasic milieu (molar ratio  $n(\text{KNH}_2)/n(\text{InCl}_3) > 3$ ), no InN was obtained, while under ammonoacidic conditions (molar ratio < 3) elemental indium next to small amounts of InN was found. Earlier we have observed formation of In<sub>3</sub>Ni<sub>2</sub> in reactions without use of a liner and thus direct contact of the reactants with the inner metallic autoclave surface.<sup>32</sup> Therefore, ceramic liners with lid were applied.<sup>30</sup> In the early experiments BN was used as liner material, while Si<sub>3</sub>N<sub>4</sub> was used in the later experiments. Most successful experiments were conducted with molar ratios of exactly  $n(\text{KNH}_2)/n(\text{InCl}_3) = 3$ , thus close to an ammononeutral range in a solution of effectively KCl and ammonia. Products obtained from synthesis using boron nitride liners always contained three phases, namely InN, KCl and In<sub>2</sub>O<sub>3</sub> according to PXRD patterns. SEM revealed octahedral KCl crystals, which grow up to several  $\mu$ m in size. Fig. 1 shows such

octahedral crystals next to spherical aggregates of hexagonal plates, rods, and truncated pyramids. Fig. 2 gives an enlarged detail of these spherical InN aggregates. InN crystallites within these aggregates typically show sizes of up to about 500 nm. We suspect that In<sub>2</sub>O<sub>3</sub> serves as nucleation centers and finally rests in the centers of these spherical aggregates. The InN was always found in the hot zone of the autoclave, where the initial InCl<sub>3</sub> was placed, indicating either an exothermic transport to the hot zone or the absence of effective transport under the applied conditions.

The most likely source of oxygen impurities is the porous boron nitride liner. Thus, for a second row of experiments we applied liners manufactured from silicon nitride (Si<sub>3</sub>N<sub>4</sub>), which provides a surface with significantly less porosity. Additionally, the liner was vacuum-heated at 423 K for 12 h and exclusively handled strictly inert prior use. This operation successfully led to samples without any noticeable In<sub>2</sub>O<sub>3</sub> impurities according to PXRD (Fig. 3). At temperatures of 773 K we obtained isolated hexagonal needle-shaped InN crystals with high aspect ratio and dimensions up to 2.5 µm in length and 0.4 µm in diameter (Fig. 4). The absence of oxygen in the bulk product was proven by hot gas extraction measurements, which revealed only small amounts of H and O (w(H) = 0.085 % and w(O) = 0.427 %) probably caused by the transfer from inert storage to the measurement device. Fig. 3 shows the PXRD pattern of the product from synthesis using a silicon nitride liner. Unit cell parameters of *a* = 3.534(5) Å and *c* = 5.712(5) Å from least-square refinements agree well with literature data (*a* = 3.533(4) Å and *c* = 5.693(4) Å) from samples obtained by Juza and Hahn from the antmonolysis of (NH<sub>4</sub>)<sub>3</sub>InF<sub>6</sub>.<sup>34,35</sup>

Lower synthesis temperatures of 663 K again applying the  $Si_3N_4$ -liner produced InN crystals of different shape and size. We observed crystals with low aspect ratio and hexagonal platelet shape up to 2.0 µm in diameter shown in Fig. 5 (663 K for 10 h and subsequent cooling for 96 h) Page 7 of 18

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and isolated hexagonal rod-shaped InN crystals with high aspect ratio and dimensions up to 4.0  $\mu$ m in length and 1.0  $\mu$ m in diameter shown in Figs. 6 + 7 (slow heating to 663 K in 48 h, 663 K for 24 h and cooling duration of 4 h). However, in several experiments, we have observed that a variation of the heating and cooling duration had shown no significant influence on the maximum crystal size, as long as the overall synthesis duration including heating and cooling sequence is around 100 h. Furthermore, it can be stated that the formation of InN starts in the first 15 h of the synthesis. In a short experiment of only 15 h entire reaction duration (maximum temperature of 663 K for 5 h), hexagonal plates with dimensions of up to 1  $\mu$ m formed.

With the aim to further increase the crystal sizes we have combined the two successful synthesis temperatures (663 K for 10 h followed by 773 K for 10 h) and obtained isolated hexagonal needle-shaped InN crystals with dimensions up to 5.2  $\mu$ m in length and 0.4  $\mu$ m in diameter (Fig. 8). Long heating durations at 773 K (over 150 h) resulted in decomposition of InN, evidenced by observation of small metallic In spheres. PXRD revealed metallic indium next to potassium chloride as products. The decomposition upon enlarged heating durations can be accorded to the metastable character of InN.<sup>21</sup>



**Figure 1:** SEM image of the obtained bulk material at 773 K (t = 24 h, natural cooling, BN-liner). The octahedral crystals represent the well crystalized KCl as a coproduct of the reaction of indium chloride with potassium amide.



**Figure 2:** Detailed SEM image of the spherical InN aggregates, obtained at 773 K (t = 24 h, natural cooling, BN-liner).



**Figure 3:** PXRD pattern of the initial ammonothermal reaction of InCl<sub>3</sub> with KNH<sub>2</sub> using the Si<sub>3</sub>N<sub>4</sub>-liner (T = 773 K, t = 24 h); upwards: measured pattern, downwards: *h*-InN (calc.),<sup>35</sup> \* KCl.



Figure 4: SEM image of InN rods from synthesis at 773 K (t = 24 h, cooling rate 0.11 K/min,

Si<sub>3</sub>N<sub>4</sub>-liner).



**Figure 5:** SEM image of InN platelets from ammonothermal synthesis at 663 K (t = 10 h, cooling rate 0.06 K/min, Si<sub>3</sub>N<sub>4</sub>-liner).



**Figure 6:** SEM image of InN from ammonothermal synthesis at 663 K (t = 100 h, cooling rate 0.26 K/min, Si<sub>3</sub>N<sub>4</sub>-liner).



Figure 7: SEM image of InN from ammonothermal synthesis at 663 K (t = 24 h, cooling rate

1.54 K/min, Si<sub>3</sub>N<sub>4</sub>-liner).



**Figure 8:** SEM image of InN from ammonothermal synthesis at 663 K and 773 K (t = 10 h at both temperatures each, cooling rate 1.6 K/min, Si<sub>3</sub>N<sub>4</sub>-liner).

#### Conclusion

 The ammonothermal method can be successfully applied to obtain InN crystals. We have obtained crystals with sizes in the range of up to 5.2 µm in length or up to 2.0 µm in diameter depending on the synthesis temperature. Lower temperatures (663 K) favor the growth of hexagonal platelet crystals and rods with a low aspect ratio, while a temperature increase to 773 K leads to hexagonal needles. Further optimization of reaction conditions is required to increase the crystal size. In contrast to GaN, which is grown either in ammonobasic or ammonoacidic milieu, it seems that the ammononeutral regime is most promising for InN crystal growth. For growth of larger crystals, particularly exclusion of oxide impurities and avoiding the direct contact to the reducing metallic autoclave surface appeared of utmost importance. Variation of starting materials and mineralizer may open ways to more favorable temperature conditions for InN crystal growth. Experiments to explore the chemical processes are currently underway.

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#### Synopsis

InN crystals with hexagonal shapes up to several  $\mu$ m in size were grown ammonothermally at around 280 MPa in an essentially ammononeutral milieu. The crystal morphology varies with maximum synthesis temperature in size and aspect ratio between hexagonal platelets and rods.