

Review

Progress in Ammonothermal Crystal Growth of Gallium Nitride from 2017–2023: Process, Defects and Devices

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Abstract: Gallium nitride continues to be a material of intense interest for the ongoing advancement of electronic and optoelectronic devices. While the bulk of today's markets for low-performance devices is still met with silicon and blue/UV LEDs derived from metal–organic chemical vapor deposition gallium nitride grown on foreign substrates such as sapphire and silicon carbide, the best performance values consistently come from devices built on bulk-grown gallium nitride from native seeds. The most prominent and promising of the bulk growth methods is the ammonothermal method of high-pressure solution growth. The state-of-the-art from the last five years in ammonothermal gallium nitride technology is herein reviewed within the general categories of growth technology, characterization and defects as well as device performance.

Keywords: gallium nitride; ammonothermal crystal growth; wide band gap semiconductors; defects; high-power electronics

1. Introduction

From the first measurements of gallium nitride (GaN) material properties over 50 years ago, the potential for advancements in device performance in optoelectronic and electronic devices has driven a massive global effort for the development and commercialization of gallium nitride wafers [1]. Early work focused on the opportunity for ultraviolet (UV) and blue-light-emitting diodes (LEDs) and led to the proliferation of GaN grown by metal–organic chemical vapor deposition (MOCVD) on epi-ready foreign substrates such as silicon, sapphire and later silicon carbide [2]. The epitaxy of InGaN and AlGaN on sapphire created LEDs that worked astonishingly well, given that their dislocation densities (10^8 – 10^{12} /cm²) far exceeded what was considered to be workable for a semiconductor device. The commercial markets for white LED lighting supported the growth of an industry that gained access to economies of scale and continuous improvement through incremental engineering advances.

In the meantime, the bulk growth community has proven that the material and device properties available from high-quality material open the door to new markets including high-power laser diodes, vertical high-power transistors (both needing conductive substrates) and lateral power devices (needing semi-insulating or SI-GaN). Three methods vie for the bulk market: hydride vapor phase epitaxy (HVPE), sodium flux and ammonothermal growth. HVPE has something of a toehold in the higher-power GaN laser market, but several ammonothermal groups are working to break out. Improvements in HVPE have decreased defect densities to $<10^6$ dislocations/cm² and improved crystal curvatures to the >5 meter-range with linear growth rates around 100–200 $\mu\text{m/h}$ [3,4]. While cost is an open question and sales volumes are nearly impossible to ascertain, it seems that a modest market exists today for 2-inch GaN wafers and that 4-inch to 6-inch wafers of high quality would be met with enthusiasm in the semiconductor market.

While maintaining something of its original blue aura, GaN is far from the only material in contention in these markets. The SiC market has grown exponentially in the



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last decade, while diamond, gallium oxide and potentially cubic boron nitride could all claim space in different applications, though primarily power electronics. Two widely cited figures of merit (FOM) for material quality in this domain are the Baliga FOM (BFOM) and the Johnson FOM (JFOM), which combine parameters including band gap (E_g), breakdown voltage (V_{BD}), carrier mobility (μ_e), dielectric constant (ϵ) and saturation velocity (v_{sat}) [5,6]. Specifically,

$$BFOM = E_g^3 \mu_e \epsilon = V_{Br}^2 / R_{ON} \quad (1)$$

$$JFOM = V_{BD} v_{sat} \quad (2)$$

It is worth noting that the second equality in Equation (1) is the formulation used for vertical p-n junction diodes. In Figure 1, the BFOM parameter is mapped against the current commercialization state for various materials. The two properties that make GaN stand out the most relative to the competition are (1) a high electric breakdown field and (2) the ability to tune the bandgap through the near-seamless integration with epitaxial InGaN (toward the visible) and AlGaN (further into the UV). Within the nascent ammonothermal GaN (Am-GaN) market, the strongest players commercially contending in ~2-inch wafers include NL-3 (from the Institute for High Pressure Physics or IHPP, also comprising what was formerly AMMONO), SixPoint, Kyocera (formerly Sora) and Mitsubishi Chemical Corp.

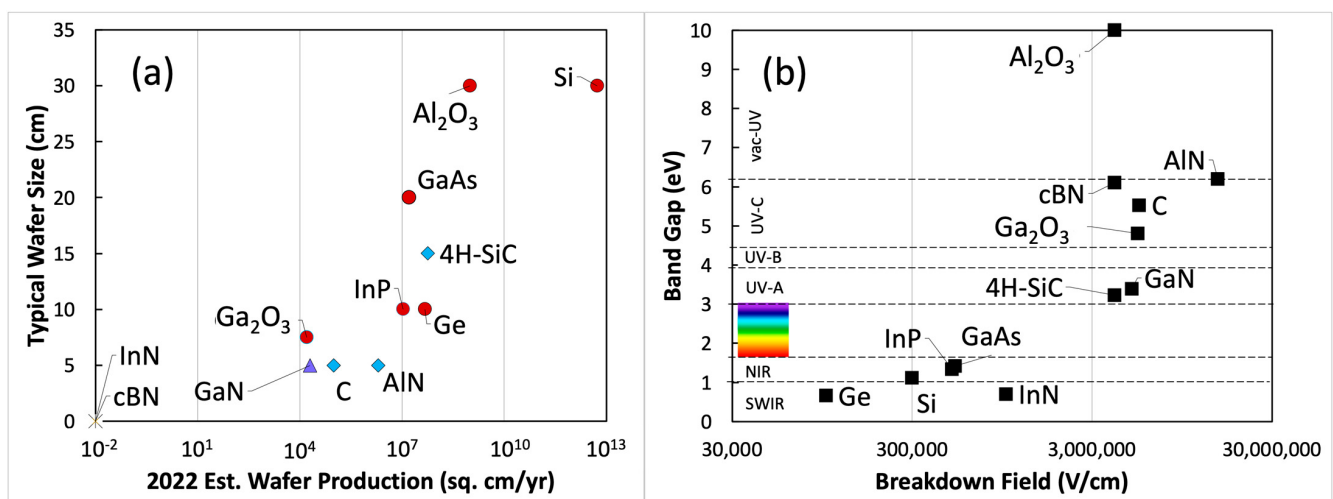


Figure 1. Comparison of relevant semiconductor substrates for electronic and optoelectronic applications. (a) Production wafer nominal dimension vs. area of wafers produced in 2022 (est.). Dot shape corresponds to primary growth method, with circles for melt growth, diamonds for vapor deposition, triangles for solution growth. InN and cBN are insufficiently developed to specify a method. (b) Semiconductor band gap vs. reverse-bias diode breakdown field. Optical bands are delineated with horizontal dotted lines. Generally, materials with the weakest production metrics in (a) have the highest performance potential in (b). Sapphire is a notable outlier, but it is not generally suitable for electronic devices. Data sources from [7,8] and industry reports.

The primary challenge in creating GaN crystals derives from the tendency of GaN to want to decompose. Since the triple-bonded N₂ molecule is tremendously stable, it becomes thermodynamically favorable to decompose the nitride into the metal and nitrogen gas at relatively low temperatures under moderate pressures. GaN is no exception and unfortunately decomposes at a temperature below its melting temperature at ambient pressures. The ability to compensate with high nitrogen overpressure is only feasible to a point. As a result, GaN has to be formed through either vapor deposition or solution growth methods in oxygen-free atmospheres. HVPE has reached a performance plateau

with limitations on crystal thickness due to edge stress and facet-driven area reduction. In solution growth, while at least one group continues to pursue a solution growth in a sodium flux [9], a significant research effort has gone into high-pressure ammonothermal solution growth, which will be the focus of this review [10,11].

A large commercial industry exists growing quartz via analogous hydrothermal methods, but nitride materials need ammonia to be the solvent. Crystal growth takes place by establishing a solubility gradient within a volume, where the source material is placed in the high solubility zone and the seed crystals are placed in the low solubility zone, as seen in Figure 2. Natural convection drives the flow of dissolved constituents and crystal growth rates depend on absolute solubilities, solubility gradients, mass transport and kinetic factors at the seed surface. In order to boost the lack of solubility for GaN in pure NH_3 , mineralizing agents are added to form intermediary species with gallium, thereby increasing solubility. These mineralizers can either induce basic pH values (alkali and alkaline earth metals) [12] or acidic pH values (halides) [13] within the ammonia solution. In practice, the basic ammonothermal GaN (Am-GaN-B) processes typically run at 2000–6000 atmospheres and 400–650 deg. C as compared with acidic (Am-GaN-A) processes at 1000–1500 atmospheres, 350–600 deg. C. Relatively few materials can withstand these combinations of temperatures, pressures and chemistry, so autoclave design is an important piece of the technology. For a more detailed introduction to ammonothermal GaN techniques, see [14].

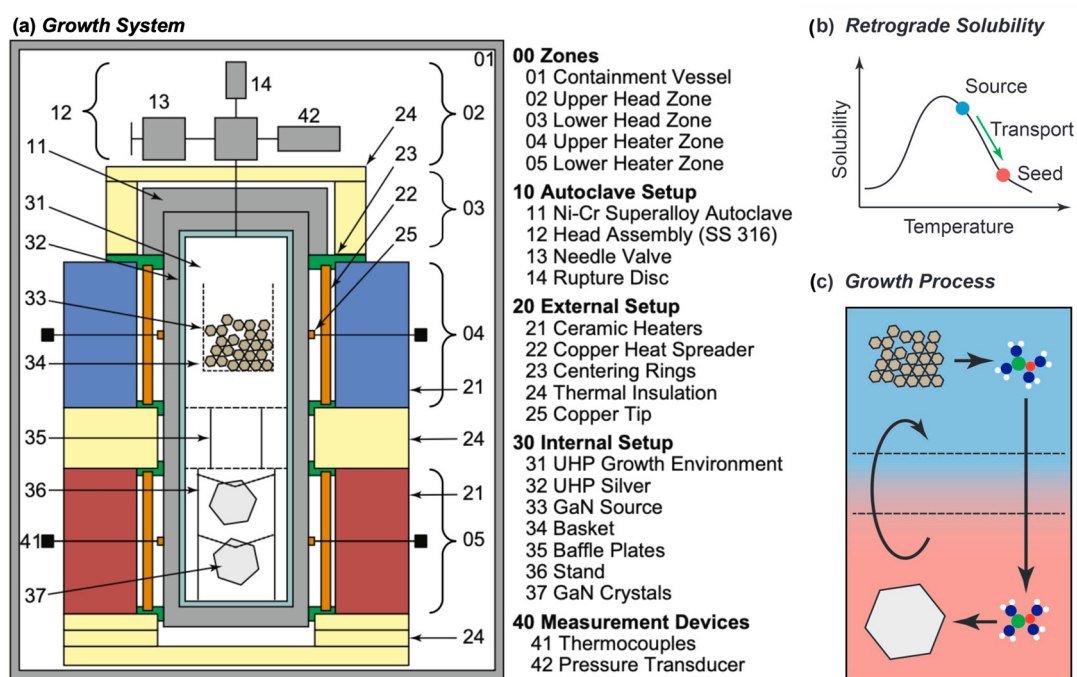


Figure 2. (a) Key parts of an ammonothermal growth system. Two thermal zones are formed (red and blue regions) with a temperature gradient of 30–100 deg. C. In the case of basic mineralizers and fluorine, the feedstock is dissolved at a lower temperature and crystal growth takes place at a higher temperature, as shown in (b). In other acidic mineralizers, the temperature gradient is inverted, but the hot zone is still kept in the lower position. In (c), supercritical ammonia fills the cavity and gravity-driven thermal buoyancy effects provide the main convective transport of growth species from the source reservoir to the crystal seed. Reproduced from [15,16].

The primary technical hurdles between Am-GaN and widespread commercialization remain (1) scaling to a larger wafer size, (2) improving wafer throughput and (3) yield, all while maintaining or improving the bulk crystal quality. There are good review articles summarizing the state-of-the-art in ammonothermal growth up through early 2018 [16–18], so this review will focus on advances in the last five years, looking at the following

areas: (1) growth methods and technology, (2) characterization methods and GaN material properties focusing on defects and (3) device performance results based on latest substrates.

2. Growth Methods and Technology

2.1. Progress in Growth Methods

The central delineator in growth technology is generally taken to be the mineralizer used. Groups from Poland (NL-3 at the IHPP) [17], Germany (University of Erlangen, University of Stuttgart) [19], China (Chinese Academy of Science) [20] and the USA (Six-Point [21], UCSB/Lehigh [22]) generally take the basic approach. Kyocera/Soraa (USA) [23] and the groups from Japan (Nagoya, MCC, Tohoku) [24,25] have opted for the acidic approach. Sodium is the most commonly cited mineralizer in the literature, although references can be found for other alkali options. Table 1 summarizes the most recently reported parameters from a number of different groups.

Table 1. Typical growth parameters for GaN growth reported in the last five years from different technical approaches described in this section.

	Units	IIHP/NL3	SixPoint	Tohoku/MCC	Soraa/Kyocera	Competition
Method		Am-GaN-B	NEAT	SCAAT/LPAAT	SCoRA	HVPE
Chemistry		Basic	Basic	Acidic	Acidic	GaCl ₃ -NH ₃
Wafer Size	cm	50–60	50–100	50–60	50 (2015)	50–150
Growth Rate	mm/day	24–60	30	170–205	700	2400
Temp. Range	deg. C	400–750	450–600	550–625	650–800	900–1100
Press. Range	MPa	100–600	100–300	100–200	100–600	Low
Oxygen	atoms/cm ³	10 ¹⁸ –2 × 10 ¹⁹	2–8 × 10 ¹⁸	-	10 ¹⁸	10 ¹⁷ –10 ¹⁹
DD	defects/cm ²	10 ³ –5 × 10 ⁴	10 ⁵	1–5 × 10 ⁴	10 ⁵	5 × 10 ⁶ –10 ⁸
Curvature	m	>20	20	1460	>20	1–5
Rocking Width	arcsec	<30	20–50	20–30	<30	30–80
Boule Thickness	mm	3–4	1–3	2–3	>2	3–4
Crystals/run	#	36	50	-	-	1

A recent paper from SixPoint outlines the performance from their “Near-Equilibrium Ammonothermal” or NEAT process [21]. The process reportedly involves growing at “near-equilibrium” conditions with a somewhat reduced growth rate compared to other sources. The lower growth rate and low crystal growth driving force are proposed to allow for long and stable growth runs of many crystals in parallel. From pilot production, many 2'' wafers and one 4'' wafer are presented, appearing to range from 1 to 3 mm thick, as seen in Figure 3.

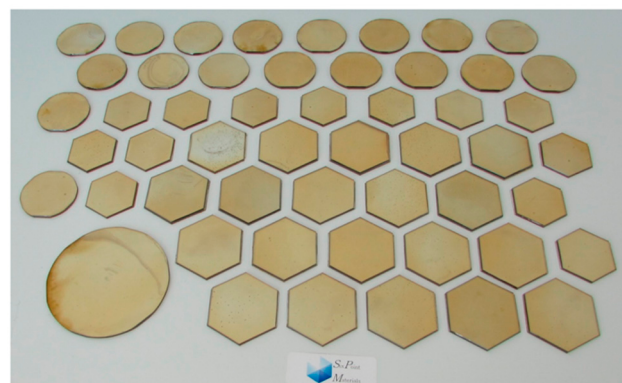


Figure 3. Crystals grown from a single batch at SixPoint ranging from 40 to 100 cm in lateral dimension. Reproduced from [21].

It is not mentioned whether the 4'' crystal is the result of incremental lateral expansion over long periods of time or whether it is the result of growing on a 4-inch diameter single crystal seed. Oxygen is reported to have been reduced to the low 10^{18} cm^{-3} range and optical clarity looks good while X-ray-based dislocation analysis on two areas suggests a mid- $10^5/\text{cm}^2$ dislocation density.

Recent papers from the IHPP at the Polish Academy of Sciences (former AMMONO, now NL3) also point to promising progress from basic Am-GaN [26–29]. They report results using basic mineralizers for their process, but do not specify which one they prefer. One of the hallmarks of their method is a two-stage growth process, as seen in Figure 4. In the first stage, a narrower rectangular seed is grown in a primarily lateral (although somewhat vertical or [000-1]) direction. The material generated from this lateral growth is presented to be consistently better in structural quality than the seed crystal, as seen in Figure 5, with dislocation densities as low as 10^2 cm^{-2} . It is well established that the lateral growth and vertical growth have drastically different levels of impurity uptake, causing internal stress when together [17]. The second step of growing the crystal thickness is accomplished using metal seed holders that inhibit growth in non-preferred directions. In all cases, the (0001) or bottom-facing direction of the seed crystal is masked. In the second stage runs, the edges are also masked to inhibit growth on non-polar and semipolar planes.

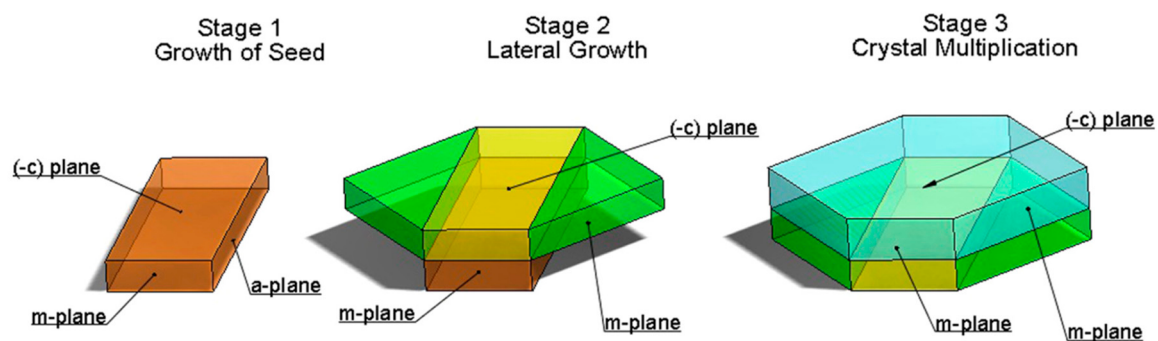


Figure 4. Schematic of 2-stage ammonothermal growth process with labeled facet directions, from [29].

One of the most recent papers compares crystals grown with flat edges to those grown with circular cross-sections [27]. The use of a circular edge mask constrains the crystal to maintain a circular cross-section. Meanwhile, the circular shape is credited with cutting down on edge stresses and resulting in crack nucleation points. As a result, the process yield increased significantly while the growth speed could be simultaneously increased by a factor from 2 to $60 \mu\text{m}/\text{day}$. Additionally, the authors also report on growth from multiple seeds tiled together. A small gap exists between the two seeds that are well-aligned, but it is not perfect. The gap is overgrown and the crystals merged by lateral growth, which is followed up by vertical growth across the entire two-seed cross-section.

Apart from these headline results, steady progress has been reported in understanding the influence of mineralizers in the ammonothermal process. In a study comparing different sodium sources, crystals were grown using sodium amide, sodium azide and sodium metal [30]. The form factors of the source materials are reported to play a significant role, with the amide and azide powders being significantly more oxygen-contaminated than bulk sodium metal. In the resulting crystals, the amide-assisted GaN surface is covered in small hillocks while the azide-assisted surface has long creviced trenches. The crystals from sodium metal runs, by contrast, had nearly featureless surfaces.

A further study examined rubidium and cesium as mineralizers [31]. They each tend to form heavy liquids that are fully miscible with liquid ammonia at room temperature. Through a combination of Raman and nuclear magnetic resonance (NMR) spectroscopy, they are able to identify specific molecular constituents present in the liquids and determine which molecules are most responsible for gallium transport under different ammonia concentrations.

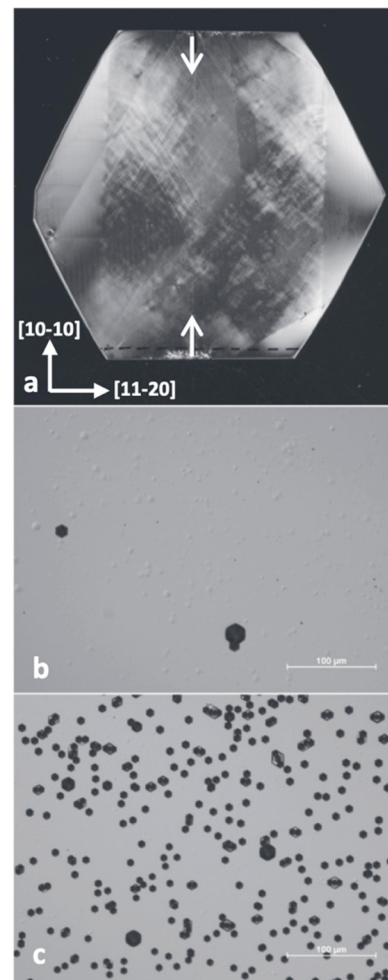


Figure 5. A GaN crystal with laterally grown wings (left and right) showing no stress-induced polarization under Nomarski microscopy (a). Dislocation etching of wing regions (b) and central region (c) indicate nearly two orders of magnitude of improvement in dislocation density. From [27].

Groups coming out of Japan (Tohoku University, Nagoya, Mitsubishi Chemical Corporation) have opted for the acidic mineralizers, most typically NH_4F . Notably, while early papers from Sora (now Kyocera) tout their ability to grow using basic or acidic environments, their published results as of 2017 use acidic mineralizers. While the pressure requirements for these acidic environments are generally lower than in the Am-GaN-B world, the halides are somewhat more chemically aggressive toward the metals in the autoclaves. Apparently expensive platinum-based liners have been used, but in a 2020 paper, Tomida et al. describe the use of a silver liner in a 60 mm inner diameter autoclave to both provide some protection to the autoclave and improve the impurity concentrations in the grown crystals [25]. Earlier papers described a Super-critical Acidic Ammonothermal (SCAAT) process, but the authors report a lower pressure regime here (100–120 MPa) and dub the process Low-Pressure Acidic Ammonothermal (LPAAT). The reported crystal growth rates are remarkably high compared with the basic techniques, up to 170 microns per side per day. Meanwhile, other quality metrics seem to be mostly on-par, except for possibly elevated dislocations. In a follow-up, further improvements are described including nearly bow- and mosaic-free $60 \times 60 \text{ mm}^2$ crystals with dislocation density as low as 10^4 cm^{-2} [24].

Most of the groups contributing to the ammonothermal literature have been working on the technology for more than a decade, but some new papers have come from a group at the Chinese Academy of Science using basic ammonothermal chemistry. One focus has been surface morphology influences on crystal growth, including both semi-polar and

non-polar faces [20,32,33]. Their most recent paper looks at the evolution of V-pits during growth [34]. Gaps initially present from HVPE growth defects become filled in via lateral and oblique growth planes as growth proceeds. The trend of lower dislocations in the laterally grown material mentioned earlier is confirmed, with a factor of 10 improvement in dislocation density.

2.2. *In Situ Measurements of Ammonothermal Growth*

Some of the most interesting science in the Am-GaN space comes from the application of novel in situ measurements to the high-pressure growth environment. The autoclave itself is not a welcoming environment for measurement techniques due to thick walls, temperatures in the >500 deg. C range and the risk of ammonia leakage from the vessel. Nevertheless, multiple methods have been proposed and reduced to practice to penetrate the autoclave wall: internal temperature measurement, ultrasonic probing, X-ray transmission measurements through sapphire windows and X-ray-computed tomography through the entire autoclave set up.

In a 2018 paper, Griffiths et al. place a sheathed thermocouple inside the autoclave bore to become as close as possible to the thermodynamics of the process [35]. Detailed analysis was applied to the temperature fields and compared with growth/etch-back measurements to identify a critical fluid density difference needed for the given baffle design to drive source material transport. Furthermore, the activation energy for growth on the c-plane and m-plane was estimated to be 140 kJ/mol and 190 kJ/mol, respectively.

The fluid dynamics and etch/growth behavior were also the primary target of a study that placed a specially designed active autoclave in an X-ray beam [36]. The experiment did not involve a full-fledged two-zone crystal growth autoclave, but rather an “optical cell” with a sapphire window especially designed for placement in the beam line. The optical cell cavity and heating was designed for long-term steady state conditions with uniform temperature distribution and minimal convection in order to maximize the chances of obtaining meaningful images given a relatively long image acquisition time (several minutes). Both basic and acidic environments were tested under crystal-dissolving conditions. Due to the relatively high atomic number of gallium, it was possible to see not only the change in the outlines of the crystal, but also the dispersion of gallium-containing species into the nearby ammonia solution. Based on X-ray absorption measurements over time, both the concentration of Ga-carrying species in the solvent and the diffusivity of those species were estimated, with values of 0.28 mmol/mL and $1.76 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively. Based on the analysis, the role of convection (absent in these experiments) was confirmed as critical to the gallium transport in the ammonothermal method.

In a separate but related experiment, Schimmel et al. worked to take the X-ray techniques to the next level by using a computed tomography (CT) approach [37]. In a comprehensive study, many experimental parameters (autoclave alloy, wall thickness, X-ray wavelength, image time, liner material) were optimized to provide the best possible contrast of the GaN elements within the autoclave. By taking a series of slices at different rotational angles around the autoclave, detailed images of the interior were produced using 300–600 kV X-rays, as seen in Figure 6.

It is further projected that applying X-ray CT to acidic growth autoclaves with minimized wall thickness could allow for the visualization of gallium-containing fluid flow.

To complement these efforts at experimentally peering inside the autoclave, numerical modeling of thermally driven convective flow patterns continues to suggest new insights. Researchers from Nagoya, Tohoku and Erlangen collaborated for a 2021 review of the field [38]. Since then, at least two noteworthy papers were published. In the first, Han et al. report on a crucible design that is indicated to improve convective flow and gallium uptake in computational fluid dynamics (CFD) simulations [39]. Adding a hole to the center of the basket containing the GaN feedstock, they predict improved nutrient dissolution and transport of gallium-containing species to the growth zone. With the assumption that mass

transport is the rate-limiting factor in the crystal growth, they conclude that enhanced crystal growth rates should result.

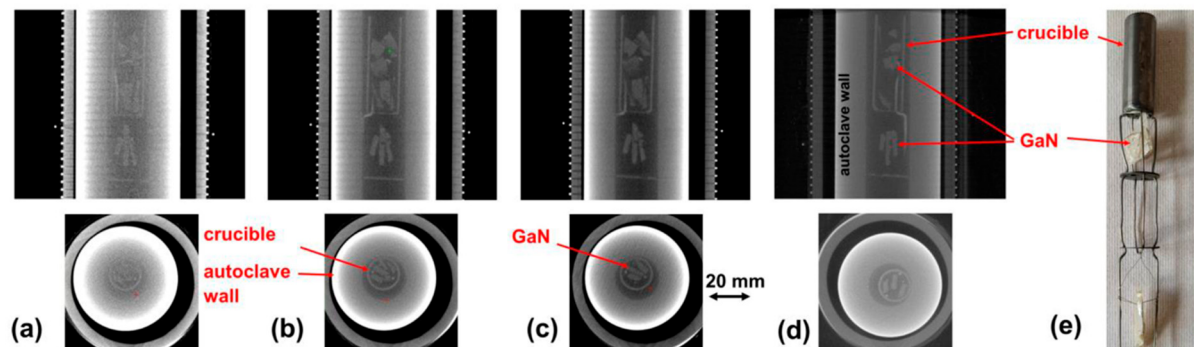


Figure 6. CT images of gallium nitride and Inconel support structures inside of an autoclave. (a) through (c) are Inconel 718 autoclaves while (d) is Haynes alloy. X-ray energies are (a) 300 kV, (b) 550 kV, (c), 600 kV, (d) 590 kV. (e) is a photograph of the internal parts present in the autoclaves. From [37].

In the second paper, Schimmel et al. report on numerical simulations of the transition period between seed etch-back and growth, examining behavior as a function of position within the autoclave [40]. The transition phase from etch-back to growth has been identified elsewhere as a potential culprit in defects incorporated into Am-GaN crystals. The system must transit from a gradient in one direction to a stronger gradient in the opposite direction, causing transitory thermal and convection states in the supercritical ammonia. The ends of the autoclave generally see the largest changes in absolute temperature, while the center regions likely see the greatest fluctuations in convective fields. Larger crystals will see a greater variation in behavior from one end to the other. Heat is being driven from the outside of the autoclave, so large gradients can arise between centrally positioned seeds and the autoclave wall. Overall, for a 90-min programmed transition, it is predicted to take 2–3 h for the internal states to truly stabilize in the growth temperature distribution. In the meantime, seed temperatures can vary from 20 to 70 K relative to the surrounding fluid, leading to parasitic growth conditions in some vertical zones of the autoclave.

Although much of autoclave design remains secretive within different groups, several insights are available in the literature. It has already been mentioned that silver linings have proven useful in the LPAAT method [25]. Cobalt alloys are also mentioned as an alternative to nickel–chromium superalloys while ceramic–steel composites are mentioned in regard to the growth of other nitride materials, while Malkowski et al. worked with molybdenum as an autoclave material despite its lower yield strength and toughness values in the 500–900 deg. C range [18,41,42].

3. Characterization Methods and GaN Material Properties

The fate of every good crystal is to be judged or even defined by its defects. GaN is no different. From the earliest days, dislocations have been a primary focus for device performance. While determining local dislocation densities is relatively straightforward using defect etching and optical microscopy, a quantitative method for mapping large areas of wafers has only been approximated using techniques such as cathodoluminescence and X-ray topography. In addition to estimating densities, the typing of dislocations is equally important.

3.1. Structural Defects

Table 2 provides an overview of dislocation characterization methods discussed here. It is worth noting that transmission electron microscopy is not listed here since it is virtually useless for dislocation densities lower than 10^6 cm^{-2} and covers areas at tiny fractions of a square millimeter.

Table 2. Metrics of importance in choosing an effective method for characterizing structural defects.

Dislocation Method	Units	Confocal Raman	Synchrotron XRT	Defect Etching	CL	PL	Bevel Etching	Borrmann XRT	HR-XRD
Sample Area	mm ²	0.0025	2500	0.25	2500	2500	0.25	2500	4
Dislocation Typing?		Yes	Yes	No	No	No	Yes	Yes	No
Destructive?		No	No	Yes	No	No	Yes	No	No
In-line Potential?		No	No	No	Maybe	Yes	No	Yes	Yes
Range Capability	Disl/cm ²	<10 ⁶	10 ² –10 ⁶	10 ² –5 × 10 ⁶	-	-	-	<10 ⁵	>10 ⁴
Measurement Depth		Surface	Full Depth	Surface	Surface	Full Depth	Full Depth	Full Depth	Full Depth
3D Depth Contrast	mm	2–25	N/A	N/A	N/A	N/A	5–400	N/A	N/A

In a paper developing confocal 3D Raman scattering, Holmi et al. are able to probe edge and mixed-type threading dislocations volumetrically [43]. Using diffraction-limited all-optical scanning, the authors probe dislocations as they move down through at least 20 microns of the sample depth and could determine the Burgers vector direction based on the orientation of compressive and tensile contrast for well-separated individual dislocations. There was no indication for ability to detect pure screw-type dislocations, and the areas of study were still rather small with 50-micron by 50-micron raster areas, but the depth contrast appears to be unique among the methods.

A study of synchrotron-based X-ray topography (XRT) from a large group of collaborators imaged 25 and 50-mm diameter wafers from HVPE and Am-GaN-B [44]. Their images were compared against a series of ray-tracing simulations for screw-type, edge-type and six varieties of mixed-type threading dislocations. In a survey of five areas on a wafer, they found an average of 96.3% of dislocations to be mixed-type while 3% were pure edge-type and the remaining 0.8% were screw dislocations in a wafer with a low overall concentration of defects ($5 \times 10^3/\text{cm}^2$). A second recent paper explores strain mapping using X-ray rocking curve topography in a synchrotron beam [45]. While the efforts here demonstrate the comprehensive characterization power of the synchrotron XRT method, the method itself is very challenging to introduce in any type of regular quality control feedback for crystal growers.

Dislocations are well-known to be the result of stress relaxation in the crystal lattice under plastic deformation conditions. While they partially relieve stress, they also retain distinctive stress fields that interact in increasingly complicated ways as the spatial density increases. Grabianska et al. have studied residual stress and dislocation densities using a combination of cross-polarized optical microscopy (Nomarski contrast) and defect etching to characterize an effect they term Stress-Induced Polarization Effect or SIPE [26]. This defect shows up clearly in the Nomarski microscope in areas of vertical growth, but only at the crystal position in the autoclave directly under the baffle, as seen in Figure 7.

In neither crystal did the laterally grown material exhibit any SIPE. Further cross-sectional analysis and UV illumination pointed to growth from areas of the surface roughened by uneven etch-back. In the regions grown above these rough patches, the dislocation density was found to be an order of magnitude higher than that in the seed crystal. Unstable convection during etch-back and the transition from etch-back to growth in the near-baffle region is implicated as the root cause of the process instabilities. In this case, the polarized image contrast roughly correlates with dislocation density, but would not be useful for detecting dislocation distributions that are not associated with the rough growth features.

A more direct method for evaluating structural defects is possible with XRT taking advantage of the Borrmann Effect [46]. Using a transmission geometry, this method relies on the anomalous transmission of X-rays that would normally be absorbed due to distortions about the perfect crystal reflection range, provided that the defects are sparse enough not to overlap. As with many XRT techniques, a relatively large area can be sampled in a single image capture, but the image will be dense with highly resolved local information that is available under magnification. Individual threading dislocations are visible as “rosettes” of light and dark contrast. A wide range of other defects are discernible as well, including honeycomb defects (hexagonal dislocation structures, dislocation bundles, growth bands,

dislocation walls, subsurface damage, seed tiling boundaries). It is not unreasonable to think that an advanced image analysis tool could be applied to these images and provide quantitative feedback for every crystal in a production run. The issue of defects from seed tiling are also explored at some length. The practice of seed tiling appears to be somewhat common in the pursuit of larger wafers. Typically, seeds are placed adjacent to one another with a best-effort applied to alignment, then allowed to grow together based on lateral growth from an inclined facet. As pointed out in the paper, seeds can be misaligned in three independent angles: in-plane pole rotation, roll-rotation (with an axis parallel to the seam line) and pitch rotation (out of plane but with an axis perpendicular to the seam). Depending on the degree of misorientation, defects can range from periodic arrays of dislocations to small-angle grain boundaries (SAGBs) to full-fledged grain boundaries. In Figure 8, an optical microscope cross-section of a crystal grown from two tiles is reproduced from the Appendix of Kirste et al. [46].

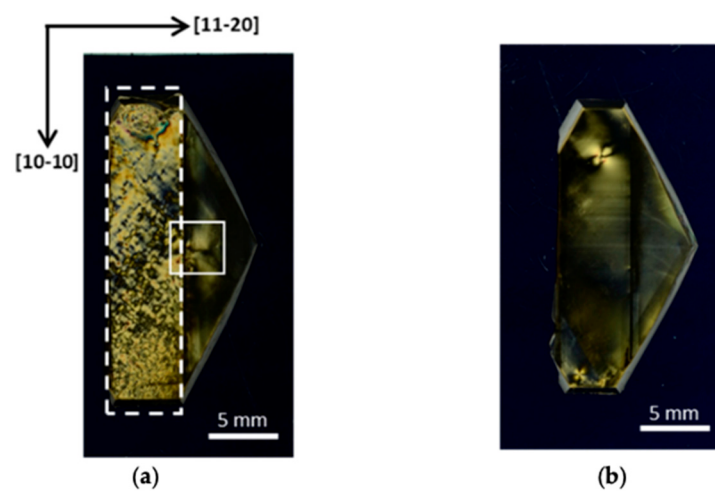


Figure 7. Optical images of two GaN crystals grown from rectangular seeds imaged under cross-polarized illumination. The crystal on the left (a) was grown directly under the baffle in the center of the autoclave. The dotted line demarcates the original seed geometry. The crystal on the right (b) was grown at a position near the bottom of the autoclave. From [26].

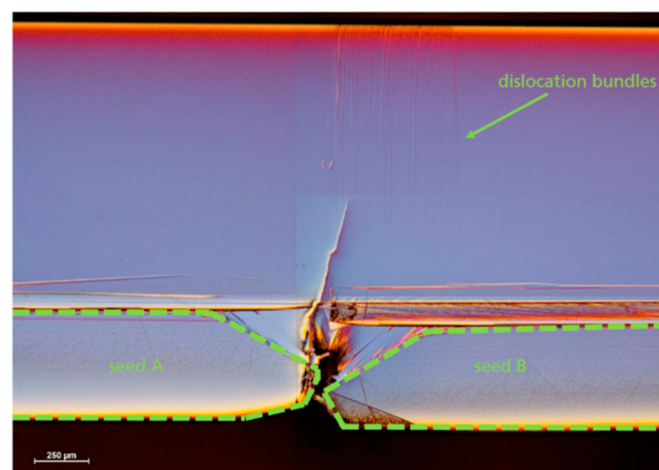


Figure 8. Optical microscope image of a GaN crystal grown from two seeds tiled together (A, B). After consolidation of the grown crystal, dislocation bundles propagate upwards. From the Appendix of [46].

Seed tiling and its defects have been studied heavily in other materials, notably silicon ingots grown for solar. In these applications, crystals would need to grow much thicker than typical GaN growth (from 200–500 mm), and dislocation bundles would frequently

devolve during growth into huge dislocation cascades with mosaic structure SAGBs. Many techniques were investigated to minimize this behavior that may be useful to the GaN community. In some cases, specific misorientations (such as a $\Sigma 5$ or $\Sigma 13$ grain boundary) were found to grow stably with a lower chance of decomposition than a boundary with slight but unintentional misalignment. In other cases, wafer segments were placed on-end between two seed crystals to form two parallel grain boundaries that would both grow in a predictable vertical direction and also functionally contain structural defects to the thin zone between the two tiles, protecting the remainder of the crystal [47–52].

Not all dislocations derive from crystal growth. The wafer-cutting process induces significant amounts (up to 10s of microns) of sub-surface damage in the form of dislocations. Removal of this process damage is critical to device performance. In a 2019 paper, Hashimoto et al. use glancing-angle X-ray rocking curves to assess the extent of sub-surface damage through grinding, lapping, polishing and chemical–mechanical polishing (CMP) processes [53]. In the end, the sub-surface damage is completely removed and the rocking curve full-width at half maximum (FWHM) matches that of an as-grown crystal.

3.2. Doping

The presence of oxygen in GaN crystals provides effective n-type doping from substitutional incorporation on nitrogen sites. Typically, uncontrolled oxygen sources cause doping levels to be higher than those desired by device makers, especially since the presence of high levels of oxygen typically affects optical clarity and coloration. Methods to control oxygen sources are therefore sought after, including noble metal liners as previously mentioned [15,24].

In a 2019 proceeding, Hashimoto et al. report on successful oxygen reduction in SixPoint GaN, decreasing from initial levels of 2×10^{19} atoms/cm³ to 7×10^{18} atoms/cm³ with a corresponding improvement in 450 nm optical absorption coefficient to 5.6 cm^{-1} , following a linear relationship on a log-log graph [54]. No insight is provided as to what process improvements were used to cause this improvement.

A 2018 paper from Tomida et al., on the other hand, provides details on efforts to reduce oxygen during crystal growth through the use of an oxygen gettering material [55]. They chose several metals known to have a high oxygen affinity ($\text{Ca} > \text{Al} > \text{Ti} > \text{Si}$) and added them to their acidic Am-GaN process. While reporting a marked decrease in growth rates for all options in m-plane orientation, Ti and Si also showed no appreciable oxygen gettering. Ca was expected to be effective based on its oxygen affinity, but it was found to react aggressively with the NH_4F to form CaF_2 . Aluminum was found to be effective as an oxygen getter, producing crystals with higher clarity, better UV fluorescence and photoluminescence without any reported negative impacts. The magnitude of oxygen reduction was not measured specifically, but is presumed to be causal to the other benefits.

Apart from oxygen, other impurities can be intentionally added to manipulate electronic doping levels. Manganese and magnesium are both known p-type dopants in that area often used to compensate oxygen in the growth of semi-insulating crystals. A 2020 study examines material incorporating these two dopants using positron annihilation [56]. Positrons are a useful tool for detecting vacancies on cation sites. When irradiating a material with positrons, the lifetime of the positron will be slightly but measurably longer when it becomes trapped in a negatively charged vacancy. The length of time of prolonged positron life can be correlated to properties of the vacancy. While both Mn and Mg dopants are capable of acting as effective counter-dopants for semi-insulating substrates, their behaviors with regard to gallium vacancies are markedly different. Manganese doping seems to encourage vacancy incorporation, to the extent wherein $1\text{--}5 \times 10^{16} \text{ cm}^{-2}$ fluences of irradiation do not further increase positron lifetimes (indicating that the samples are vacancy saturated as-grown). Doping with Mg, on the other hand, causes very low increases in positron lifetime compared to “defect-free” reference material, while irradiation clearly introduces significant amounts of new vacancies.

Zinc doping has been speculated as a p-type option, and its action as a p-type dopant is confirmed for the first time by Zajac et al. [57]. Zinc is shown to be not very effective

as a dopant, and a poor choice relative to Mg or Mn. At Zn concentrations as high as 10^{20} atoms/cm³, the hole concentration does not exceed 4×10^{15} cm⁻³. A carrier mobility of 3 cm²/V/s is measured in the sample, and the position in the band gap is determined to be relatively deep at 260 meV above the valence edge. Despite this, Zn is shown to occupy substitutional sites and induce a degree of p-type compensation.

3.3. Point Defects and Impurities

In addition to the doping elements already discussed, a number of other impurities are relevant to the performance of GaN devices. Secondary Ion Mass Spectroscopy (SIMS) is the primary method for evaluating impurity profiles. The impurities of greatest concern form deep level carrier traps in the band gap, typically electron-rich transition metals. Carbon, silicon and mineralizers are also of interest. Suikhonen et al. provide a good summary of reported results up to 2017 [16]. There have not been many papers focused on this recently, but in 2019 Amilusik et al. report on impurities measured in Am-GaN-B material used as seeds for HVPE [58]. Impurity ranges are shown in Table 3.

Table 3. Elements detected by SIMS in Am-GaN-B samples (from [16,58]).

Element	Typical Range (atoms/cm ³)	Amilusik Range (atoms/cm ³)	Change
H	1×10^{19} to 6×10^{20}	4×10^{18} to 5×10^{19}	Improvement
C	High 10^{16} to Low 10^{17}	8×10^{16} to 1.5×10^{18}	Similar to worse
Si	Low 10^{18}	1×10^{17} to 2×10^{18}	Similar
Na	1×10^{16} to 1×10^{19}	1×10^{16} to 7×10^{17}	Similar to better
Mg	High 10^{16} to Low 10^{17}	5×10^{15} to 8×10^{17} (dopant)	Similar
Mn	3×10^{16} to 2×10^{18}	6×10^{15} to 1×10^{18} (dopant)	Similar
Fe	$\sim 10^{16}$ to Low 10^{17}	3×10^{15} to 2×10^{16}	Improvement
Zn	Not reported	8×10^{16} to 2.5×10^{18}	N/A

In earlier work, the use of a silver liner inside a Ni-Cr alloy autoclave was shown to reduce [Al] by a factor of 2, while [Si], [Fe] and [Mo] were all reduced below the SIMS detection limit [15].

Complexes between gallium vacancies (V_{Ga}) and hydrogen can be electrically active as well. Vacancies are generally difficult to detect, but there are at least two methods that can shed light on these point defects. Reschikov et al. use photoluminescence (PL) to assess defect complexes [59]. One of the main questions with V_{Ga} is how interstitial hydrogen (H_i) and substitutional oxygen (O_N) interact with them to form complexes of the form V_{Ga} -nH and V_{Ga} -mO_N where n and m vary from 1–4. With annealing at temperatures from 300–1400 deg. C and with pressures both at atmospheric pressure and under high pressure, the authors correlate specific defect complexes with atomistic simulations to PL defect bands. A YL2 peak arises in lower oxygen Am-GaN at 600–800 deg. C and then drops sharply above 1050 deg. C. It matches simulated behavior for a V_{Ga} -3H_i complex. No peak is observed in high oxygen material. OL3 and RL4 peaks are present in both types of samples, but a broad rise and fall centered around 950 deg. C in low oxygen material transforms into sharp peaks at ~ 1120 deg. C in the high oxygen sample. The RL and OL peaks are not typical of material assessed in prior analysis. The RL4 peak matches reasonably well to simulations of a V_{Ga} -3O_N complex and its thermal behavior makes sense. The origin of the OL peak is unknown but is speculated to be a V_{Ga} -O-H complex.

These complexes have also been investigated using Fourier Transform Infrared Spectroscopy (FTIR). In a 2017 paper, the group from Soraa reported the first direct evidence for V_{Ga} -H-O complexes using FTIR, with Hall measurements showing their compensatory electronic nature [60]. Their results suggest that V_{Ga} -O-H and V_{Ga} -O-2H comprise the bulk of the defects in Am-GaN with mid-level oxygen concentrations and correlates to the 423 nm luminescence and optical absorption behavior. These observations complement earlier work focused more directly on V_{Ga} -nH complexes [61,62].

Apart from FTIR and PL, device-based electrical methods can be a powerful method for investigating electronic substrate quality. In a 2018 paper, results on Ni Schottky diodes with indium ohmic contacts have been reported [63]. In I-V and C-V measurements during temperature sweeps from 77 K to 500 K, the defects in the band gap were characterized using Photoinduced Current Transient Spectroscopy (PICTS), a variant on Deep-Level Transient Spectroscopy (DLTS). The m-plane-oriented Am-GaN material was found to be semi-insulating p-type with the Fermi level pinned at around 0.9 V above the valence band edge. Weak deep-level hole traps were detected with band gap positions of 0.7, 0.9 and 1.2 eV above the valence band. The defect concentrations are measured to be 5.4×10^{13} , 190×10^{13} and $5.4 \times 10^{13} \text{ cm}^{-3}$, respectively, with the $E_v + 1.2 \text{ eV}$ defect having the largest capture cross-section at $4 \times 10^{-12} \text{ cm}^{-2}$. In an additional finding, no significant electron traps were detected at all, indicating that this material may be suitable for non-polar lateral devices such as AlGaIn/GaN high electron mobility transistors (HEMTs).

4. Device Performance Results

All of this work ultimately culminates in the use of the best Am-GaN samples in devices. Device results prior to 2018 are nicely summarized in [17]. The last five years have seen some impressive progress in the main metrics of device quality, including breakdown voltage, ideality and on resistance.

Working with GaN on Am-GaN P-I-N diodes, Chen et al. report favorable results [64]. Working with a vertical mesa diode, an on-state resistance of $0.31 \text{ m}\Omega/\text{cm}^2$ is measured, while the device breakdown voltage measures up to 3.04 kV. The diode ideality was measured at around 2.2. Putting these together, a Baliga FOM value of $29.7 \text{ GW}/\text{cm}^2$ is obtained. In the same year, authors from SixPoint reported on P-I-N devices made on their material [65]. Using substrates grown in a batch of a material from a lightly filled reactor, they produced diodes with an ideality of 2.08, a breakdown voltage of 1430 V and a Baliga FOM greater than $9.2 \text{ GW}/\text{cm}^2$.

In a study using vertical P/N mesa diodes, Taube et al. reported on high current injection and high breakdown voltages [66]. In a device with five layers of epi-GaN, six guard rings and polyimide passivation, bright electroluminescence was seen under forward bias. The spectra revealed strong near-band-edge emission and only weak, broad bands related to defects, consistent with high structural quality material. The maximum current densities were in the range of $9\text{--}10 \text{ kA}/\text{cm}^2$. On/off current ratios exceeded 10^{13} . Ideality factors ranged from 2.3 for diodes with 360 nm etch depth to 1.5 for the 550 nm etch depth device. Specific ON resistance also varied with etch depth, from around $0.4 \text{ m}\Omega/\text{cm}^2$ for the 360 nm etch depths to as low as $0.007 \text{ m}\Omega/\text{cm}^2$ for the 550 nm etch depth devices, which is the lowest value reported to date for high breakdown voltage vertical GaN p-n diodes. The exceedingly good performance is attributed to a high efficiency of photon recycling in this low-defect material. The breakdown voltage does not follow the same trend as the previous parameters, reaching its peak at 1940 V for the middle etch depth case (450 nm), with lower values on either side. Overall, the high current injection measurements result in a BFOM that was the highest reported as of the end of 2022 for this type of device.

A very recent study reports further improvements in device performance [67]. In a vertical device on a bulk GaN substrate, the authors report the use of an optimized guard ring structure aimed at maximizing breakdown voltage. With the addition of a very low doping ($\sim 10^{15} \text{ cm}^{-3}$) drift layer and excellent ohmic contacts, a breakdown voltage of 4900 V is reported. With this record high voltage and a specific on-resistance of $0.9 \text{ m}\Omega/\text{cm}^2$, the Baliga FOM reaches $27 \text{ GW}/\text{cm}^2$.

5. Conclusions

The technology associated with ammonothermal GaN crystal growth is undeniably challenging. With pressures and temperatures that test the limits of even the strongest materials and chemical environments that are highly corrosive to most materials, finding a process window that can simultaneously deliver reasonable growth rates and high-quality

crystals is a daunting task that has been taken head on by several groups around the world. The fans of acidic mineralizers have a well-established advantage in growth rate, but the quality from processes with basic mineralizers are reported to be more consistent. In growth techniques, a process constraining growth to a cylindrical shape seems to be a stand-out in decreasing stress and improving yield, while the use of a silver liner in the Am-GaN-A process has cut the autoclave cost while producing excellent quality. Efforts to observe in situ the convection and crystal growth within the autoclave have made advances through the application of X-rays, both through sapphire windows and using computed tomography.

The study of GaN defects has progressed as well. While growth process improvements continue to steadily lower dislocation rates, the very lowest values now extend to the 10^2 cm^{-2} range. Bow process-induced crystal stress and stress-induced polarization effect also have seen improvements, underpinned by improvements in the understanding of their generation mechanisms. The Borrmann effect XRT was shown to be a particularly good tool for imaging defects. Zinc was measured for the first time to induce p-type doping in GaN, while Mn doping was shown to be correlated with significant vacancy incorporation. Oxygen concentrations are reported to be lower from several sources, and aluminum was demonstrated to act as an effective oxygen gettering agent in the ammonothermal process.

These advances have culminated in setting new standards for quality in vertical devices, with breakdown voltages reported from 1940 to 4900 V and BFOM values demonstrated in the 27–30 GW/cm² range with lowest-defect material leading the way.

In the meantime, there is constant pressure to obtain a product to market before advances in the incumbent technologies or the emergence of another wide band gap substrate squeeze out the business case for Am-GaN wafers. The shining example of the successful hydrothermal quartz industry continues to motivate ammonothermal growers, and industrial players do seem to be delivering on the long-promised ability to grow many crystals in parallel. Perhaps the greatest development challenge continues to be the very long growth times associated with this technology, fundamentally limiting the pace at which technical advancements can be made. The ability to peer into the process in situ is invaluable, potentially reducing the turn time on experimental results by an order of magnitude. In the next five years, the race to 75 and 100 mm diameter wafers is on, and there is good reason to believe that the teams that can get there will not be too late to find a market that they can grow into.

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