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Development of Cost-Effective Native Substrates for Gallium Nitride-Based Optoelectronic Devices via Ammonothermal Growth

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1. Introduction

Since the realization of blue light emitting diodes (LEDs) in 1991 (Nakamura et al., 1991), GaN-based optoelectronic devices have been widely developed and commercialized. Adding blue and green colors to the existing red LEDs enabled full-color displays and white light sources. Blue LEDs were also combined with yellow phosphor to achieve solid-state white light sources. Another major application of GaN-based materials is blue laser diodes (LDs). After the first lasing in 1996 (Nakamura et al., 1996), blue LDs were intensively developed to commercialize high-density digital video disks (HD-DVDs). Starting from its applications to indicators, traffic lights, cell phone back-lighting, and HD-DVDs, GaN-based optoelectronic devices are now used in general lighting and replacing conventional electric light sources using vacuum tubes.

Due to the lack of native substrates (e.g., GaN or AlN) in the 1980s and early 1990s, GaN-based devices were developed on heterogeneous crystalline substrates such as c-plane sapphire and c-plane silicon carbide. After the commercialization of free-standing GaN substrates grown by hydride vapor phase epitaxy (HVPE) on gallium arsenide (Motoki et al., 2007), blue LDs have been developed on GaN substrates because highly dislocated devices on heteroepitaxial substrates were susceptible to degradation caused by high current density (1~10 kA/cm²) in laser devices. Nevertheless, people have not switched to GaN substrates for LED applications because of the following reasons: 1) extremely high cost of GaN wafers ($5,000~$10,000 per 2” in 2008) does not fit the cost structure of LEDs; and 2) dislocations do not have deteriorating effects on LEDs owing to the low current density. However, to realize solid-state lighting which replaces existing light bulbs, HB-LEDs are required to handle higher current than conventional LEDs. State-of-the-art HB-LED chips carry 1 A in 1 mm² chip (Cree, 2009), which corresponds to 0.1 kA/cm². Although power saturation at high current injection called “droop” is not an easy problem to solve (Stevenson, 2009), each HB-LED chip will be required to handle even higher current densities to achieve significant reduction of lumen cost in the near future. When the current density becomes comparable to that of LDs, GaN substrate will be indispensable to ensure the reliability of the device. With an increasing demand for low-cost GaN substrates, several
methods such as HVPE (Hanser et al., 2008; Fujito et al., 2009), high-pressure solution growth (Porowski, 1999; Inoue et al., 2001), flux method (Yamane et al., 1998; Kawamura et al., 2003) and ammonothermal method (Dwiliński et al., 1998; Ketchum et al., 2001; Purdy et al., 2002) have been researched to grow bulk GaN. Among these methods, the ammonothermal growth of bulk GaN has a potential to provide cost competitive GaN wafers for lighting LEDs due to its excellent scalability.

This chapter first explains the ammonothermal growth including its development history and current major research activities. Second, a physicochemical aspect of the method is described. The ammonothermal growth of GaN is categorized into the basic and acidic ammonothermal growth. Owing to their physicochemical properties, these two conditions exhibit a significant difference in terms of the phase selection, solubility, and chemical compatibility with reactor materials. The third section covers recent results of GaN growth by the basic ammonothermal method. Crystal quality characterized with x-ray diffraction (XRD), transmission electron microscopy (TEM), Nomarski differential interface contrast microscopy (Nomarski microscopy), secondary ion mass spectroscopy (SIMS), photo absorption spectroscopy, and four-probe measurement is discussed. The last section concludes with a summary and future prospect. The progress in the ammonothermal growth promises cost-effective GaN wafers for solid-state lighting LEDs.

2. Ammonothermal growth

2.1 Fundamentals of ammonothermal growth

A method of growing crystals in supercritical solvent is generally called solvothermal growth. The solvothermal growth utilizes an autoclave which can contain supercritical solvent at high-pressure and high-temperature. The most successfully commercialized solvothermal growth is hydrothermal growth of $\alpha$-quartz, in which silica is dissolved in supercritical water and recrystallized on seed crystals. The solvothermal growth has an advantage of scalability over other crystal growth methods. Nowadays, a hydrothermal quartz autoclave can grow over 1,000 crystals in one batch. Ammonothermal growth is one type of solvothermal growth using ammonia as a solvent, which is mainly used to grow nitride materials. In general, growth mechanism of GaN in ammonothermal growth is explained as follows: 1) nutrient such as metallic Ga or polycrystalline GaN placed in a nutrient region dissolves in supercritical ammonia under high-pressure (100~400 MPa) and high-temperature (400~600 °C); 2) the dissolved solute is transported by the convective flow of solvent (i.e. supercritical ammonia) to a seed region; 3) the solvent becomes supersaturated in the seed region under different temperature and/or pressure condition from the nutrient region; and 4) GaN crystallizes on seed crystals. Schematic drawings of typical ammonothermal growth setups are shown in Fig. 1. An autoclave heated by external heaters houses internal components and source materials. The heater is divided into two or more regions; the lower region is usually maintained at higher temperature than the upper region. The configuration differs depending on the acidity because temperature dependence of solubility varies with the acidity of the supercritical ammonia. In the case of basic ammonothermal growth, the nutrient is located in the upper region of the autoclave and the seed crystals are located in the lower region of the autoclave as shown in Fig.1 (a). By contrast, the seed crystals are located in the upper region and the nutrient is located in the lower region for the acidic ammonothermal growth as shown in Fig.1 (b).
2.2 Development history and current activities of the ammonothermal GaN growth

The first ammonothermal growth of group III nitride crystals was synthesis of AlN reported in 1990 (Peters, 1990). Surprisingly, the result in this report has already implied the retrograde solubility of group III nitride materials in ammono-basic solutions. In 1995, synthesis of GaN in the ammono-basic environment was reported (Dwiliński et al., 1995), followed by reports in the ammono-acidic environment (Purdy, 1999) and the ammono-basic environment (Ketchum et al., 2001). After these pioneering works of microcrystalline GaN synthesis, the research started to focus on seeded growth of GaN via fluid transport (Callahan et al., 2004). Retrograde solubility of GaN in ammono-basic solution was reported in a technical journal in 2005 (Hashimoto et al., 2005) as well as in a patent application (Dwiliński et al., 2001), while research on ammono-acidic conditions revealed normal dependence of solubility on temperature (Kagamitani et al., 2006). In 2007, the main focus of the ammonothermal GaN growth has shifted from thick-film growth to bulk growth (Hashimoto et al., 2007) and an exceptionally high-quality GaN bulk crystal was demonstrated in 2008 (Dwiliński et al., 2008). Since these reports on bulk-shaped GaN were published, the ammonothermal growth has drawn more attention in the research body of GaN crystal growth.

Currently, there are several companies and institutes researching and developing the ammonothermal growth of GaN such as Ammonoz Oo. in Poland, SixPoint Materials, Inc. in the U.S.A., Mitsubishi Chemical Corp. in Japan, Soraa, Inc. in the U.S.A., the University of California, Santa Barbara (UCSB) in the U.S.A., the Air Force Research Laboratory (AFRL) in the U.S.A., Tohoku University in Japan, and Asahi Chemical Corp. in Japan. There are mainly three different approaches to grow GaN in supercritical ammonia: 1) basic
ammonothermal with external heaters; 2) acidic ammonothermal with external heaters; and 3) acidic high-temperature ammonothermal with internal heaters. Table 1 summarizes typical growth configurations, conditions and research groups.

<table>
<thead>
<tr>
<th>Growth configuration</th>
<th>Basic</th>
<th>Acidic</th>
<th>Acidic high-temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seeds: lower region</td>
<td></td>
<td>Seeds: upper region</td>
<td>Seeds: upper region</td>
</tr>
<tr>
<td>Nutrient: upper region</td>
<td></td>
<td>Nutrient: lower region</td>
<td>Nutrient: lower region</td>
</tr>
<tr>
<td>Temperature range (°C)</td>
<td>400~600</td>
<td>400~600</td>
<td>600~1500</td>
</tr>
<tr>
<td>Pressure range (MPa)</td>
<td>100~400</td>
<td>100~400</td>
<td>100~400</td>
</tr>
<tr>
<td>Mineralizers</td>
<td>Alkali metals and their compounds</td>
<td>Halide compounds</td>
<td>Halide compounds</td>
</tr>
<tr>
<td>Research institutes</td>
<td>Ammono z o. o. AFRL</td>
<td>Tohoku University</td>
<td>Asahi Chemical Corp. Soraa, Inc.</td>
</tr>
<tr>
<td></td>
<td>Mitsubishi Chemical Corp.</td>
<td>UCSB</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SixPoint Materials, Inc.</td>
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<td></td>
</tr>
</tbody>
</table>

Table 1. Summary of current major activities of the ammonothermal growth.

3. Physicochemical properties of the ammonothermal growth

The ammonothermal method is divided into two categories in terms of acidity of supercritical ammonia: the basic ammonothermal method and the acidic ammonothermal method. These two methods exhibit quite different physicochemical properties. A chemical additive called a mineralizer determines the acidity of the fluid. Basic mineralizers are alkali metals and their compounds such as potassium (K), sodium (Na), lithium (Li), potassium amide (KNH₂), sodium amide (NaNH₂), lithium amide (LiNH₂), and sodium azide (NaN₃). Acidic mineralizers are halide compounds such as ammonium fluoride (NH₄F), ammonium chloride (NH₄Cl), ammonium bromide (NH₄Br), ammonium iodide (NH₄I), and gallium iodide (GaI₃). In addition to controlling acidity of fluid, mineralizers play an important role of increasing the solubility of GaN in the supercritical ammonia. Mineralizers also have an influence on phase selection of GaN; that is, formation of hexagonal wurtzite GaN or metastable cubic zinc-blende GaN. In this section, physicochemical properties of ammonothermal growth are discussed in terms of phase selection, solubility, and impact on reactor material.

3.1 Phase selection of GaN in ammonothermal synthesis

In addition to the stable wurtzite structure, GaN represents two other phases: zinc-blende structure and rocksalt structure. Rocksalt GaN is only observed under an extremely high pressure (Xia et al., 1993), whereas zinc-blende structure is a low-temperature metastable phase and more frequently observed for GaN grown at relatively low temperature (Wu et al., 1996) or grown on zinc-blende templates (Mizuta et al., 1986). Since the growth temperature of GaN in the ammonothermal method falls in the temperature range at which
metastable zinc-blende GaN is frequently formed, it is of great interest to investigate the phase of GaN synthesized in the ammonothermal growth. Fig. 2 illustrates X-ray $2\theta$-$\omega$ scan for microcrystalline GaN powders synthesized by the ammonothermal method with various mineralizers. As shown in the figure, microcrystalline GaN powder synthesized with acidic or neutral mineralizers contained both wurtzite and zinc-blende phases. On the contrary, GaN powder synthesized with basic mineralizers contains negligible amount of zinc-blende GaN. Similar result was reported in literature (Dwiliński et al., 1995; Purdy et al., 2002). Considering the temperature range of GaN syntheses in this experiment, it is quite natural that the microcrystalline GaN contains zinc-blende phase. Therefore, we argue that some kinetics have a dominant influence on the selection of wurtzite phase in the basic environment. From an industrial point of view, basic mineralizers have a great advantage because a potential inclusion problem of metastable phase can be avoided. Ammonothermal growth with acidic mineralizers requires a delicate optimization of growth condition to eliminate phase inclusions (Ehrentraut et al., 2008a).

Fig. 2. X-ray $2\theta$-$\omega$ scan for microcrystalline GaN powders synthesized with various mineralizers. Both wurtzite (WZ) and zinc-blende (ZB) GaN were synthesized with acidic or neutral mineralizers, while wurtzite GaN was synthesized with basic mineralizers.

### 3.2 Solubility of GaN in supercritical ammonia

It is indispensable to understand the solubility of GaN in supercritical ammonia for successful development of ammonothermal GaN growth. Several groups have reported solubility data; however, the reported data are scattered possibly due to different conditions, immaturity of measurement technique, and measurement errors. Fig. 3 shows one example of solubility curve as a function of temperature. GaN was dissolved in supercritical ammonia at 76±12 MPa with 1.5 mol% of NaNH$_2$ as a mineralizer for 120
hours, and the weight loss of GaN was measured after a sudden release of ammonia. The solubility increases as a function of temperature until around 500 °C, and then, decreases at higher temperature. The increase in solubility can be explained with increased kinetic energy, while the retrograde solubility can be explained with one or combination of the following three reasons. The first reason is the dissociation of NH$_3$ at high temperature. The solubility decreased in the temperature range at which NH$_3$ starts to dissociate into N$_2$ and H$_2$. If NH$_3$ dissociates into N$_2$ and H$_2$, the total amount of NH$_3$ to dissolve GaN decreases, causing underestimation of solubility in the experiment. The second reason is preferred formation of gallium amide or gallium imide compounds from GaN at lower temperature. The third possible reason is the effect of entropy in dissolution process. The standard free energy of solution, $\Delta G$ is expressed as follows:

$$\Delta G = \Delta H - T \Delta S,$$

where $\Delta H$ and $\Delta S$ are changes in enthalpy and entropy associated with dissolution, and $T$ is temperature. In dissolution of ionic salts, an entropy contribution to the free energy cannot be neglected since the enthalpy changes associated with dissolution process are usually comparatively small. It is reported that the entropy of solution is exceedingly negative when the anion and cation that would be formed on dissociation are both triply charged (Johnson, 1968). This might be the case in GaN dissolution; i.e., the entropy of GaN dissolution into NH$_3$ is negative, resulting in higher free energy at higher temperature. In the experiment shown in Fig. 3, up to 1.2 wt% of GaN dissolved in supercritical ammonia with 1.5 mol% of NaNH$_2$ at 76 MPa and 550-600 °C. Other solubility value for basic supercritical ammonia available in literature is 3 mol% (∼15 wt%) with KNH$_2$:NH$_3$ = 0.07 at 340 MPa and 400 °C (Dwiliński et al., 2001), 13 wt% at 350 °C and 1 wt% at 560 °C for 2-4 molar KNH$_2$ solutions (Callahan et al., 2006). Unlike ammono-basic conditions, GaN does not show retrograde solubility for ammono-acidic conditions. It was reported that up to 0.25 mol of GaN dissolved in supercritical ammonia with 0.127 mol NH$_4$Cl at 67.7~100.9 MPa and 550 °C (Ehrentraut et al., 2008b). Considering the temperature limitation of the autoclave materials, the retrograde solubility for basic conditions is beneficial; seed temperature can be maintained as high as possible to grow better quality GaN crystals.

![Fig. 3. Solubility of GaN in supercritical ammono-basic solutions as a function of temperature. The pressure was 76±12 MPa (11000±1800 psi) and the mineralizer was 1.5 mol% of NaNH$_2$.](www.intechopen.com)
3.3 The impact of acidity on the autoclave material
Ammonothermal autoclaves are usually constructed with Ni-Cr based superalloy because the growth temperature higher than 500 °C is preferred to grow GaN crystals. Although Ni-Cr superalloy presents excellent corrosion resistance against water and salt water, it is seriously corroded when exposed to acidic supercritical ammonia. To avoid corrosion of the autoclave, the acidic ammonothermal method employs Pt-based liner (Kagamitani et al., 2006). In addition to extreme cost of the liner, it is quite challenging to cover all wet surfaces of high-pressure components such as valves, safety rupture discs, and pressure transducers. In the case of acidic high-temperature ammonothermal method, all growth components are housed in a capsule made of a noble metal to protect internal heater and high-pressure enclosure (D’Evelyn et al., 2004). Conversely, Ni-Cr based superalloy withstands corrosion against supercritical ammono-basic solutions. From an industrial point of view, basic ammonothermal method is advantageous over acidic conditions for simpler and inexpensive autoclave design.

4. Characteristics of GaN crystals grown by the basic ammonothermal method
Recently, the crystal quality of GaN grown by the ammonothermal method has become sufficient for successive device fabrications. In our group, GaN crystals are usually grown on c-plane GaN seed crystals prepared by a vapor phase method. Given the polar nature of wurtzite GaN, crystals grown on the Ga-polar side exhibit different characteristics from that on the N-polar side. Here, structural characteristics and surface morphology are compared between crystals on the Ga-side and the N-side, followed by impurity analysis, optical characterization, and electrical characterization for crystals grown on the N-side.

![XRD rocking curve](https://www.intechopen.com)

Fig. 4. XRD rocking curves of 002 reflection from crystals grown on Ga-side and N-side with an unoptimized condition.

4.1 Structural characteristics and surface morphology
In the basic ammonothermal method, crystals grown on the N-side tend to present better structural quality than that on Ga-side. Fig. 4 shows an example of XRD rocking curve...
measured for 002 reflection from Ga-polar and N-polar crystals. The crystal grown on the Ga-side in this sample contained numerous poorly aligned grains, although structural quality was acceptable on the N-side. It was demonstrated, however, that high-quality crystals can be grown on both sides with optimized conditions as presented in Fig. 5. The full width half maximum (FWHM) of the 002 XRD rocking curve became as narrow as ~60 arcsec. Surface morphology on the Ga-side has a strong correlation with FWHM of the 002 XRD rocking curve. Fig. 6 (a) and (b) show Nomarski microscopy images of the surface on the Ga-side for the unoptimized and optimized growth conditions, respectively. The Ga-polar surface exhibits smooth humps when 002 XRD FWHM became 200 arcsec or less. By contrast, the N-polar surface is covered with large hillocks [Fig. 7 (a)] with microscopic dots [Fig. 7 (b)] regardless of 002 XRD FWHM. Threading dislocation density of crystals grown on N-polar surface is typically under the detection limit of TEM, which corresponds to the order of $10^6$ cm$^{-2}$. Generation of new dislocations at the interface between the seed crystal and the grown crystal was not observed.

Fig. 5. XRD rocking curve of 002 reflection from crystals grown on Ga-side and N-side with an optimized condition.

Fig. 6. Morphology of Ga-polar surface observed with Nomarski microscopy for crystals grown with (a) an unoptimized condition and (b) an optimized condition.
4.2 Impurity analysis, characterization of optical and electrical property

GaN grown by the basic ammonothermal method contains relatively higher impurities than crystals grown by other methods. The main reasons are as follows: 1) lower growth temperature than other methods; 2) oxygen contamination caused by oxidation of mineralizers; and 3) incorporation of heavy metal elements from the reactor wall. Table 2 presents an example of impurity concentration in a GaN crystal on the Ga-face and N-face. The crystal grown on the Ga-side contains more Na and heavy metals than that on the N-side, whereas the Ga-side incorporates less O than the N-side. It is surmised that internal polarization field attracts cation on the Ga-side and anion on the N-side. We also demonstrated that annealing of the crystals at 1200 °C induced accumulation of alkali metal impurities on the Ga-polar surface. This phenomenon is tentatively explained by thermally enhanced drifting of alkali metals under internal electric field. Some amount of alkali metal impurities can be removed through annealing followed by lapping of the top Ga-polar surface. Note that annealing at 1100 °C or lower did not cause the migration of alkali metals, which implies that the alkali metals do not migrate into device layers during the epitaxial growth process on the ammonothermal GaN wafers.

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>O</th>
<th>Heavy metals (Ni, Cr, etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga-face</td>
<td>$2 \times 10^{18}$ cm$^{-3}$</td>
<td>$7 \times 10^{18}$ cm$^{-3}$</td>
<td>$10^{15}$~$10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>N-face</td>
<td>$2 \times 10^{16}$ cm$^{-3}$</td>
<td>$2 \times 10^{19}$ cm$^{-3}$</td>
<td>$10^{15}$~$10^{19}$ cm$^{-3}$</td>
</tr>
</tbody>
</table>

Table 2. Example of impurity concentrations in a GaN crystal grown by the basic ammonothermal method.

Although the ideal GaN crystal is transparent, GaN grown by the ammonothermal method looks yellowish, brownish, or blackish, depending on growth conditions. Fig. 7 (a) shows one example of bulk GaN crystal. The origin of color is attributed to impurities and/or vacancies. Brownish crystals usually yield yellowish wafers after slicing [Fig. 7 (b)]. In order to use GaN wafer for white LEDs, optical absorption at around 450 nm must be minimized to maximize optical output. To date, the smallest optical absorption coefficient at 450 nm obtained from sliced and polished GaN wafer is 8 cm$^{-1}$.

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The crystal is electrically conductive with n-type conduction. Resistivity measured by the four-probe method was $10^{-2} \Omega \text{ cm}$ or less, which is low enough for LED and LD applications. Fig. 8 demonstrates LED devices fabricated on a GaN wafer sliced from an ammonothermally grown bulk GaN crystal. GaN wafers produced by the basic ammonothermal method have sufficient quality for successive device fabrication.

Fig. 8. Photograph of LEDs on a GaN wafer produced by the ammonothermal method.

5. Conclusion

Motivated by the successful mass production of quartz crystals by the hydrothermal growth, we have been developing the ammonothermal growth of GaN. It has been demonstrated that the ammonothermal method can produce device-quality GaN wafers. Fundamental research for over a decade has revealed general physicochemical properties of the ammonothermal GaN growth. Structural quality of GaN crystals evaluated with XRD FWHM and TEM has been improved to the acceptable level for successive device fabrications. However, there remain several challenges to bring this technology into
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industrial mass production of GaN wafers. First, more detailed knowledge on chemistry and crystal growth mechanism is indispensable. In particular, solubility reported in literature seems highly scattered, although it is one of the most important parameters to optimize crystal growth conditions. A more comprehensive study on solubility for various conditions is strongly demanded. Since the reaction occurs in a “black box,” it is quite challenging to obtain an idea of what is happening in the reactor. Accurate control of the crystal growth process will require fundamental knowledge on the relationship among pressure, volume, and temperature for supercritical ammonia with mineralizers. Growth mechanisms and kinetics are also poorly understood. It is preferable to develop an in-situ technique to analyze or observe the growth process. Second, the grown crystals still contain a large amount of impurities and point defects, which is the cause of colored crystals. Optical absorption coefficient as low as 1~2 cm$^{-1}$ is requested for LED applications. Purification of the process as well as searching for an effective dopant are necessary to achieve colorless GaN wafers. Third, seed crystals with large surface area are needed to achieve large diameter wafers because lateral expansion is quite slow in the ammonothermal growth. It would be necessary to combine other growth methods such as HVPE and flux methods to obtain high-quality, large-area seed crystals. Lastly, more time and efforts are required to develop large-capacity autoclaves. Development of large diameter superalloy billets is one of the keys for the success of the ammonothermal mass production. Also, complete safety assessment against potential blast hazards and toxic gas hazards becomes a critical issue for large-capacity autoclaves. Despite the above-mentioned challenges, the outstanding scalability of the ammonothermal method makes it one of the most promising pathways to achieve low-cost, high-quality GaN wafers. The entire GaN industry strongly expects successful development of the ammonothermal method for mass production of GaN wafers.

6. References


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