

Advances in Bulk Crystal Growth of AlN and GaN

Dirk Ehrentraut and Zlatko Sitar

Abstract

Aluminum nitride (AlN) and gallium nitride (GaN) play an essential role in modern electronics, particularly in optoelectronics. Highly efficient light-emitting devices covering the ultraviolet to green spectral region are fabricated from these materials. Despite all efforts, the growth of large-size and high-quality AlN and GaN crystals for substrates, which are thermally and lattice-matched to the AlGaIn-based device structures, is still in its infancy. This is due to the high equilibrium vapor pressure of nitrogen above these compounds, which requires growth techniques employing either the vapor phase or liquid solutions. The best commercially available GaN substrates show a high dislocation density of $>10^5$ per cm^2 and strong bowing with a radius of curvature smaller than 10 m. This article reviews current growth techniques that look promising and may become commercially viable.

Introduction

Due to their exceptional properties (direct bandgap spanning from 6.1 to 0.8 eV), high breakdown voltage (several MV/cm), high electron mobility (several $1000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), and high saturation velocity ($>10^7 \text{ cm s}^{-1}$), semiconducting Group III nitride compounds have become the base for a multibillion dollar device market throughout the world during the past two decades.

The complete miscibility of the pure phases of AlN-GaN and partial miscibility of InN-GaN allows the tuning of physical properties over a wide range. This offers an enormous variety of possible applications as light-emitting diodes (LEDs) and laser diodes (LDs) covering the spectral wavelength from far red to ultraviolet. It is anticipated that solid-state lighting devices such as LEDs will replace incandescent light bulbs and fluorescent lamps for energy savings and lifetime considerations. Other applications of Group III nitrides involve high electron mobility transistors, high-power amplifiers, solar-blind detectors (devices that can detect radiation in the narrow wavelength window of 240–285 nm, a UV absorption band at the surface of the earth, without interference from the sun), and heat sensors, to name a few.

In contrast to other semiconductor technologies such as Si and GaAs, which strongly rely on their respective native substrates, AlGaInN device technology, although highly developed, is nonetheless limited by the lack of native substrates. The lack of thermally and lattice-matched substrates presents a major roadblock for the development of high-performance devices with improved efficiency and long lifetime. The worldwide demand for native aluminum nitride (AlN), gallium nitride (GaN), and indium nitride (InN) substrates is forecast to exceed \$400 million in 2010.¹ Currently, only GaN substrates are being used in commercial device fabrication, AlN substrates are under development, and InN crystals have not been grown in any significant size, primarily due to the extremely high equilibrium vapor pressure of N_2 over the InN compound. This article illustrates the state-of-the-art in the crystal growth of AlN and GaN and discusses critical issues that need to be solved to pave the way toward fabrication of large-size wafers (diameter ≥ 2 in.).

The Group III nitrides crystallize in the wurtzite structure, space group P6₃mc, which consists of two interpenetrating hexagonal, close-packed lattices (Figure 1).

The atoms are arranged in bilayers on the (0001) basal plane, one containing the cations and the other anions. The topmost species in the bilayer defines the polar orientation: III-polar [$+c$ orientation, (0001)] or N-polar [$-c$ orientation (000 $\bar{1}$)]. Polar orientation should not be confused with surface termination, as each orientation may be terminated with either species. The two polarities are related by an inversion operation, which is a true symmetry operation. The surface atomic configuration and neighboring atom arrangements are different for the two polar orientations, which results in a different surface chemistry. Thus, the crystal growth mode and impurity incorporation will strongly depend on polar orientation.

Physical Vapor Transport Growth of Aluminum Nitride Single Crystals

Although the first AlN was synthesized in 1862² by the reaction between molten aluminum and nitrogen, it took more than a century before any sizeable single crystals of AlN were grown.³ Past efforts to grow AlN bulk crystals included sublimation of AlN,⁴ vaporization of Al,⁵ and solution routes,⁶ with sublimation yielding the most voluminous ($> 15 \text{ cm}^3$) AlN crystals to date. In recent years, several research groups^{7–10} independently developed processes and models for growth of AlN crystals via physical vapor transport (PVT), which all converge to the same basic growth principle and process parameter space. All of these efforts clearly demonstrate that PVT can produce AlN bulk crystals of very high quality and of sizes appropriate for use as Group III nitride substrates.

In a typical PVT process, an AlN powder source is sublimed within a closed or semi-open crucible following the reaction $\text{AlN} \rightarrow \text{Al} + \frac{1}{2}\text{N}_2$. The vapors are subsequently transported in a temperature gradient, through nitrogen at subatmospheric pressure, to a seed held at a lower temperature than the source, where they recrystallize. A typical growth configuration and growth equation (Figure 2) driving the process is

$$v_G = k \frac{\exp\left[\frac{\Delta S - \frac{\Delta H}{T}}{RT^{1.2}P^{1.5}}\right] \Delta T}{\delta} \quad (1)$$

AlN growth can be achieved at temperatures as low as 1800°C; however, temperatures in excess of 2200°C are required to achieve commercially viable growth rates of $\sim 500 \text{ }\mu\text{m/hour}$ and desired boule shapes and crystal quality. The upper temperature limit of this process is

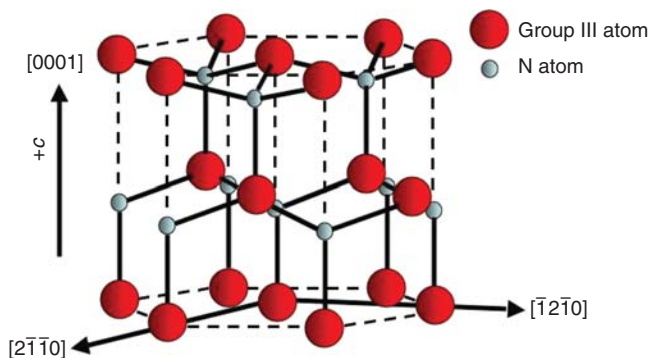


Figure 1. A schematic of the wurtzite structure for space group P63mc. The sequence of anions and cations in the III-N bilayer determines the crystal polarity.

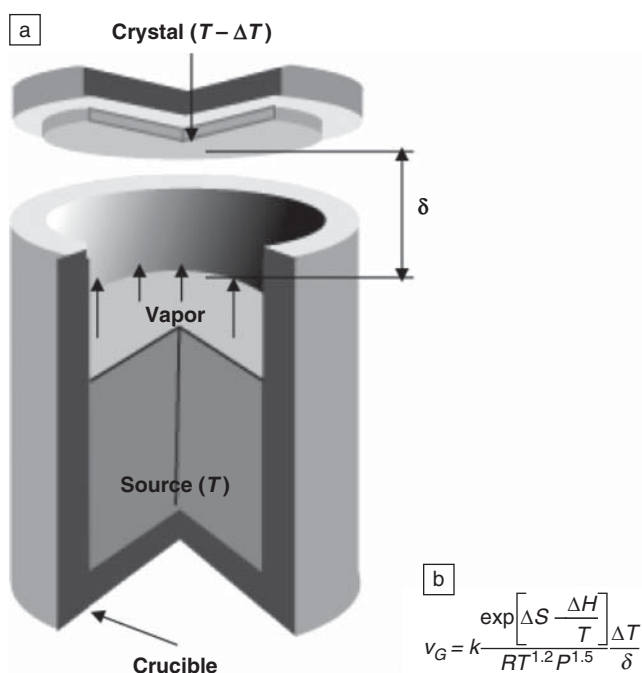


Figure 2. (a) Typical growth configuration in physical vapor transport of AlN. (b) Dependence of growth rate, v_G , on controllable parameters: pressure, P , temperature, T , and gradient, $\Delta T/\delta$, where δ is the distance between the source and the seed. The pre-exponential term k contains the diffusion coefficient of Al; ΔS and ΔH are the entropy and enthalpy of sublimation, respectively; and R is the universal gas constant.

~2500°C, when the Al vapor pressure reaches 1 atmosphere.

The very high process temperatures make furnace design and materials selection critical to the success of the overall process, both for achieving durability of growth hardware and keeping crystal impurity levels low. In particular, crucible materials must be (1) inert to chemically aggressive Al vapor, (2) a negligible source of contamination to the growth process, (3) reusable for multiple growth runs, (4) relatively inexpensive, and (5) manufacturable in various shapes and dimensions.¹¹ The

available data show that graphite¹² and boron-containing¹³ crucibles should be avoided, whereas solid tungsten^{3,14} and sintered TaC¹¹ crucibles, the latter being more stable but more difficult to come by, offer acceptable performance in terms of lifetime and impurity incorporation.

Self-Seeded Growth of AlN Bulk Crystals

Several groups reported on self-seeded growth of AlN,^{9,15,16} and noticed that the crystal shape changed from long needles to well-faceted crystals as the growth temper-

ature was changed from 1800 to 2200°C. AlN boules up to 10 mm in diameter were produced by this method in conical crucibles.¹⁵ No seed crystals were used in the growth process and, typically, several nuclei formed on the crucible walls during the early stages of growth; growth competition between different nuclei resulted in single crystal regions of varying sizes and orientations. Step flow growth resulted from screw dislocations intersecting the growing surface. The screw dislocation density was estimated at $5 \times 10^4 \text{ cm}^{-2}$.

Seeded Growth of AlN Bulk Crystals

Seeded growth of AlN on SiC has been studied as a way to exploit the availability of large, high-quality SiC substrates and to control the polarity and orientation of AlN crystals.¹⁷ Due to the high process temperatures involved and the difference in thermal expansion between AlN and SiC, the stability of the SiC seeds and the cracking of the AlN layers are important issues that need to be addressed in establishing a reproducible seeded growth process on SiC. In contrast, seeded growth on recently available AlN native seeds eliminates many of the problems associated with heteroepitaxial growth, but this technique is only beginning to be investigated and exploited. Techniques to avoid renucleation and to maintain stable growth have been developed and led to considerable single crystal size expansion (up to 2 in.).^{18,19} However, several questions, such as which orientation is most favorable for growth, still need to be addressed.

Growth on SiC Seeds

The growth of AlN crystals seeded on SiC substrates was first reported by Balkas et al.²⁰ and more extensively investigated at Kansas State University.²¹⁻²³ Experiments were carried out in tungsten crucibles placed within the axial temperature gradient of a resistively heated furnace. Direct growth on as-received Si-face SiC resulted in the formation of discontinuous hexagonal islands, while no growth was observed on C-face SiC. To promote two-dimensional growth on Si-face SiC substrates, a 2 μm -thick AlN buffer layer was deposited by metalorganic chemical vapor deposition. Continuous growth was achieved by the use of the buffer layer, and atomic force microscopy images indicated that AlN grew by the step-flow growth mode. Stress-induced cracks were always observed in the AlN crystals grown on SiC. It was predicted²⁴ that AlN grown on 6H-SiC should be at least 2 mm thick to avoid cracking during cool down from a growth temperature of 2000°C.

Dalmau et al.²⁵ developed a two-step process for deposition of thick AlN layers on SiC and for reduction of cracks in the grown layers. AlN layers up to 3 mm thick were grown on on-axis and off-axis, (0001)-oriented, Si-face SiC seeds. During the growth, the SiC seeds were gradually decomposed at high temperature, yielding freestanding AlN crystals up to one inch in diameter. As-grown surfaces of layers on on-axis SiC seeds were characterized by hexagonal hillocks, suggesting a dislocation-mediated island growth mode, whereas layers grown on off-axis seeds exhibited steps aligned perpendicular to the off-axis direction, characteristic of the step-flow growth. Crack-free AlN crystals were obtained from both on- and off-axis layers and used to fabricate AlN wafers. Synchrotron white beam x-ray topography (SWBXT) indicated that some strain-free crystals were obtained, but in all samples, the density of dislocations was relatively high ($>10^6 \text{ cm}^{-2}$), just at the theoretical limit for thick films grown on mismatched substrates. Elemental characterization showed impurity concentrations comparable to those found in the AlN source powder, indicating negligible incorporation of C and Si during growth.

Sarney et al.²⁶ grew bulk AlN on on-axis and 3.5° off-axis, *c*-oriented 6H-SiC seeds. Sublimation from an AlN powder source in N_2 atmosphere was performed in the temperature range of 2150–2200°C with 4 mm of separation between the source and seed. The AlN grew well-aligned with the substrate. Epelbaum et al.²⁷ studied AlN crystal growth on SiC substrates of different orientations. Layers of 200–500 μm thickness were deposited at seed temperatures around 2000°C in 350 mbar N_2 pressure. Growth on Si-face, *c*-oriented substrates was characterized by many hexagonal hillocks on the surface. In contrast, growth on on-axis and 10° off-axis *a*-plane substrates resulted in more stable growth. The smoothest morphology, typical of step-flow growth, was obtained with on-axis *a*-plane substrates; however, cracking problems persisted.

Growth on AlN Seeds

Reports on AlN growth on native seeds are limited, as these seeds have only recently become available by growth of sizable, spontaneously grown crystals. Schlessner et al.¹⁰ reported for the first time seeded growth of AlN on native seeds by PVT. This work identified that growth rates on the two *c*-faces of opposite polarity differed by a factor of 2–3, with the Al polarity showing slower and smoother growth. X-ray rocking curves around the (0002) reflection varied from 25 to 45 arc-

sec, confirming the very high crystalline quality of the material grown by seeded growth.

Noveski et al.¹⁶ achieved a major breakthrough in seeded growth by demonstrating a process for continuous growth of AlN on previously deposited material, resulting in significant expansion of single crystalline grains. During the early stages of each run, the crystal growth region was maintained in an inverted temperature gradient, effectively desorbing surface contamination and part of the previously grown layer. Centimeter-sized, single-crystal grains were observed in polished cross sections of boules, and epitaxial regrowth was demonstrated regardless of the orientation of individual grains.

To overcome problems associated with the formation of cracks in these polycrystalline boules, large single-crystal grains were harvested and used to prepare seeds for subsequent seeded growth.^{28,29} To ensure epitaxial regrowth, seeds were etched in a phosphoric and sulfuric acid mixture, dipped in diluted hydrofluoric acid prior to loading into the system, and maintained in an inverted temperature gradient during the ramp to the growth temperature. This cleaned the surface and eliminated the native oxide layer. Crystal growth was performed in an axial temperature gradient of 5–10°C/cm, maintaining the source temperature at 2200–2250°C and reactor pressure at 400–900 Torr. A seed was expanded from 10 to 18 mm after several consecutive growth runs, representing a 45° crystal expansion angle (Figure 3).

In related work, Herro et al.^{19,30} investigated seeded growth along the two (0001) polar directions and determined that more stable growth was obtained on N-polar seeds. The growth surface of N-polar crystals was controlled by a single

growth center, which led to a mirror-like growth facet. Atomic force microscopy studies revealed single unit cell-high steps on both surfaces, but the 200–250 nm terrace width on N-polar AlN (Figure 4a) was much larger than the 50–70 nm width observed on Al-polar AlN (Figure 4b). Since seeded growth was performed on seeds of both polarities using the same growth conditions, thus ensuring equal supersaturation of Al vapor, these differences were attributed to the surface energy difference of the N- and Al-polar facets.

Fabrication of AlN Wafers

There are several reports on fabrication of AlN wafers. SWBXT studies of these crystals show formidable characteristics: visible Pendellösung fringes, indicative of high crystalline perfection; triple-crystal x-ray rocking curves as narrow as 7.2 arc-sec, marginally larger than the theoretical limit; and overall dislocation densities below 10^3 cm^{-2} , with some crystals virtually dislocation free.^{53,54} Chemo-mechanical polishing (a technique used in semiconductor fabrication for planarizing a semiconductor wafer or other substrate) processes have been developed for basal plane substrates that produce atomic level steps and root mean squared roughness smaller than 0.2 nm. One issue with AlN wafers is spontaneous surface oxidation, which can be managed by passivating the wafer with a stable hydroxide layer that can be easily removed *in situ* prior to epitaxial growth.

However, despite a few commercial efforts with exciting results (Crystal IS: 2-in. wafers with up to 85% useful area [Figure 5],³¹ HexaTech: 1-in. wafers with 100% useful area), the availability of AlN wafers remains scarce, and the cost is extremely high.

Conclusion and Outlook for AlN

AlN crystal growth is a challenging task that has been attempted in the past via a variety of growth methods. Although several issues remain, PVT growth of AlN at high temperatures shows the most promising results and is the only growth technique that can produce high-quality, low dislocation density 2-in. crystals. The recent demonstration of seeded growth with subsequent crystal size expansion is certainly a crucial milestone for future development of this technology that could lead to further expansion of single crystal size. Lifetime and stability of growth crucibles and reactor parts remain a challenge that will need to be addressed in the quest for high-purity crystals and lower production cost.

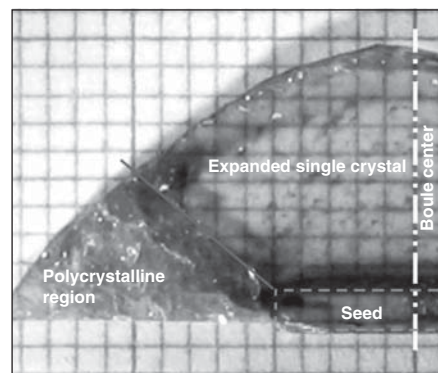


Figure 3. Longitudinal cut of a crystal boule after several growth runs showing the crystal expansion angle. Grid size = 1 mm.

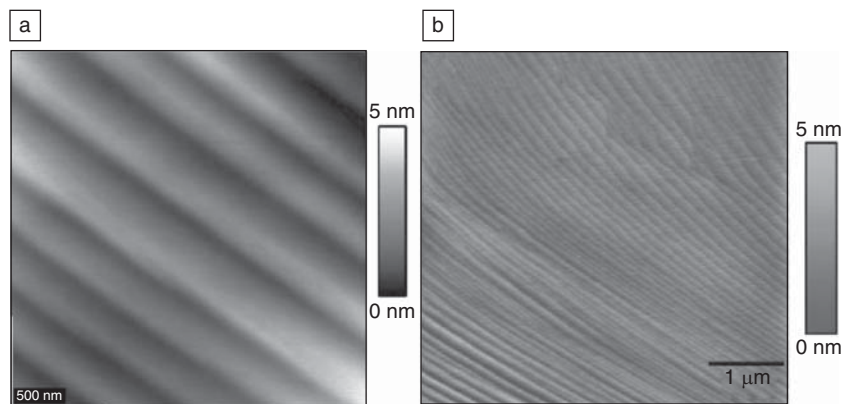


Figure 4. Atomic force microscopy micrographs taken on as-grown AlN surfaces: (a) N-polar orientation; (b) Al-polar orientation. In both cases, single unit cell-high steps were observed.

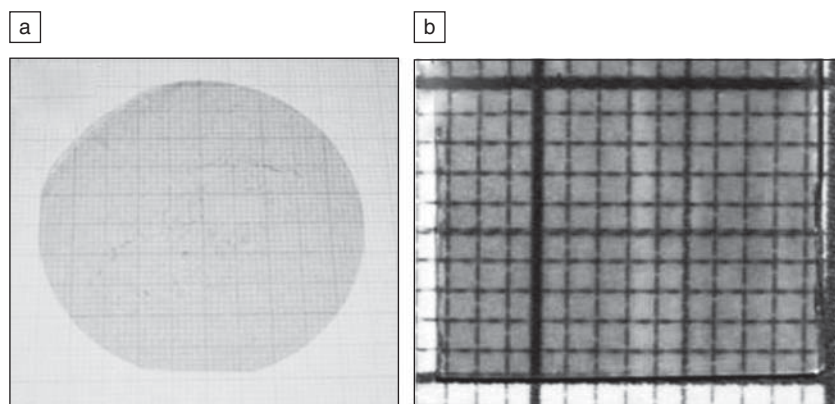


Figure 5. Optical images of single-crystal AlN wafers: (a) on-axis 2-in. wafer, (b) *m*-plane wafer. Grid size = 1 mm. Images courtesy of Crystal IS. Reprinted with permission.

Growth of GaN Single Crystals

At approximately 900°C, GaN decomposes to give 1 bar (10^{-4} GPa) N_2 pressure,³² therefore it cannot be grown from the stoichiometric melt without employing an extreme pressure of >6 GPa and temperature of 2220°C.³³

The industry requires GaN as a large-size wafer (minimum 2 in. in diameter), consequently, only techniques employing the liquid or vapor phase are appropriate for the economic growth of GaN. The following discusses GaN growth techniques, which already have been demonstrated to be able to produce bulk crystals and are considered promising for fabrication of GaN wafers.

Growth from Liquid Solution

Growth from a liquid solution is generally regarded as a superior technique in terms of achieving high structural crystal

quality because the growth takes place near thermodynamic equilibrium. At the equilibrium, neither growth nor dissolution of the seed crystal occurs. This approach comprises the high-pressure solution (HPS) technique, the ammonothermal technique, and the Na flux method.

Among the solution growth techniques, the HPS technique employs a diluted solution of atomic nitrogen in liquid gallium under a pressure of ≤ 2 GPa and temperature of $\leq 1700^\circ\text{C}$.³⁴ Excellent crystals have been prepared at high growth rates of 0.1 mm/h in the directions perpendicular to the *c*-axis, the highest rate among the techniques employing a solution. However, the growth is strongly anisotropic and does not exceed 1 $\mu\text{m}/\text{h}$ along the *c*-axis. Figure 6a shows a specimen of a 2-cm large hexagonal GaN crystal. The crystal thickness (along the *c*-axis) is typically about 0.1 mm, which makes it nearly

impossible to prepare wafers for device production. Figure 6b illustrates a thin wafer produced from a HPS GaN crystal ready for subsequent epitaxial growth (epi-ready wafer). Laser diodes have been demonstrated on a laboratory scale on such wafers with a defect density as low as 10^2 per cm^2 , to compare them with conventional laser diodes prepared from GaN on sapphire substrates.³⁵ So far, no thick GaN crystals, suitable to prepare several wafers per one grown crystal, could be obtained. Moreover, the application of high pressure requires the use of special vessels, which impedes the scale up to mass production.

The ammonothermal growth technology has similarities with the well-established hydrothermal growth technology for quartz (SiO_2) crystals. The polar solvent in the case of GaN is ammonia (NH_3), which transitions into a supercritical state with increased chemical reactivity at 11.2 MPa and 132°C . A mineralizer of either acidic (such as NH_4Cl in the ammonoacidic technique) or basic (such as NaNH_2 or KNH_2 in the ammonobasic technique) nature is utilized to greatly enhance the solubility and transport of GaN in NH_3 . The solution is encapsulated in an autoclave and produces pressures up to 400 MPa at temperatures up to 600°C during the crystal growth, a bit lower than for the HPS technique. The chemical equilibrium of species during the crystal growth is not well understood at present. A significant difference is the solubility behavior of GaN, which is of retrograde and regular character for the basic and acidic mineralizers, respectively.³⁶ In other words, supersaturation increases, and crystal growth is initiated inside the autoclave in the zone with a higher temperature or under temperature increase if a basic mineralizer is employed. Conversely, the crystal growth of GaN will commence in the colder zone or under a temperature decrease if an acidic mineralizer is applied. Whatever mineralizer is used, the growth rates are quite similar and up to 0.1 mm per day for the $\langle 0001 \rangle$ direction,³⁷ about a factor of 25 lower than the HPS technique.

Figure 7a shows a 2-in. (5 cm), as-grown crystal, and Figure 7b shows an epi-ready (0001) GaN wafer prepared from a crystal grown under ammonobasic conditions by Ammono Sp. z o. o., a GaN crystal growth company located in Poland. It took about 15 years to develop the crystal size from the μm - to the cm-scale.^{38,39} A remarkably low etch pit density of the order of $5 \times 10^3 \text{ cm}^{-2}$ and perfect flatness with wafer bending of the order of $\geq 10^2 \text{ m}$ was attained. The ammonoacidic technique

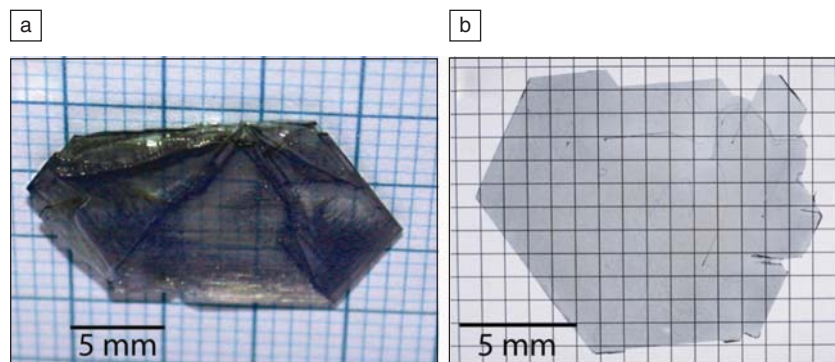


Figure 6. (a) As-grown GaN crystal prepared by the high-pressure solution growth technique. (b) Epi-ready wafer prepared from an as-grown GaN crystal. Figures are courtesy of I. Grzegory and M. Bockowski, Institute of High Pressure Physics, PAS, Warsaw, Poland. Reprinted with permission.

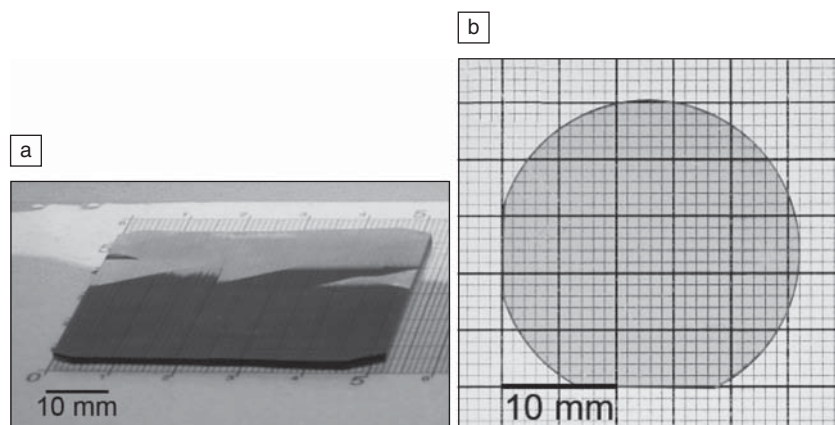


Figure 7. (a) As-grown GaN crystal grown from the ammonobasic technique at Ammono Sp. z o.o. (b) An epi-ready (0001) GaN wafer prepared from an as-grown crystal. Figures are courtesy of Ammono Sp. z o.o., Warsaw, Poland. Reprinted with permission.

was recently employed to grow thick (on the order of mm) GaN films and small bulk crystals (about 5–7 mm) on GaN seed crystals.^{40,41} Owing to the acidic medium, the inner wall of the autoclave is protected by a thin platinum-based liner to prevent container corrosion.

In general, the scalability of the autoclave and the number of crystals grown per cycle is an enormous advantage of the ammonothermal technique when compared to any other growth technique. For example, with the hydrothermal growth of SiO₂, more than 1,000 crystals are simultaneously grown;⁴² it is becoming clear that the ammonothermal growth has a strong industrial potential.

The Na-flux method was first applied to GaN by Yamane et al., who prepared free-standing crystals and platelets up to 10 mm in the longest direction under pres-

sure of around 5 MPa and temperatures of 600–800°C.^{43,44} Figure 8 shows some spontaneously nucleated GaN crystals synthesized at a pressure of 9.5 MPa and temperature of 900°C. The crystals are typically of excellent structural quality, with a full width at half maximum of 25–55 arcsec as measured by the x-ray rocking curve technique for the (0002) reflection.

The Na-flux method was further developed, and recently a 2-in. diameter and 3-mm thick crystal has been grown on a (0001) sapphire substrate, which was covered by a thin GaN film to initiate nucleation.⁴⁵ The same research group has expanded the use to other group I and II metals, such as lithium, calcium, and strontium as the solvent and recently used carbon as an additive to greatly suppress parasitic nucleation and dislocation generation.

Growth from the Vapor Phase

Growth from the vapor phase generally operates far away from thermodynamic equilibrium under high supersaturation but involves fewer reactants and offers somewhat higher purity grown crystals.

Hydride vapor-phase epitaxy (HVPE) has been investigated for about four decades,⁴⁶ the longest period among all techniques suitable for bulk GaN, and is presently the sole technology to deliver GaN wafers of relatively high optical and structural quality at reasonable growth rates.⁴⁷ Crystals as thick as 2 mm can be grown at growth rates of 100–500 μm/h along the crystallographic (0001) direction.⁴⁸ A severe limitation to the HVPE technique is the problem of dislocation generation (>10⁶ cm⁻²), and inverted pyramidal pits may lead to a change in the growth mode at the growing interface. Another concern is related to parasitic nucleation—uncontrolled, often highly defective, nucleation that may happen on the seed crystal as well as on any other place where the temperature is lowered. In both cases, the problem becomes severe for GaN layers exceeding about 100 μm in thickness.

Routes have been developed to mitigate high dislocation density; however, a dislocation density in the range of 10⁵–10⁶ cm⁻² is at the theoretical limit of this technique due to the use of mismatched foreign substrates. Lowering the growth rate below 100 μm/h and using template substrates have both been attempted to deal with the problem. The current most successful way is to use a template substrate to grow GaN to a thickness of just a very few wafers. Sumitomo Electric is applying the A-DEEP (advanced defect elimination by epitaxial growth with inverse pyramidal pits) technology by using GaAs (111)A substrates (which represent the Ga-polar face of the (111) GaAs substrate) to grow up to 1.5-mm thick GaN.⁴⁹ Another approach was developed by Hitachi Cable, who uses their void-assisted separation (VAS) technique to grow a 3-in. diameter and up to 600-μm thick GaN crystal on a sapphire-based template covered with a TiN nanonet layer.⁴⁹

The latest development is directed toward fabricating large-sized nonpolar (10 $\bar{1}0$), so called *m*-plane wafers, to enable the manufacture of structures free of electrostatic fields and therefore improved quantum efficiency for light-emitting devices.⁵⁰ Mitsubishi Chemical and Kyma Technologies have demonstrated the growth of up to 12- and 10-mm thick (0001) GaN crystals, respectively, from which *m*-plane wafers are prepared by slicing the crystal vertically.^{51,52}

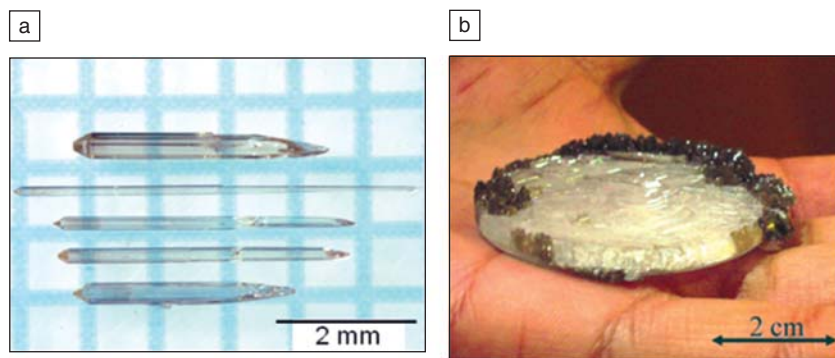


Figure 8. (a) GaN prismatic needle crystals prepared by the Na flux method at 900°C and 9.5 MPa for 400 h. (Image courtesy of H. Yamane, Tohoku University, Japan. Reprinted with permission) (b) A 3-mm thick GaN crystal grown by liquid phase epitaxy on a 2-in. substrate. (T. Sasaki, *J. Cryst. Growth* **310**, 1288 (2008). Reprinted with permission. © 2008, Elsevier Publishers.)

Next Challenges in Bulk GaN Technology

Several methods are currently employed for the growth of bulk GaN crystals. None of them has fully developed the potential for cost-effective mass production of high-quality material. The HVPE technique takes the major share, despite the small bending radius below 10 m and dislocation density around 10^6 cm^{-2} , even for the best commercially available material.

The ammonothermal technique provides the crystals with the highest structural quality; however, production costs have to be drastically lowered to provide competitive GaN wafers. This may be achieved by scaling up to larger autoclaves.

The industry demands the manufacturing of 4-in. epi-ready GaN substrates. This may give an advantage to those methods that combine a high throughput with high crystal quality.

Summary

Recent progress in the growth of AlN and GaN crystals has been briefly reviewed. Several crystal growth techniques are currently applied to produce high-quality bulk AlN and GaN crystals to supply device makers with thermally and lattice-matched substrates. However, it is noted here that the general problem of manufacturing low defect wafers of desired size is still an open issue. Presently, the physical vapor transfer approach to AlN crystal growth seems to be the most promising; it delivers high-quality, low dislocation density ($<10^3 \text{ cm}^{-2}$) substrates, but still requires a lot of tedious engineering work to increase the yield and scale the process beyond 1 in. In the case of GaN, the currently used

hydride vapor-phase epitaxy process offers an intermediate solution and modest crystal quality, while, with further development, the ammonothermal route could become a future leading technology in terms of crystal size, quality, and scalability. It could also assist with the economic and environmental issues of future high-volume production.

References

1. *Semicond. Today* **1**, 23 (2006).
2. F. Briegleb, A. Geuther, *Ann. Chem.* **123**, 228 (1862).
3. G.A. Slack, "Aluminum Nitride Crystal Growth," Final Report, Contract No. F49620-78-C-0021, 1 (1980).
4. V. Noveski, R. Schlesser, S. Mahajan, S. Beaudoin, Z. Sitar, *J. Cryst. Growth* **264**, 369 (2004).
5. R. Schlesser, Z. Sitar, *J. Cryst. Growth* **234**, 349 (2002).
6. C.O. Dugger, *Mater. Res. Bull.* **9**, 331 (1974).
7. J.C. Rojo, G.A. Slack, K. Morgan, B. Raghathamachar, M. Dudley, L.J. Schowalter, *J. Cryst. Growth* **231**, 317 (2001).
8. J.H. Edgar, L. Liu, B. Liu, D. Zhuang, J. Chaudhuri, M. Kuball, S. Rajasingam, *J. Cryst. Growth* **246**, 187 (2002).
9. M. Bickermann, B.M. Epelbaum, A. Winnacker, *Phys. Status Solidi C* **7**, 1993 (2003).
10. R. Schlesser, R. Dalmau, Z. Sitar, *J. Cryst. Growth* **241**, 416 (2002).
11. R. Schlesser, R. Dalmau, D. Zhuang, R. Collazo, Z. Sitar, *J. Cryst. Growth* **281**, 75 (2005).
12. C.M. Balkas, Z. Sitar, T. Zheleva, L. Bergman, R. Nemanich, R.F. Davis, *J. Cryst. Growth* **179**, 363 (1997).
13. D.W. Brenner, R. Schlesser, Z. Sitar, R. Dalmau, R. Collazo, Y. Li, *Surf. Sci.* **560**, L202 (2004).
14. B. Liu, J.H. Edgar, Z. Gu, D. Zhuang, B. Raghathamachar, M. Dudley, A. Sarua, M. Kuball, H.M. Meyer, *MRS Internet J. Nitride Semicond. Res.* **9**, 6.6 (2004).

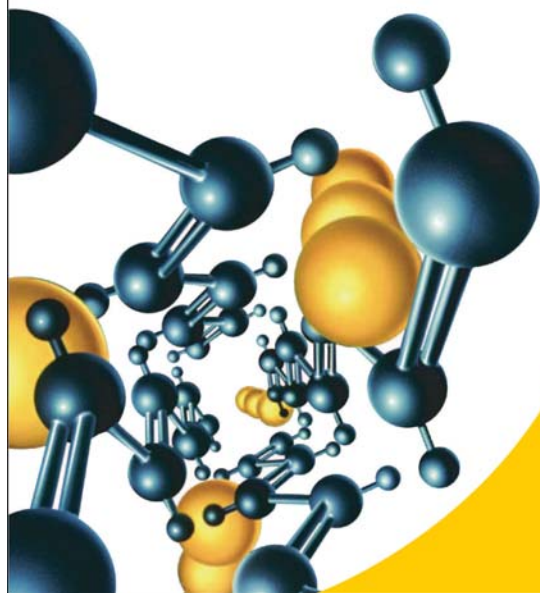
15. L.J. Schowalter, J.C. Rojo, N. Yakolev, Y. Shusterman, K. Dovidenko, R. Wang, I. Bhat, G.A. Slack, *MRS Internet J. Nitride Semicond. Res.* **5S1**, W6.7.1 (2000).
16. V. Noveski, R. Schlesser, B. Raghathamachar, M. Dudley, S. Mahajan, S. Beaudoin, Z. Sitar, *J. Cryst. Growth* **279**, 13 (2005).
17. R. Dalmau, R. Schlesser, B.J. Rodriguez, R.J. Nemanich, Z. Sitar, *J. Cryst. Growth* **281**, 68 (2005).
18. D. Zhuang, Z.G. Herro, R. Schlesser, B. Raghathamachar, M. Dudley, Z. Sitar, *J. Electron. Mater.* **35**, 1513 (2006).
19. Z.G. Herro, D. Zhuang, R. Schlesser, R. Collazo, Z. Sitar, *J. Cryst. Growth* **286**, 205 (2006).
20. C. Balkas, Z. Sitar, T. Zheleva, L. Bergman, I.K. Shmagin, J.F. Muth, R.M. Kolbas, R.J. Nemanich, R.F. Davis, *Mater. Res. Soc. Symp. Proc.* **401**, 41 (1997).
21. Y. Shi, Z.Y. Xie, L.H. Liu, B. Liu, J.H. Edgar, M. Kuball, *J. Cryst. Growth* **233**, 177 (2001).
22. L. Liu, B. Liu, Y. Shi, J.H. Edgar, *MRS Internet J. Nitride Semicond. Res.* **6**, 7.1 (2001).
23. P. Lu, J.H. Edgar, C. Cao, K. Hohn, R. Dalmau, R. Schlesser, Z. Sitar, *J. Cryst. Growth* **310**, 2464 (2008).
24. L. Liu, B. Liu, J.H. Edgar, S. Rajasingam, M. Kuball, *J. Appl. Phys.* **92**, 5183 (2002).
25. R. Dalmau, R. Schlesser, Z. Sitar, *Phys. Status Solidi C* **2**, 2036 (2005).
26. W.L. Sarney, L. Salamanca-Riba, T. Hossain, P. Zhou, H.N. Jayatirtha, H.H. Kang, R.D. Vispute, M. Spencer, K.A. Jones, *MRS Internet J. Nitride Semicond. Res.* **5S1**, W5.5.1 (1999).
27. B.M. Epelbaum, M. Bickermann, A. Winnacker, *Mater. Sci. Forum* **433–436**, 983 (2003).
28. D. Zhuang, Z.G. Herro, R. Schlesser, Z. Sitar, *J. Cryst. Growth* **287**, 372 (2006).
29. M. Strassburg, J. Senawiratne, N. Dietz, U. Haboeck, A. Hoffmann, V. Noveski, R. Dalmau, R. Schlesser, Z. Sitar, *J. Appl. Phys.* **96**, 5870 (2004).
30. Z.G. Herro, D. Zhuang, R. Schlesser, R. Collazo, Z. Sitar, *Mater. Res. Soc. Symp. Proc.* **892**, FF21.01.1 (2006).
31. S.B. Schujman, L.J. Schowalter, R.T. Bondokov, K.E. Morgan, W. Liu, J.A. Smart, T. Bettles, *J. Cryst. Growth* **310**, 887 (2008).
32. J. Karpinski, J. Jun, S. Porowski, *J. Cryst. Growth* **66**, 1 (1984).
33. W. Utsumi, H. Saitoh, H. Kaneko, T. Watanuki, K. Aoki, O. Shimomura, *Nat. Mater.* **2**, 735 (2003).
34. S. Porowski, *J. Cryst. Growth* **166**, 583 (1996).
35. I. Grzegory, M. Bockowski, S. Porowski, in *Bulk Crystal Growth of Electronic, Optical and Optoelectronic Materials*, P. Capper, Ed. (Wiley, Chichester, UK, 2005) p. 173.
36. D. Ehrentauf, K. Kagamitani, C. Yokoyama, T. Fukuda, *J. Cryst. Growth* **319**, 891 (2008).
37. B. Wang, M.J. Callahan, *Cryst. Growth Des.* **6**, 1227 (2006).
38. R. Dwilinski, R. Doradzinski, J. Garczyński, L.P. Sierzputowski, A. Puchalski, Y. Kanbara, K. Yagi, H. Minakuchi, H. Hayashi, *J. Cryst. Growth* **310**, 3911 (2008).
39. R. Dwilinski, R. Doradzinski, J. Garczyński, L. Sierzputowski, J.M. Baranowski, M. Kamińska, *Mater. Sci. Eng.* **B50**, 46 (1997).

40. Y. Kagamitani, D. Ehrentraut, A. Yoshikawa, H. Hoshino, T. Fukuda, S. Kawabata, K. Inaba, *Jpn. J. Appl. Phys.* **45**, 4018 (2006).
41. D. Ehrentraut, H. Hoshino, Y. Kagamitani, A. Yoshikawa, T. Fukuda, H. Itoh, S. Kawabata, *J. Mater. Chem.* **17**, 886 (2007).
42. D. Ehrentraut, H. Sato, Y. Kagamitani, H. Sato, A. Yoshikawa, T. Fukuda, *Prog. Cryst. Growth Charact. Mater.* **52**, 280 (2006).
43. H. Yamane, M. Shimada, S.J. Clarke, F.J. DiSalvo, *Chem. Mater.* **9**, 413 (1997).
44. M. Aoki, H. Yamane, M. Shimada, S. Sarayama, F.J. DiSalvo, *J. Cryst. Growth* **242**, 70 (2002).
45. F. Kawamura, M. Morishita, M. Tanpo, M. Imade, M. Yoshimura, Y. Kitaoka, Y. Mori, T. Sasaki, *J. Cryst. Growth* **310**, 3946 (2008).
46. H.P. Maruska, J.J. Tietjen, *Appl. Phys. Lett.* **15**, 327 (1969).
47. D. Gogova, D. Siche, R. Fornari, B. Monemar, P. Gibart, L. Dobos, B. Pécz, F. Tuomisto, R. Bayazitov, G. Zollo, *Semicond. Sci. Technol.* **21**, 702 (2006).
48. B. Łuczniak, B. Pastuszka, I. Grzegory, M. Boćkowski, G. Kamler, E. Litwin-Staszewska, S. Porowski, *J. Cryst. Growth* **281**, 38 (2005).
49. K. Motoki, T. Okahisa, R. Hirota, S. Nakahata, K. Uematsu, N. Matsumoto, *J. Cryst. Growth* **305**, 377 (2007).
50. P. Waltereit, O. Brandt, A. Trampert, H.T. Grahn, J. Menninger, M. Ramsteiner, M. Reiche, K.H. Ploog, *Nature* **406**, 865 (2000).
51. *Compound Semiconductor* **14**, 8 (2008).
52. D. Hanser, M. Tutor, E. Preble, M. Williams, X. Xu, D. Tsvetkov, L. Liu, *J. Cryst. Growth* **305**, 372 (2007).
53. B. Raghoechamachar, W.M. Vetter, M. Dudley, R. Dalmau, R. Schlessner, Z. Sitar, E. Michaels, J.W. Kolis, *J. Cryst. Growth* **246**, 271–280 (2002).
54. B. Wu, R. Ma, Hui Zhang, M. Dudley, R. Schlessner, Z. Sitar, *J. Cryst. Growth* **253**, 326–339 (2003). □

Organic Microelectronics and Optoelectronics Workshop V

A Joint Workshop of ACS / IEEE / MRS

July 6-9, 2009
Marriott San Francisco
San Francisco, CA, USA



The workshop will bring together a broad spectrum of chemists, materials scientists, physicists, and engineers from both industry and academia in a stimulating forum to share information and ideas in the emerging fields of Organic Microelectronics and Optoelectronics. The goal is to build an interdisciplinary community working on applications such as RFIDs, displays, sensors, photovoltaics and optical devices while addressing some of the common scientific and manufacturing challenges to help these technologies advance in a more rapid, effective, and economical manner.

The technical program will focus on the areas of synthesis, theory, novel processing/patterning/fabrication and device physics through a series of presentations by renowned invited speakers and poster sessions.

Edwin Chandross, General Chair

Mary Galvin, Air Products

John Kymissis, Columbia University

Iain McCulloch, Imperial College

Register by June 1, 2009 and SAVE! After June 1, 2009

| | | |
|-------------------------|-------|-------|
| ACS, IEEE or MRS Member | \$650 | \$850 |
| Non-member | \$750 | \$950 |
| Invited Speaker | \$450 | \$450 |

For more information on the Organic Microelectronics and Optoelectronics Workshop V visit www.mrs.org/org_micro5



Your RF Power Source Partner for Precision
Induction Heating Solutions in Crystal Growing Applications

Visit Us: crystals.ameritherm.com

solar collectors

semiconductor fab

electronics

Call Us: +1.585.889.9000