

GaN single crystals grown on HVPE seeds in alkaline supercritical ammonia

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Ammonothermal growth (synthesis in supercritical (*sc*) ammonia fluid) has the promise of producing large low defect gallium nitride crystals through the application of techniques similar to those used in hydrothermal growth. Retrograde solubility of GaN greater than 5% by weight using group I amides as mineralizers is demonstrated in high nickel content autoclaves at pressures of one to three kilobars and temperatures between 300 to 600°C. The above conditions were optimized to grow single-crystal GaN at rates up to 40 μm per day on one cm^2 seeds. Gallium nitride Hydride Vapor Phase Epitaxy (HVPE) seeds are placed in the higher temperature zone below the nutrient basket employing the same configurations used in reverse gradient hydrothermal growth of berlinite (AlPO_4). GaN single crystals grown by the ammonothermal technique were characterized by X-ray diffraction, photoluminescence, scanning electron microscopy (SEM), atomic force microscopy (AFM), and chemical etching. The nitrogen-terminated face tends to exhibit a flatter surface morphology than the gallium-terminated face, which is made up of a series of hexagonal columns. Major impurities in the crystal include potassium from the mineralizer, metals from the autoclave, and oxygen. The nitrogen-terminated face incorporated a lower level of metallic impurities in comparison with the gallium-terminated face. Finally, several process phenomena such as ammonia decomposition, parasitic nucleation of GaN on the autoclave walls, impurity incorporation, and defect generation in single-crystal GaN layers grown on HVPE seeds are identified and their possible mechanisms are discussed. © 2006 Springer Science + Business Media, Inc.

1. Introduction

The gallium nitride material system including gallium, indium, and aluminum ternary nitrides, has received a great amount of attention in the last decade. Current and potential GaN based devices include green-UV LEDs, detectors, and laser diodes; IR and terahertz devices; and high power electronic devices that operate at frequencies above 10 GHz. The annual commercial market for GaN devices is expected to rise to \$5B by 2007 [1].

Traditional molten techniques used to produce Si and GaAs boules for substrates cannot be applied to GaN because of the extremely high pressure and temperature needed to melt GaN [2]. Therefore, the majority of nitride devices are manufactured on heterogeneous substrates such as sapphire or SiC. The resulting large number of defects in the device active layer(s) degrades lifetimes, lowers efficiencies, and decreases product yields [3]. Because of the emerging nitride market and the deleterious effects of using non-native substrates there

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has recently been great interest in developing a low cost process to produce GaN substrates. Several researchers have grown centimeter-diameter GaN platelets by flux growth, wherein a few percent of nitrogen is soluble in molten gallium at tens of kilobars of pressure and temperatures of 1500-2000°C, but this method is cost-prohibitive [4]. Sublimation, alkali flux growth, and HVPE have been employed for growth of GaN, but these methods have yet to produce substrates of acceptable size and quality, at a reasonable price [5-7].

Growth in high-pressure supercritical ammonia fluids (ammonothermal growth) is an attractive technique for achieving high volume production of GaN substrates. Ammonia has many similarities with water. Both are polar solvents, have high dielectric constants, and dissolve a variety of inorganic compounds. A chart of the physical properties of ammonia and water is shown in Table I.

Ammonothermal growth is the analog of hydrothermal growth, which has been used to produce hundreds of bulk oxide crystals of varying crystalline and molecular structure over the last 100 years. Millions of kilograms of low-defect-density hydrothermal quartz are produced annually with diameters up to 15 cm. Nitrogen compounds can be synthesized in ammonia solvents, much as oxides are synthesized in aqueous solutions, by dissolution and precipitation mechanisms. The solvation properties of water and ammonia can be increased by introducing an ionizing acid or base to increase the number of cations or anions in a particular solution. These ions break the bonds of solute molecules by lowering the electrostatic forces in the crystal. Thus, intermediate ionized complexes are formed in solution. A comparison of the water/ammonia dissolution mechanism is in Table II.

Despite the similarities between the hydrothermal and ammonothermal growth methods, the ammonothermal technique has not been exploited for large-scale synthesis of bulk nitride crystals in the same way that large oxide crystals have been grown hydrothermally. However, ammonia is the most studied and best known non-aqueous solvent. A large body of research, stretching from 1900 to the present day, has characterized many chemical, physical, and mechanical properties of ammonia solutions such as viscosity, electrical conductivity, and density. Many inorganic and organic compounds have been synthesized in ammonia-based solvents, but the majority of the research was performed at temperatures and pressures below the critical point of ammonia, and concentrated on forming submicron powders.

Recently, liquid ammonia has been used in catalytic reactions for medical applications, waste treatment processes, and synthesis of nitrates for fertilizers. Investigation of precipitating nitride powders in *sc* ammonia was first attempted by Jacobs in the 1960s and 1970s [8]. Peters reacted aluminum metal with *sc* ammonia and potassium in order to obtain AlN powder, and suggested the reaction

TABLE I Properties of ammonia and water

Property	Ammonia NH ₃	Water H ₂ O
Boiling point (°C)	-33.4	100
Freezing point (°C)	-77.7	0
Density (g/ml)	0.68(-33°C)	0.96(100°C)
ΔH _{vap} (kcal/mol)	5.58	9.72
ΔH _{fus} (kcal/mol)	1.35	2.0
Dielectric constant	22(-33°C)	80(0°C)
Dipole moment, Debye units	1.46	1.84
Polarizability, cm ³ (10× ²⁴)	2.25	1.49
Spec. conductance (ohm ⁻¹ cm ⁻¹)	4 × 10 ⁻¹⁰	4 × 10 ⁻⁸
Viscosity at 25 °C, cP	0.135	0.891

TABLE II Comparison of dissolution processes in hydrothermal and ammonothermal solvents

Hydrothermal: Oxides	Ammonothermal: Nitrides
2H ₂ — H ₃ O ⁺ + OH ⁻	2NH ₃ — NH ₄ ⁺ + NH ₂ ⁻
Ga ₂ O ₃ in alkali water solution: Ga ₂ O ₃ + 7H ₂ O + 2OH ↔ 2Ga(H ₂ O) ₂ (OH) ₄	GaN in ammonobase solution GaN + (x-3)NH ₂ + 2NH ₃ ↔ Ga(NH ₂) _x ^{3-x} NH ₂
Mineralizers Acids: HNO ₃ , HCl, HI Bases: KOH, NaOH, LiOH	Mineralizers Acids: NH ₄ Cl, NH ₄ I, HCl, HI Bases: KNH ₂ , NaNH ₂ , LiNH ₂

was endothermic, with retrograde grade solubility [9]. Lan showed similar results for reacting gallium with lithium and *sc* ammonia to obtain GaN powder [10]. Dwinlinski not only reacted aluminum, gallium, and boron to obtain the corresponding nitrides in alkaline *sc* ammonia, but also dissolved GaN and AlN powder in the same solutions [11-14]. Recently, several groups have dissolved and precipitated submillimeter-size GaN spontaneously in both alkaline and acidic *sc* ammonia, but did not deposit material on a seed. Kolis has transported milligrams of GaN to a seed, using azides and amides mixed with halides as mineralizers, but growth was limited [15].

Here we present experiments that both confirm retrograde solubility of gallium nitride in *sc* ammonia with alkali amides as mineralizers, and data for the growth of gallium nitride on HVPE seeds. Although further work must be done in kinetics, phase relationships, solubility, and fluid dynamics, this present work serves as a starting point for developing a methodology for producing large-area GaN bulk crystals in high pressure ammonia fluids.

2. Experimental methods

All work was performed at the U.S. Air Force Research Laboratory facilities at Hanscom Air Force Base, MA, USA. The ammonothermal growth was performed in high-strength nickel alloy autoclaves. Solubility

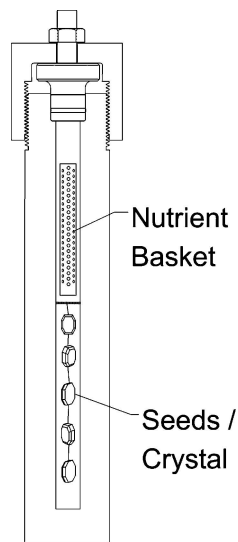


Figure 1 Autoclave configuration for ammonothermal growth of GaN with retrograde solubility.

experiments were conducted in 15 cc autoclaves with a 1 centimeter internal diameter. Seeded growth experiments employed autoclaves with a 2.2 cm internal diameter and 140 ml volume. Both sets of autoclaves are capable of sustained operation at 600°C and pressures up to 4 kbars. Polycrystalline GaN, synthesized by an in-house vapor process, was suspended in a scaffold near the bottom of the autoclave to obtain solubility data. An orientation of seeds with respect to nutrient that was consistent with retrograde soluble materials was employed for the seeded growth experiments, so that density-driven convective flow could be obtained (Fig. 1).

Single crystal “free standing” gallium nitride up to 200 μm thick and up to one centimeter square, grown by Hydride Vapor Phase Epitaxy (HVPE) and supplied by Richard Molnar of MIT Lincoln Laboratory, were used as seeds and suspended by a wire scaffold near the bottom (warmer portion) of the autoclave. Polycrystalline GaN (typically 5–10 grams) was used as the source material (nutrient) and was suspended in a basket in the top (colder) portion of the autoclave. Baffles were placed between the nutrient and the seeds to create a steeper temperature gradient between the dissolution and crystallization zones.

The material was placed in one of the autoclaves, which was then loaded into a glove box. Depending on the autoclave used, the desired percent fill of ammonia, and the concentration of amide desired, 0.5–6 grams of alkali metal and/or alkali amide were added. Typical amide concentrations were 2–4 molar. The autoclave was then removed from the dry box, chilled in a bath of 2-propanol and solid carbon dioxide, attached to a filling station, and evacuated. Once the autoclave temperature fell below minus 50° C, liquid ammonia was condensed into the autoclave to achieve the desired fill rate (0.65–0.85 moles for the smaller autoclaves and 3–4 moles for the larger

autoclaves). The autoclave was then removed from the filling station and weighed on a scale accurate to $\pm 0.2\text{g}$ to determine the amount of ammonia transferred.

The autoclave was then placed in an enclosed fume cabinet to ensure that any escaped ammonia went to exhaust. Sufficient insulation was packed around the autoclave to prevent an excessive load on the heaters. The autoclave was then heated to between 300 and 600°C while monitoring pressure. A temperature gradient was maintained such that the top of the autoclave was colder than the bottom. Experiments continued for 3–7 days at temperature for the solubility experiments and 20 days or more for the seeded experiments.

At completion of the run the autoclave was cooled to room temperature and the ammonia was evaporated into a water bath. The autoclave was then opened, and the nutrient basket and/or scaffolding were removed. For solubility experiments the remaining portions of the GaN nutrient were weighed to determine the amount of dissolved material. Any material that nucleated on the walls of the autoclave was collected, filtered, and weighed. For seeded growth experiments, the ammonothermal crystals were removed from the scaffolding and etched in an aqua regia solution to remove any metallic or oxygen impurities from the surface.

Scanning electron microscopy (SEM), atomic force microscopy (AFM), high resolution X-ray diffraction, and photoluminescence (PL) measurements were performed on the GaN crystals that had grown on the HVPE seeds by the ammonothermal technique. SEM measurements were performed on a JOEL JSM-840 scanning electron microscope. Double-axis rocking curves were performed with a Phillips PW1830 high-resolution four-circle X-ray diffractometer system with a 1×3 mm spot size. Atomic force microscopy was done on a Digital Instruments Nanoscope 3A. The impurity concentrations in the starting material, in heterogeneously nucleated GaN, and in GaN nucleated on HVPE seeds were analyzed by glow discharge mass spectrometry (GDMS) by Shiva Technologies Incorporated and secondary ion emission spectroscopy (SIMS) by Evans Analytical Incorporated. Finally PL was performed with a 0.25 meter grating monochromator, CCD detector, and a 325 nm CW helium-neon laser source.

3. Results

The solubility of gallium nitride in supercritical ammonia solutions in the presence of alkali amide mineralizers was determined to decrease with increasing temperatures, a characteristic of retrograde solubility. GaN solubility from 1–14% weight was obtained in 2–4 molar amide ammonia solutions (Fig. 2). The volume of liquid ammonia condensed into 15 ml autoclaves had an uncertainty of $\pm 5\%$ and the temperature gradient was 5–25°C/cm for

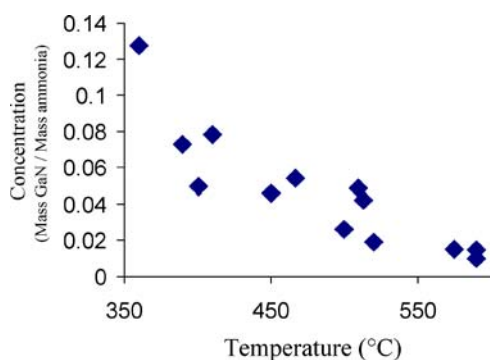


Figure 2 Solubility of gallium nitride in supercritical alkaline ammonia.

the experiments shown in Fig. 2. Experiments where the ammonia is measured with greater precision and the temperature is closer to isothermal conditions are currently being conducted to obtain more accurate solubility data for potassium amide and other mineralizers.

Several experiments confirmed that hexagonal GaN was thermodynamically favored over ammoniate or amide complexes above 300°C in solutions of ammonia with alkaline mineralizers, in agreement with previous work [11, 16]. Furthermore, little transport and GaN formation was evident in experiments conducted below 400°C, suggesting the need to grow at higher temperatures. Equipment limitations prevent long-term growth at temperatures greater than 600°C, effectively placing the temperatures of interest between 400°C and 600°C for seeded growth of gallium nitride in autoclaves.

Gallium nitride nutrient was partially, and in some cases totally, dissolved at the completion of the experiment. Transported material nucleated on the walls or furniture of the autoclave and on the GaN HVPE seeds. Single-crystal growth on the seeds occurred at rates of up to 40 μm per day. In one experiment, growth approaching 1 mm in thickness was achieved on multiple c-plane HVPE seeds. GaN that had nucleated on the walls of the autoclave, as well as single-crystal growth on a HVPE seed is shown in Figs. 3a and b respectively.

The weight of heterogeneously nucleated materials recovered from the lower walls (crystallization zone) was often 8–10 times more the weight gain of the seeds. Heterogeneous nucleation as well as the occurrence of seeded growth in the hottest area of the autoclave confirms that gallium nitride has retrograde solubility under these conditions. Etching studies determined the polarity of the crystalline surfaces. Previous work [17] demonstrated that the c⁺ face (gallium-terminated face) of GaN shows little erosion when exposed to phosphoric acid etchants compared to the c⁻ face (nitrogen-terminated face). SEM pictures were taken of unetched ammonothermal GaN crystals and ammonothermal GaN crystals etched in 85% phosphoric acid at 140°C for 120 min for comparison (Fig. 4). The nitrogen-terminated face is shown both be-

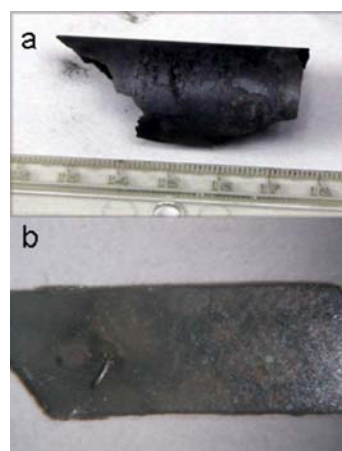


Figure 3 (a) Heterogeneously nucleated material recovered from the walls of the autoclave (centimeter scale shown). (b) Ammonothermal crystal (gallium-terminated face up) grown on HVPE seed.

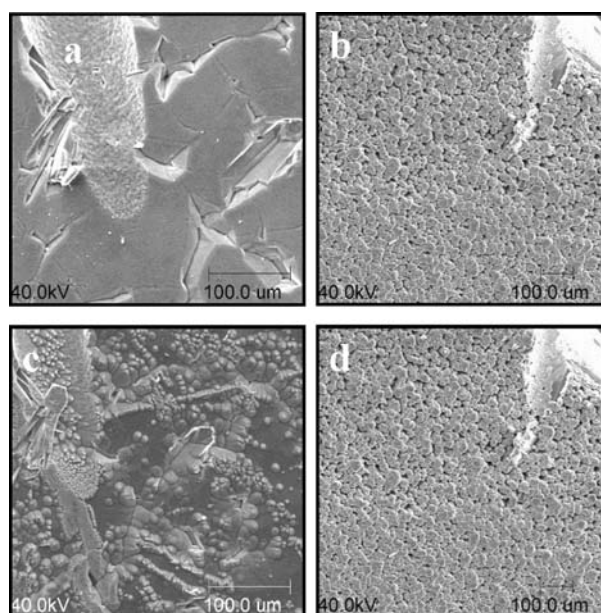


Figure 4 Etching studies of opposite faces of gallium nitride grown on HVPE seeds in 85% H₃PO₄ at 140°C for 120 min (a) N-terminated face: Flat surface with valleys before etching (b) Ga-terminated face: rough surface with apparent columnar growth before etching (c) N-terminated face: flat surface eroded substantially by etchant (d) Ga-terminated face: etching had little effect.

fore etching (Fig. 4a); and after etching (Fig. 4c), where erosion is evident. The gallium-terminated face shows no significant erosion from etching (Figs 4b and d).

The gallium-terminated face of an ammonothermal crystal is shown in Figs 5a and b. The surface has a matted or rough morphology consisting of hexagonal columns that are partially or totally coalesced (Fig 5b). The columns range in diameter from 20 to 30 μm and the column tops are flat with small prismatic facets. Sections of the gallium-terminated crystal surface are flat

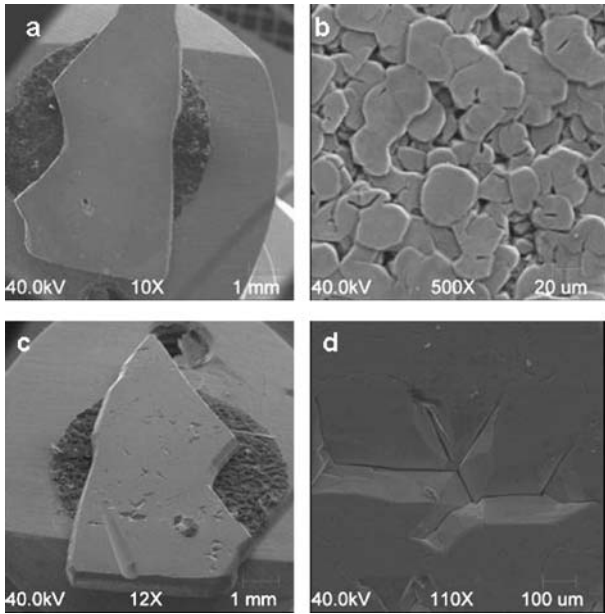


Figure 5 Scanning electron microscope images of gallium-terminated and nitrogen-terminated faces of a gallium nitride crystal grown by the ammonothermal technique. (a) Gallium face (b) Gallium face magnified (c) Nitrogen face (d) Nitrogen face magnified.

and 50 to 100 μm in diameter, due to columns having coalesced, leaving only the occasional valley to identify the previous location of a column separation. The gallium face is generally clear, but has a frosty appearance due to surface roughness. Larger hexagonal columns protrude from the edges of the HVPE seed because of the large tilt and misorientation in the gallium nitride HVPE seeds (not shown). The nitrogen-terminated face of an as-grown ammonothermal GaN crystal is shown in Figs 5c and d. The surface is flat and dark in appearance, with opaque patches covering 30 to 60% of the surface. The most apparent morphological defects are valley-like formations on the surface (Fig. 5d), having typical widths of $100\mu\text{m}$. The origin of these defects is not known.

The surface morphology was also analyzed by atomic force microscope (AFM) images. The morphology of the different crystallographic faces of the ammonothermal GaN crystals was affected by the temperature gradient ($>5^\circ\text{C}/\text{cm}$) in the crystallization zone. There was considerable variation of the surface roughness of both faces, depending on the location of the HVPE seeds in the autoclave, as seen in Table III. The crystal-to-crystal variability of the surface roughness indicates that the fluid dynamics and temperature gradients need further optimization to improve crystal structure. AFM images of both the gallium face and the nitrogen face for crystals grown at different locations (temperatures) in the autoclave are shown in Fig. 6.

A cleaved cross section of an ammonothermal gallium nitride crystal is shown in Fig. 7. Columnar growth is evident in both the C^+ and C^- directions, with

TABLE III Atomic force microscope values identifying absolute maximum and minimum, as well as average surface roughness of growth on two HVPE seeds placed in the same autoclave

Crystal One	Gallium Face	Nitrogen Face
Image Z range	171.49 nm	281.89 nm
Image RMS	18.41nm	36.85 nm
Crystal Two	Gallium Face	Nitrogen Face
Image Z range	346.33 nm	114.92 nm
Image RMS	53.73 nm	7.18 nm

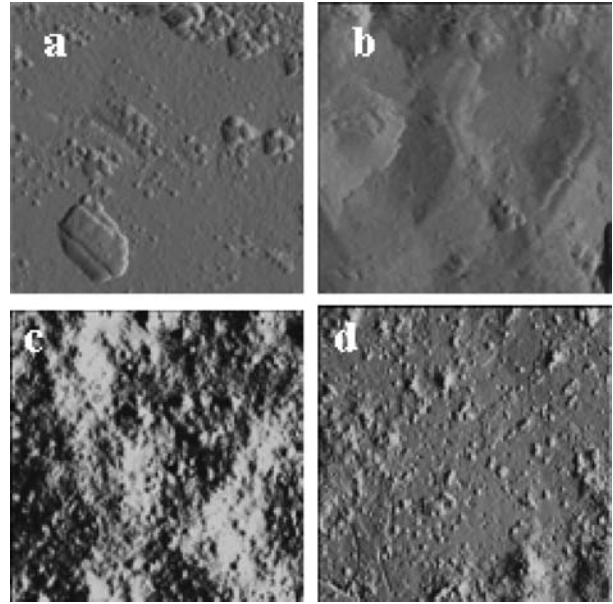


Figure 6 AFM Images of a $10\mu\text{m}^2$ area of samples from two positions in the autoclave: (a) Gallium face of crystal one in Table III (b) Nitrogen face of crystal one in Table III(c) Gallium face of crystal two in Table III (d) Nitrogen face of crystal two in Table III.

the C^+ direction having larger columns and more pronounced grain boundaries. Maximum growth rates approached $40\mu\text{m}/\text{day}$ on several experiments, but generally averaged $25\mu\text{m}/\text{day}$. Growth rates in the C^+ and C^- directions differed under different experimental conditions, with generally higher rates in the C^- di-

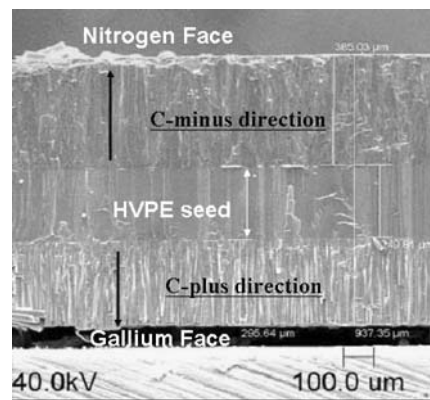


Figure 7 SEM image of a cleaved cross section of gallium nitride grown on a HVPE seed.

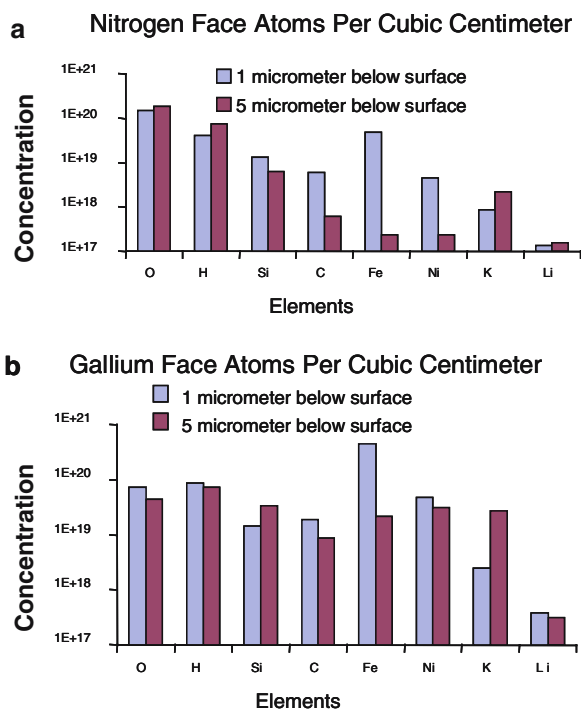


Figure 8 Concentration of atoms/cm³ at 1 and 5 μm below the surface of gallium nitride crystal (a) results for the nitrogen-terminated face (b) results for the gallium-terminated face.

rection. Substantial growth in the M direction was also observed.

Impurity concentrations for gallium nitride that nucleates heterogeneously on the walls of the autoclave were analyzed by glow discharge mass spectrometry (GDMS). The GDMS results indicate that several elements have impurity concentrations greater than 10¹⁷ atoms/cm³. Oxygen was detected above 10²⁰ atoms/cm³, with C, K, and Si in the low 10¹⁹ range. Secondary ion emission spectroscopy (SIMS) was performed on gallium nitride crystal samples grown by the ammonothermal method. Results from a characteristic sample are shown in Fig. 8. Impurity incorporation differed between the nitrogen-terminated and gallium-terminated faces. In general, metallic impurities incorporated less readily on the nitrogen-terminated face than on the gallium-terminated face. Furthermore, for both surfaces the impurity density decreased as a function of distance from the surface (i.e. into the bulk of the crystal). As shown in Fig. 8, impurity levels for oxygen and hydrogen are above 10¹⁹ atoms/cm³ for both faces. Potassium impurities were 10¹⁹ atoms/cm³ near the gallium face and mid-10¹⁸ atoms/cm³ near the nitrogen face. The impurity data clearly shows a large amount of contamination in crystallized ammonothermal gallium nitride. GaN nutrient, ammonia, amide mineralizer, autoclave furniture, and the autoclave itself are being investigated for possible impurity sources.

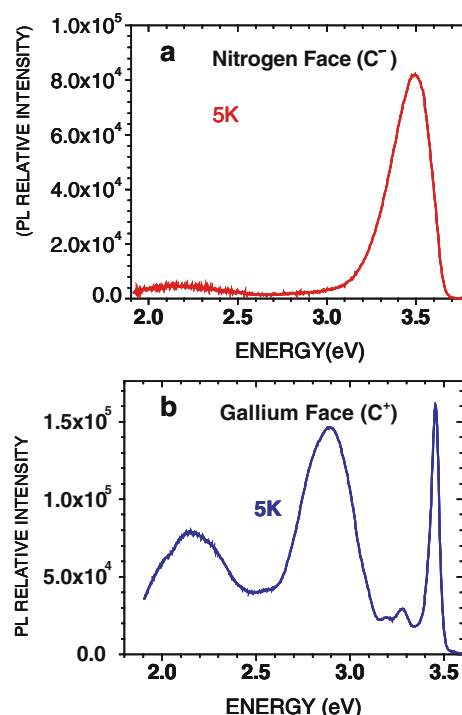


Figure 9 PL spectra of gallium nitride crystal (a) nitrogen-terminated face (b) gallium-terminated face.

The differing photoluminescence (PL) spectra of the nitrogen-terminated and gallium-terminated faces are due to the nature of various impurities and defects incorporated in the two growth planes. PL for the nitrogen face contains a lower-intensity, usually appearing in the 2.7 eV area of the spectrum (Fig. 9a). The near-band edge emission is broad. PL from the gallium face shows a wide peak in the “yellow” band centered at 2.2 eV, and an intense peak centered at 2.9 eV, consistent with what is generally considered to be defect-related or impurity-related bands. The near-band edge emission on the gallium face is significantly narrower than the near band edge emission on the nitrogen face. Two peaks that can be attributed to donor-bound excitons or phonon replicas can be seen from the PL on the gallium face, the first being at 3.28 eV, and a higher intensity peak at 3.48 eV (Fig 9b). PL measured from polycrystalline material and early growth on HVPE seeds showed reduced donor-bound exciton emission intensity, as well as larger emissions in the defect band [18]. The improvement in PL can be attributed to higher crystallinity and lower impurity incorporation in recently grown material.

X-ray powder diffraction on the gallium-terminated and nitrogen-terminated faces reveals only hexagonal (wurtzite) structure. Ammonothermally grown material typically has larger rocking curves than the HVPE seeds. Rocking curves for the HVPE seeds used are generally found to be greater than 400 arc-sec on both faces. Rocking curves for the gallium-terminated face of am-

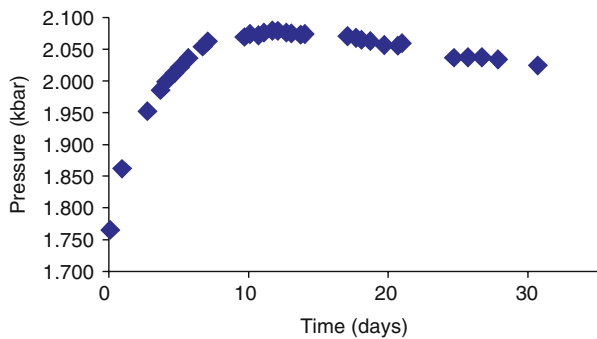


Figure 10 Pressure change inside the autoclave after reaching constant temperatures.

monothermal GaN crystals were as low as 535 arc-sec on the 002 reflection and 751 arc-sec on the 102 reflection. Additionally, the nitrogen-terminated face exhibited rocking curves of 859 arc-sec and 961 arc-sec on the 002 reflection and 102 reflection, respectively. Lattice parameters were determined to be $a = 3.186$ angstroms and $c = 5.178$ angstroms, using the Cohen extrapolation.

Pressure change typically occurred after the autoclaves reached operating temperatures. This phenomenon is in contrast to hydrothermal systems, where pressure remains constant after reaching operating temperatures. An example is depicted in Fig. 10. Ammonia decomposition into excess hydrogen and nitrogen is the primary factor contributing to pressure increase once steady state temperatures are reached. Ammonia breakdown results in thermodynamic equilibrium of different percentages of ammonia, nitrogen, and hydrogen, depending on the temperatures and pressures generated during a growth experiment [19].

4. Discussion

Dissolved impurities in the alkaline ammonia solvents affect nucleation, crystal habit, and perfection of the GaN crystals grown in our experiments. Impurities can also decrease or increase growth rates in solution growth by increasing or decreasing solubility and altering surface and diffusion kinetics [20]. The changes in nucleation and growth rates can also stabilize metastable phases [21]. Impurity absorption is affected by the number of available sites and polarity of those sites in the host lattice. Since the number and type of active sites is unique for a given growth surface, impurity incorporation differs on different crystallographic planes in anisotropic crystals. The different effects an impurity has on the growth rate of various planes can be exploited to modify faceting of crystals during growth [22]. On the other hand, if the effects are not sufficiently understood, their impact can lead to uncertainty in the outcome of shape and appearance. Impurities can halt growth altogether until a critical su-

persaturation is exceeded [23]. The increase in growth rate brought on by inordinately large supersaturation can result in crystals of irregular shape and poor quality. The difference in morphology between the gallium and nitrogen faces could also be partially influenced by impurities. The columnar growth morphology on the gallium faces of our samples may be due to a lowering of edge free energy, thereby favoring growth on kink and step faces as well as flat faces with small surface area. There is also a possibility that secondary phases, i.e. gallium oxide, are being formed at the seed interface. Reducing impurities should mitigate many of the growth issues discussed above. We believe that most of our oxygen and potassium contamination originates from the amide mineralizer. The metallic impurities are probably being leached from the autoclave. Low oxygen-content-mineralizers and autoclave liners, as well as gettering mechanisms, can be employed to lower the dissolved impurity concentrations. Even with the techniques just mentioned, impurities in the low ppm levels can still have an effect on growth kinetics. Therefore, further investigation needs to be done to gain insight into the effect impurities have on GaN crystallization in high pressure ammonia fluids. Though crystal morphology can be partially attributed to impurities in the system, there are other contributing factors. The morphology of the HVPE seeds could also play a role in the growth of ammonothermal GaN. Two features of our seeds are of particular interest. First, columnar growth of the seed itself can be discerned from the cleaved cross-section (Fig. 7). Also the pronounced “bow” in the HVPE seeds could influence morphology. Close examination of the ammonothermal crystals show a “bow” consistent with the “bow” in the HVPE seeds. Impurity incorporation and seed “bow” are possible contributing factors to the high degree of strain we observed via X-ray topography in our ammonothermal gallium nitride crystals. The strain in the crystal and the bow in the seed could also play a role in columnar growth formation. Additional considerations for the growth on HVPE seeds are the initial and final stages of growth. Initial work indicates that saturation is reached twelve to seventy-two hours after operating temperatures are reached. The autoclaves are usually brought to the desired operating temperatures over the course of a day. This leaves a window of several hours where conditions in the autoclave would remove material from the seed. Etching of the seed before supersaturation is reached could have a dramatic impact on the initial stages of growth. Several cross sections show that the interface between the seed and ammonothermal growth exhibits a dislocation density greater than that of the HVPE seed. In addition, the HVPE seeds have a large number of defects and could have phase inversions. This highly defective layer between the HVPE seed and ammonothermal growth could arise from impurities as discussed above or it could be that the seed surface is not uniform because of anisotropic

etching before growth occurs. Until low defect seeds are available, the morphology of HVPE GaN seeds must be taken into consideration for ammonothermal seeded growth.

Impurities are not the only factor that can decrease growth rate. The large amount of GaN nucleating on the walls of the autoclave limits the growth of GaN on the HVPE seeds. The amount of heterogeneous nucleation varies with temperature, the temperature gradient, and the autoclave, but at times it can account for 90% of transported material. Heterogeneous nucleation resulting in polycrystalline growth on the walls and furniture of the autoclave can be attributed to multiple physical driving forces. Our experiments have determined that gallium nitride exhibits a negative temperature coefficient of solubility. Retrograde solubility means that as temperatures increase the equilibrium concentration decreases, causing the degree of supersaturation to increase. The autoclave wall has a higher temperature than the HVPE seeds, due both to the band heaters being in direct contact with the autoclave walls and to the lower thermal conductivity of the ammonia fluid compared to the autoclave. Therefore, the fluid in close proximity of the walls will be at a higher temperature and will have a higher supersaturation than the fluid surrounding the GaN seeds. The higher supersaturation promotes wall nucleation. The composition of the autoclave wall could also lower the activation energy. The wall, or any surface, typically decreases surface free energy, depressing the energy necessary to nucleate. Further, initial investigation indicates that a NiGa alloy forms on the autoclave surface [18]. The NiGa alloy may decrease the nucleation energy just enough for heterogeneous wall nucleation to be dramatically lower than 2D homogeneous nucleation on the HVPE seeds. Therefore, temperature, supersaturation, and the autoclave surface could play a factor in fostering wall nucleation. The amount of material recovered from the walls and furniture suggests that GaN single-crystal growth is limited by precipitation kinetics in the seed zone, not by the rate of dissolution, or transport from the dissolution zone to the seed zone. Therefore, reduction of wall nucleation is critical in increasing growth rates for bulk GaN crystals. Finally, ammonia decomposition needs to be examined. Understanding the extent to which ammonia decomposes and the impact of this on quasi-steady state conditions in both the growth zone and crystallization zone is required for long-term production runs. Following LeChatelier's principle, adding energy to the system by raising the temperature pushes equilibrium in favor of nitrogen and hydrogen, at standard pressures, $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$; $H^\circ = 92.0 \text{ kJ}$.

Elevating the pressure, on the other hand, has the effect of shifting the reaction to ammonia formation. We have found that in order to achieve high growth rates, a temperature over 550°C must be employed in the growth zone.

The pressure limitation of the autoclaves of 4 kbar is not sufficient to prevent ammonia decomposition. Though the density of ammonia can be found for temperatures up to 790 K and pressures up to 5 kbar, equilibrium calculations from published data is not reliable for our current growth conditions. Mundo and Weber, and Bakemeier [24, 25] suggest that 45% of ammonia decomposes at 600°C and 1 kbar. Peters determined experimentally that at 600°C and 2 kbar, 8% of ammonia fluid decomposed without using a mineralizer and 11% decomposed employing potassium as the mineralizer [9]. Jacobs claimed that ammonia does not decompose when heated to 527°C at 6 kbar [8]. We have encountered pressures up to 341 bars after cooling the autoclave to room temperature, which indicates substantial ammonia decomposition. Variables in the process are the maximum experienced pressure, the thermal gradients and flow patterns of the fluid, the species and concentration of mineralizers, the amount of ammonia condensed in the autoclave (degree fill), and diffusion of hydrogen through the autoclave or autoclave seal. For one experiment, the decomposition of ammonia was calculated to be 21% if none of the hydrogen was lost through diffusion.

The extent of decomposition and how it changes with pressure and temperature could have dramatic effects on the viability of this technique for large-scale production of bulk gallium nitride. If uncontrolled, ammonia decomposition could limit the length of growth runs and the quality of crystals grown using the ammonothermal method. As the quantity of ammonia in the system decreases, the concentration of species dissolved in the ammonia solution increases, thereby increasing the degree of supersaturation and ultimately resulting in growth conditions that produce poor quality crystals and inordinate amounts of heterogeneous nucleation. Ammonia breakdown can be reduced by raising the operating pressure above 4 kbar, but the increased pressure might limit the use of large autoclaves. Therefore, the effects of mineralizer on ammonia breakdown, chemical additives and system modifications to reduce ammonia breakdown, and alternative high pressure-high temperature alloys must be fully investigated in order to achieve long-term stability in growing large bulk GaN crystals.

Further development of this technique for large scale production requires better understanding and control of numerous phenomena. First, more precise solubility relationships between temperature and pressure will allow better control of the growth process. Second, reducing ammonia decomposition in the presence of mineralizers would reduce crystal defects and support long-term production runs. Thirdly, an increase in growth rates can be achieved by restricting heterogeneous nucleation on the walls of the autoclave. Fourthly, close examination of seed quality and the effects of the initial and final stages of growth may yield insight into ways to improve

crystallinity. Finally, reduction of defects and a greater degree of perfection in GaN crystals will result in diminishing the unintentional inclusion of impurities during growth.

5. Conclusion

The successful determination of solubility trends has paved the way for growth experiments that yield promise for the production of bulk gallium nitride using the ammonothermal technique. The solubility of gallium nitride in supercritical ammonia solutions with alkali amides as mineralizers is retrograde from 300 to 600°C. In experiments with autoclave furnace configurations consistent with retrograde soluble growth, we have grown gallium nitride on multiple one square centimeter HVPE seeds, with growth rates of up to 40 μm per day, resulting in up to one mm of growth.

Ammonothermal technology is fertile ground for the production of many nitrogenated compounds that are difficult to synthesize by other techniques. Achieving cost-effective production of gallium nitride by the ammonothermal method will require further investigation, just as the production of quartz did in the early twentieth century. In-depth phase, solubility, growth kinetics, and fluid dynamics studies need to be completed for a multiplicity of mineralizers, and high-strength corrosion-resistant vessels must be designed for the increased pressure requirements of supercritical ammonia. The cost advantages afforded by growing on multiple seeds simultaneously make ammonothermal growth an attractive means for meeting the demand for high quality gallium nitride substrates.

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