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Abstract

An atmospheric pressure approach to growth of bulk group III-nitrides is outlined. Native III-nitride substrates for optoelectronic and high power, high frequency electronics are desirable to enhance performance and reliability of these devices; currently, these materials are available in research quantities only for GaN, and are unavailable in the case of InN. The thermodynamics and kinetics of the reactions associated with traditional crystal growth techniques place these activities on the extreme edges of experimental physics. The technique described herein relies on the production of the nitride precursor (N^{3-}) by chemical and/or electrochemical methods in a molten halide salt. This nitride ion is then reacted with group III metals in such a manner as to form the bulk nitride material. The work performed during the period of funding (July 2004-September 2005) focused on the initial measurement of the solubility of GaN in molten LiCl as a function of temperature, the construction of electrochemical cells, the modification of a commercial glove box (required for handling very hygroscopic LiCl), and on securing intellectual property for the technique.

ACKNOWLEDGMENTS

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NOMENCLATURE

DI	deionized water
DOE	Department of Energy
GaN	gallium nitride
HEMT	high electron mobility transistors
HNPSG	high nitrogen pressure solution growth
HVPE	hydride vapor phase epitaxy
KCl	potassium chloride
LED	light emitting diode
LDRD	laboratory directed research and development
LiCl	lithium chloride
ICP-MS	inductively coupled plasma-mass spectroscopy
InN	indium nitride
ppm	parts per million
SSL	solid-state lighting
SAR	synthetic aperture radar
SMU	Strategic Management Unit
SEM	scanning electron microscopy
SNL	Sandia National Laboratories
XRD	x-ray diffraction

1. INTRODUCTION

The realization of widespread implementation of high power solid-state electronics such as high electron mobility transistors (HEMTs) for applications such as Synthetic Aperture Radar (SAR), and visible light emitting diodes (LEDs) for high brightness, high efficiency lighting applications is stifled by, amongst other things, poor semiconductor material quality. The best way to improve the material quality is to grow epitaxial layers on high quality native GaN and InN substrates. However, a process that is capable of manufacturing bulk GaN has not yet emerged; those processes currently being explored suffer from extremely high process pressures (4,000 to 45,000 atmospheres) resulting from the unfortunate combination of high melting point and high equilibrium vapor pressure of nitrogen over the solid phase at the high temperatures encountered in this material system. For InN, the overpressures are much higher. In conjunction with slow kinetics, both the manufacturability and scalability of these existing processes may ultimately be limited, and the cost of such processes is potentially prohibitive when one considers the impact on a high-volume, low-cost commodity such as LEDs for the purpose of reducing the amount of energy used for lighting in the United States and the world.

Herein is described a proposed crystal growth approach that circumvents the difficulties of other bulk growth techniques by precipitating the column III nitrides from a solvent, such as a molten chloride salt, that provides an excellent host environment for the gallium nitride and indium nitride precursors. In particular, molten halide salts can solubilize both gallium (Ga^{3+}) and nitride (N^{3-}) ions (as well as indium (In^{3+})) without reacting with them to the extent that they are no longer available for reaction with each other. Reports in the literature indicate measured nitride ion concentrations in LiCl at 650°C as high as 2.8 mol%—a sufficient concentration to yield growth rates on the order of 0.01 to ~1 mm/hr under diffusion-limited growth conditions. Also, molten salts are compatible with the 450-1200°C temperatures likely to be necessary for growth of high-quality, single-crystal III-nitrides. Since they can be processed at (or close to) atmospheric pressure, scalability should not pose undue problems and manufacturability issues are thus minimized, including capital equipment costs. Although the III-nitrides cannot be float-zone refined to remove impurities due to their high melting temperatures and vapor pressures, the salts can be, thus reducing sources of impurities in the solution before growth begins. Finally, the molten salts offer a number of pathways to improve the solubility and control the growth of the III-nitrides by functioning as an electrolyte in electrochemical processes. We have demonstrated growth of wurtzite GaN particles ranging from 0.2 to 0.9 mm in two hours in our laboratory using these techniques.

The process discussed here minimizes product costs and takes advantage of the ability to use common manufacturing processes. It introduces no sources of either hydrogen or carbon for contamination, and basic and applied research alike will benefit from the availability of this material to precisely determine the effect that these impurities have on the properties of interest. Oxygen is often problematic in many high temperature growth techniques; it will be possible to do a “pre-electrolysis” to remove most, if not all, of the oxygen (and many other impurities) from the molten salt prior to growth. The lower temperatures used in this process also favor a lower oxygen content than many of the other processes currently being investigated.

The need for superior material quality as well as lower cost and improved manufacturability lie at the heart of this approach. The proposed bulk growth process is potentially scalable, manufacturable, controllable, cost-effective, and solves the problematic equilibrium vapor pressure of nitrogen issue, thus making the technique easily adapted to growth of InN and AlN, and possibly even their alloys.

This report describes the efforts from mid-July 2004 to the end of September 2005 that were funded by a late-start Laboratory Directed Research and Development (LDRD) project to investigate the possibility of using a molten salt-based approach to grow GaN and InN. Three milestones were completed by 10/01/04: the first was to measure the solubility of GaN in molten LiCl as a function of temperature; the second was to reach a decision point for the dissolution and precipitation approach; and the third was to construct a more useful electrochemical apparatus for further experiments. Additionally, there was a single milestone for FY05 which was to secure intellectual property by submitting a patent application to the U.S. Patent Office. This was completed on April 10, 2005.

2. BACKGROUND

Gallium nitride has many attractive properties that make it useful for applications in chemically and/or thermally aggressive environments. GaN is a chemically stable, high hardness, inert material with a very high melting point (~2500^{o}C). This makes it difficult to find a suitable solvent system in which to dissolve and re-precipitate GaN into large single crystals useful for substrates for thin film homoepitaxial growth for devices. To make matters worse, GaN disproportionates into gallium (Ga) metal and nitrogen gas (N_2) starting at 800°C at 1 atmosphere, and the equilibrium vapor pressure of nitrogen over the solid near its melting point is about 60,000 atmospheres, placing the melt-based growth approaches at the extremes of experimental physics. Indeed melt-based growth approaches are being pursued, either by dissolving N_2 in a gallium melt[1] (the High Nitrogen Pressure Solution Growth, or HNPSG method), or by melting and recrystallizing.[2] In either case, the pressures are extreme and the kinetics is very slow, requiring many weeks at these conditions to grow research-sized platelets. It is unlikely that either of these methods will develop into a manufacturable technique capable of satisfying the demands of US military and consumer applications.

An alternative to the melt-based approaches is the newer ammonothermal growth technique, which is an adaptation of the process used to grow quartz crystals. It is a classic dissolution and precipitation approach. In this case the chosen solvent, ammonia (NH_3), is volatile even at room temperature, thus requiring a high overpressure to maintain it in a liquid state. The high-pressure requirement is likely to limit the scalability of the process to small area crystals. A significant concern is that the nucleation step on seed crystals is essentially diffusion limited. The result has been columnar growth of poor quality GaN.[3]

The growth of crystals from solution requires supersaturation which is achieved either by slow cooling of the solution or by imposing a temperature gradient on the solution. In a recent publication, Wang et al.[4] reported growth rates of 15-20 μm/day for GaN crystals grown by the ammonothermal process on Hydride Vapor Phase Epitaxy (HVPE)-grown basal plane GaN templates. Closer examination of the grown crystals shows that the growth has a columnar structure, indicating spotty nucleation followed by preferential growth on the nuclei thus producing the structure observed. In addition, there is strong evidence that nuclei formation and growth rates are different on the Ga and N terminated faces of the seed wafer. This nucleation problem could originate from surface contamination of the seed or from non-uniform solute distribution at the growing interface. Another contributing factor for spotty nucleation could be the fact that unlike SiO_2, which has a positive solubility in hydrothermal solution growth, GaN has a negative solubility coefficient in ammonothermal solution growth, which requires the nutrient to be at a lower temperature than the seed. In this case, convective transport of nutrients away from the seeds must be minimized, requiring a very stable thermal environment. A non-trivial matter is the fact that ammonothermal growth is a slow process which requires weeks to produce useful size crystal in a closed system with no means to monitor the growth process other than pressure.

Sublimation techniques are being developed which rely on the generation of gallium vapor from molten gallium or by the thermal decomposition of GaN powder. The vapor phase Ga reacts with cracked NH_3 at a seed crystal. The driving force for the mass transfer of Ga to the substrate is a thermal gradient. This technique has the benefit of operating near atmospheric pressure, but the temperatures are high (~1200^{o}C is required to decompose the GaN powder or vaporize molten Ga, and to crack the ammonia). The growth rates are high but persistent control issues remain.[5] The difficulty lies in the fact that ammonia will crack at 300^{o}C and above, and the nature of the furnace is such that there are many hot surfaces other than the growth surface on which to crack the precursor, resulting in a deprivation of active nitrogen at the growth front.

The Sodium Flux technique is another technique that is being developed by Cornell University[6] that uses molten sodium or sodium azide (Na_3N) as the nitride source. They found that sodium can dissociate the nitrogen molecule and that GaN can be formed not only as a crust on the surface of the molten Na + Ga pool, but also within the melt.[7] Crystals have yet to reach millimeter size on a regular basis, despite long growth times (~200 hrs). Sodium azide is an explosive material and is therefore difficult to handle, and care must be taken when working with sodium metal. While these issues are resolvable, they tend to impede rapid development. Song et al. are investigating the use of a lithium flux to synthesize GaN platelets with lateral dimensions of 1-4 mm and 20-300 μm thick[8] by mixing Li_3N + Ga + N_2 at 740-800^{o}C and cooling over 2-3 days. The crystals are transparent and of high microstructural quality, indicating that lithium incorporation may not be an insurmountable problem in the process described in the report.

HVPE has been the approach of choice for producing quasi-bulk GaN over the past ten or more years. HVPE has the advantage of being able to produce thick films (up to 4 mm) at rather high growth rates. However, it is a one-dimensional growth technique that requires a seed of the same diameter as the resulting crystal. Patterned and planar sapphire, silicon, and silicon carbide substrates are used to initiate growth, typically along the (0002) direction. The lack of a compatible substrate that is readily available, inexpensive, chemically compatible with the growth process, and that has a lattice constant close to that of GaN will always plague the HVPE process.

3. DETAILED DISCUSSION OF APPROACH

Growth of bulk single crystal nitrides of any kind is hindered by the difficulties of controlling the nitrogen precursor and delivering large quantities of active nitrogen species to a growth front, either in a melt or in solution. Fast, but controllable kinetics is desirable. This report describes a technique that takes advantage of a relatively new capability to reduce nitrogen gas to an active, readily available precursor for application to bulk nitride single crystal growth.

Described below are two ways to create III-nitride precursors in, and then precipitate III-nitride crystals from, molten salt solutions. At one extreme, both precursors are created through dissolution (e.g., through dissolution of a powdered form of the III-nitride, or through dissolution of salts containing the individual chemical constituents of the III-nitride) followed by reaction and precipitation. At the other extreme, both precursors are created electrochemically, followed by reaction and precipitation. These two schemes may be combined for further control of the precursor creation/reaction/precipitation conditions.

3.1 Dissolution and Precipitation

At the one extreme, both precursors are created through dissolution. The simplest embodiment of this approach is to dissolve the material to be grown in a solvent and control precipitation of the material through use of a temperature gradient to achieve a supersaturation of the solute. While this is straightforward and this concept has been applied to growth of crystals of all kinds, our molten salt approach allows for new approaches to this concept.

As an example, $GaCl_3$ and Li_3N precursors are dissolved separately into the molten halide salt, and then allowed to react through a metathesis reaction. For our example, the reaction is thus

$$GaCl_3 + Li_3N \rightarrow GaN_{(s)} + 3\ LiCl,$$

for which the Gibbs Free Energy of the reaction is highly exothermic (~ -154 kcal/mol) at room temperature. In fact, without the LiCl solvent, the reaction is explosive.[9,10] Equilibrium conditions for this reaction require concentrations of $GaCl_3$ and Li_3N on the nanomolar scale, thus yielding slow growth rates in a diffusion-limited regime. However, if a slow growth rate were acceptable, then one might still consider this approach were it not for the problem of preventing the $GaCl_3$ precursor from reacting with (in this case) LiCl. It is well known that $GaCl_3 + LiCl \rightarrow Li^+(GaCl_4)^-$ is a very stable compound that in our laboratory experiments has been inert with respect to Li_3N at low temperatures (<250˚C). Lithium tetrachloroindate has also been synthesized in other laboratories for use as an electrolyte. Higher operating temperatures may still make this approach an option. Alternatively, other molten salt systems may be explored for use as a host solvent for the reaction (e.g., alkaline earth halide salts, etc.). Our initial experiments indicate that at temperatures above 400˚C the reaction of $GaCl_3$ with LiCl does not interfere with nitride formation.

3.2 Electrochemically Assisted Growth

At the other extreme, both precursors are created electrochemically. Rather than dissolving the compound straight into the solution and precipitating it out, the cationic (Ga^{3+}) and anionic (N^{3-}) components may be electrochemically formed in solution at locations separated by a relatively large distance in the melt to prevent premature reaction (see Figure 3.1). This alleviates the typical difficulties of solution growth associated with the reduction in driving force resulting from the removal of solute through precipitation by continuously generating precursors in solution in a controlled manner. This could be accomplished by using multiple potentiostats or power supplies, as shown in the figure, or through the use of a single potentiostat or power supply. Nitrogen can be reduced at one electrode while gallium would be oxidized at the other electrode if a single power supply were employed—these initial experiments have been demonstrated in our laboratory. If multiple power supplies are employed, then the respective half-reactions would be run, and oxidation or reduction of the proper component of the salt would take place at the opposing electrode. The concentrations of the electrochemically-generated ions would need to be maintained below the solubility limit of GaN in the salt to prevent instantaneous precipitation in the solution. The slow growth rate resulting from the low concentration of precursors could be increased by controlling the rate at which ions are transported to the growth surface via forced salt flow. A temperature gradient at the growth surface (maintained at a lower temperature than the rest of the melt) would allow precipitation due to supersaturation of the gallium nitride.

3.3 Combined Dissolution and Electrochemically Assisted Deposition

Various combinations of the two extremes described above can also be envisioned. For example, classic dissolution of GaN followed by precipitation due to supersaturation resulting from a thermal gradient also may be electrochemically enhanced. The individual ionic species (Ga^{3+} or N^{3-}) can be produced at electrodes located near the growth surface in order to tailor the V/III ratio to a desired value. In this way, the specific growth conditions may be tailored for a variety of purposes, including morphological/microstructural improvement and/or control of impurity incorporation into the solid. Thus the benefits of electrochemistry are realized while circumventing some of the material quality problems usually encountered during electroplating, while some of the most significant advantages that gas-phase deposition techniques offer are also incorporated into a solution-phase technique.

Or, for example, one of the precursors can be formed by dissolution while the other is generated electrochemically. It has been shown in the literature that a continuous, controlled supply of nitride ion (N^{3-}) may be formed in a molten chloride salt through electrochemical reduction of nitrogen gas at a nickel cathode.[11] Nitrogen gas is attractive from a crystal growth perspective as it is easily purified, inexpensive, and its introduction into the reactor is easily controlled. However, other nitrogen-containing precursors, such as nitride-containing powders (e.g., Li_3N, K_3N, NaN_3, etc.) may be dissolved in the melt as an alternative or a supplemental precursor to nitrogen gas. We have performed these experiments in our laboratory; we used a LiCl-KCl eutectic mixture at 450˚C, with Ga metal and Li_3N as the precursors. A pool of molten gallium metal was anodically reacted with N^{-3} in solution to yield multiple single crystals of GaN, the largest of these ranged from 0.5 to 0.9 mm in diameter (see Figure 3.2). The formation

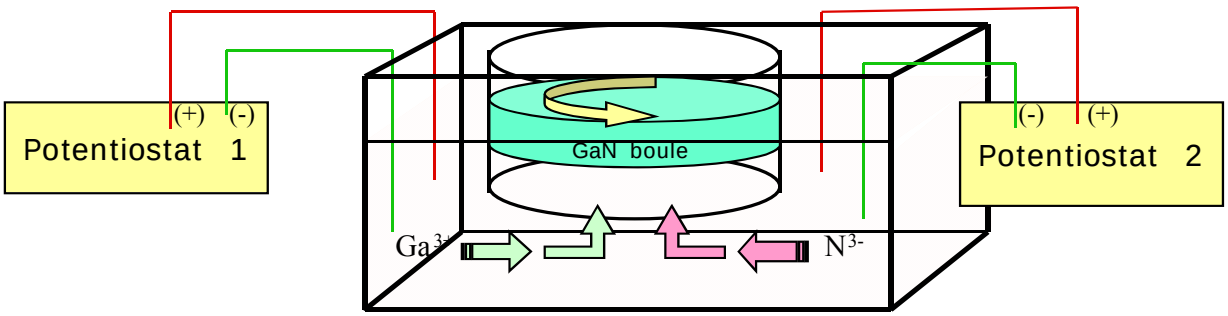
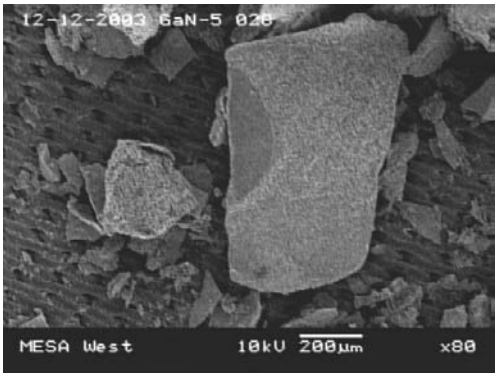
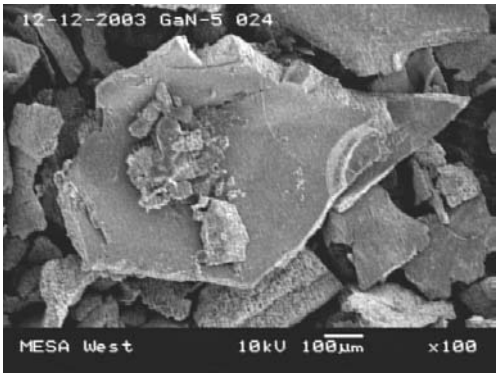


Figure 3.1 Schematic of electrochemically assisted deposition approach. A mechanism for salt (and thus precursor) transport to the growth surface is not explicitly shown.

of wurtzite GaN was verified by powder x-ray diffraction (see Figure 3.3). Voltages were maintained within the electrochemical voltage window of the salt (~3.5V), current densities ranged from microamperes/cm^2 to several amperes/cm^2, and the electrolysis was performed for about two hours at 450˚C. This procedure could very likely be performed in any of the halide salts at appropriate temperatures (i.e., hot enough to maintain a stable melt, up to the boiling point of the salt), and the metal species could be any of the group III metals, or carbon or boron. It may be possible to perform these and similar reactions in the alkaline earth halide salts as well, depending upon their electrochemical voltage windows. The growth rate and morphology of the deposit may be controlled by a number of factors, including the applied current density, the chosen geometry of the experiment, and the temperature and composition of the salt.



(a)



(b)

Figure 3.2 SEM images of selected crystals formed by electrodeposition from Li_3N and Ga metal. (a) Crystal is 900 µm lengthwise. The mesh in the background is made from stainless steel and was used to filter the crystals from an aqueous salt solution; (b) crystal is 800 µm across.

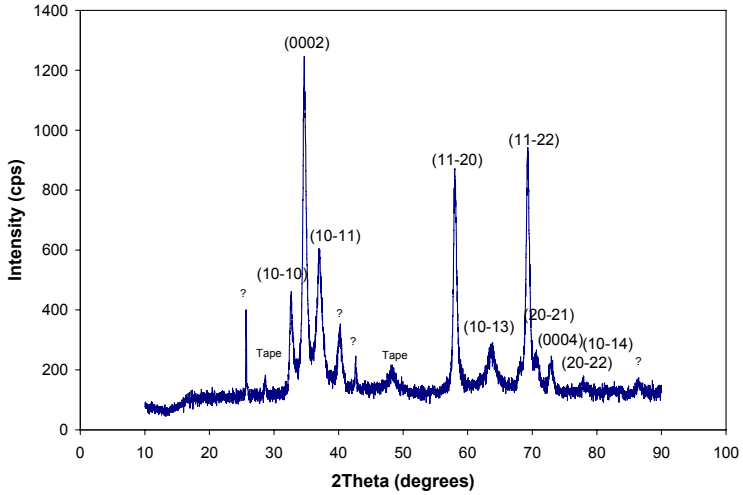


Figure 3.3 Powder XRD of GaN crystals grown from electrolysis of Ga metal and Li_3N.

4. PRESENT WORK

This section describes and discusses the results related to the three milestones that were completed by 10/01/04.

4.1 Solubility Determination of GaN in LiCl vs. Temperature

A quartz crucible was charged with approximately 15g LiCl (Alfa Aesar, 99.5%, ultra dry) under a nitrogen atmosphere and heated to 200˚C for a minimum of 48 hours at 1 x 10^{-6} Torr. The pressure was raised to 300 Torr Ar while the salt was heated to its melting point (610˚C). After melting, the reactor pressure was raised and opened to a nitrogen glove box atmosphere, and an amount of GaN powder (approximately 1g, Alfa Aesar, 99.5%, -10 mesh) sufficient to achieve saturation was added to the melt. A quartz rod was used to stir the excess GaN residing at the bottom of the crucible and the solution was allowed to settle for 30 minutes prior to salt extraction for solubility measurement. The temperature of the salt was measured prior to stirring by inserting a type K thermocouple encased in a quartz sheath (a closed end tube) into the salt, near the region where the salt would be extracted (e.g., near the top of the melt) and resting there until the temperature stabilized. The salt was extracted by briefly dipping a clean quartz rod into the solution, going deep enough to collect salt on the tube, but not so deep as to touch the bottom of the crucible where the excess GaN powder remained, thus quenching the melt on the walls of the tube. The melt was about 1-1.5" deep. Salt extractions were taken at several temperatures, including one baseline extraction at the lowest temperature of the series that was taken prior to the addition of GaN salt to get a measurement of the amount of contamination in the LiCl.

The GaN solubility was determined by measuring the gallium concentration in the salt by ICP-MS and assuming that all gallium detected resulted from dissolved GaN. Aside from any contamination in the LiCl, we believe this to be a good assumption since the equilibrium of the reaction

$$GaN + 3LiCl \rightarrow GaCl_3 + Li_3N$$

lies very far to the left and continues to move left with increasing temperature. Furthermore, $GaCl_3$ is quite volatile at the temperatures experienced in this experiment and would be expected to leave the solution preferentially. Unlike previous electrochemical experiments in which $GaCl_3$ was intentionally generated at a gallium electrode in the chloride salt, no yellow fumes were observed emanating from the melt.

The first set of salt extractions was prepared for Ga measurement by ICP-MS by scraping the solid salt from the end of the quartz extraction rod into a Nalgene™ sample bottle. The salt+GaN was weighed, and then deionized water (DI) was added and the bottle was weighed again. A few drops of HNO_3 were added to acidify the solution to prevent the metals from plating out onto the container and instrument walls. The instrument was calibrated using a series of distillations of a gallium standard (SPEX Certiprep, 1,000 ppb Ga standard) and a blank (DI water). After each measurement, a DI rinse was analyzed to determine the amount of gallium carryover from measurement to measurement. In every case the gallium carryover was below the detection limit.

Although the theoretical, ideal solubility of GaN had been calculated (Figure 4.1), the actual solubility was of course unknown. Therefore the extraction from the highest temperature (948˚C) was measured first as an upper-bound experiment. The ICP-MS detected 36 parts per million (ppm), and the calculation predicted 32 ppm. It is worthy to note that this was also a lower-bound measurement, since the salt was scraped off of the extraction tube in regular atmosphere and was collecting water during the weighing process. LiCl is extremely hygroscopic, and picks up water while sitting on the balance. Therefore, the amount of salt+GaN is actually salt+GaN+water, and is likely to be diluted more than was accounted for in the measurement. The procedure will be modified in future experiments to weigh the salt+GaN inside a dry room (<3% relative humidity).

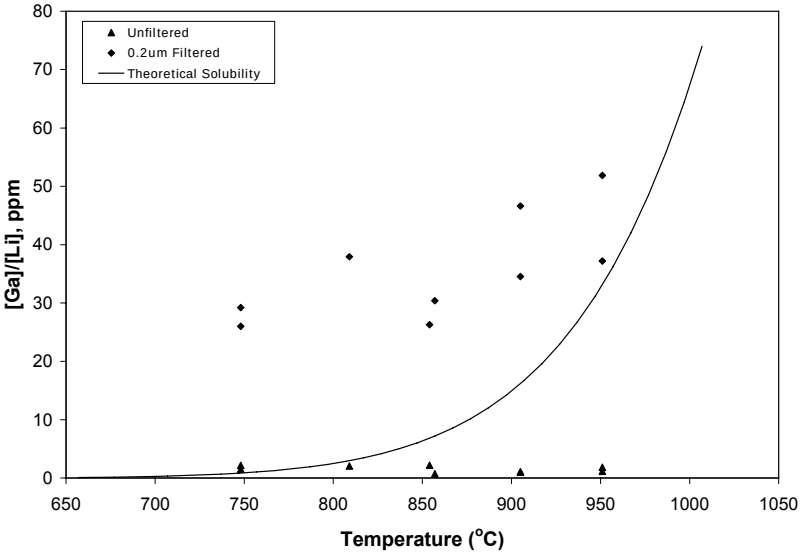


Figure 4.1 Experimental data for GaN in LiCl with and without filtering, and theoretical ideal solubility calculation.

Similar procedures were followed to dilute salt+GaN aliquots taken at the remainder of the temperature points, and the results are plotted in Figure 4.1. An irregular and irreproducible saturation of the detector on the ICP-MS led us to suspect that particulates were hitting the detector. The particulates could come from gallium buildup on the sample injector tube that unpredictably broke off and impinged onto the detector (not an uncommon event in this analysis technique), or from the solutions themselves. The solutions were filtered through a 0.2-μm filter and gallium content was measured again. The values increased substantially, indicating that material had not been reaching the detector in previous experiments.

The presence of gallium-based (presumably GaN) particulates is easily reconciled when the nature of the analysis process is considered. The GaN is dissolved in LiCl at a given temperature (>650˚C), extracted from the melt and quenched. That quenched salt solution is then dissolved in water; the LiCl dissolves readily in water, but the GaN does not and thus segregates out. No standard technique exists for wet etching GaN as for more typical compound semiconductors e.g., GaAs, InP, GaP, etc; all etching of GaN-based materials is conducted by plasma dry etching. Thus no known solvent for GaN exists. There are few reports of successfully wet etching GaN photoelectrochemically at extreme pH levels. We are considering the possibility of adapting such a technique to force the GaN into solution for concentration measurements.

There are two main points to consider regarding these data and the feasibility of the dissolution approach.

1. Colloidal suspension. One concern about the dissolution and precipitation approach is that the GaN would not dissolve in LiCl, but rather would form a colloidal suspension, thereby making precipitation of single crystal GaN impossible. In order to test for this, two or three different dilutions of the same sample were measured and were found to produce the same results each time. A colloidal suspension would be expected to have given a wide range of scatter in the results for each measurement. Furthermore, the results from two identical experiments were similar.
2. Contamination. The glove box was swiped at various locations to test for gallium (from GaN) contamination. All locations tested positive. A quantitative contamination assessment and subsequent cleanup is in progress at the time of writing. At no time after salt+GaN extraction and quenching did the quartz extraction tubes make contact with any surface except for the inside of a new Ziploc® bag. The contamination would have to have come from turbulence inside the glove box severe enough to provide a homogeneous mixture of GaN powder on each sample tube. While contamination cannot be excluded at this time, it would be expected to produce inhomogeneous results from sample to sample (for example, parts per thousand on some samples and barely detectable in others), rather than a set of clustered results as was observed in the second set of experiments.

An initial experiment was performed to gauge the solubility of InN in LiCl. The LiCl was melted under vacuum as described previously, but when InN was added, a cloud of yellow smoke was observed and the inside of the quartz tube was coated with the yellow powder. It was apparently too hot for the InN and it presumably decomposed into $InCl_3$ and probably N_2 gas. The experiment will be repeated at lower temperatures using the LiCl-KCl eutectic melt. The experiment can be conducted at temperatures as low as 375˚C. Additionally, the InN powder can be pressed into a pellet, frozen in liquid nitrogen, and immersed in the salt. The salt will freeze around the pellet and protect it while it heats up to the melt temperature and hopefully prevent the dissociation of InN.

4.2 Decision Point for Dissolution and Precipitation Approach

Although the solubility analysis method requires further attention to improve its reliability, at this time it does appear that GaN is in fact dissolving in LiCl, and at concentrations very close to or greater than the theoretically predicted concentrations. We feel that the analysis method that has been followed to date is yielding conservative results and that the numbers represent a lower bound for GaN concentrations. There is a lot to be learned still, but as the concentrations are in the ppm range (rather than ppb or below the detection limit), we feel that this approach is worth pursuing. Consider the case for the concentration at 948˚C: a GaN concentration of 36 ppm corresponds to a growth rate of about 20-50 μm/hr in a diffusion-limited process. While this is not ideal for a production process, it is a good enough start to lay the foundation for the remainder of the project. If any kind of reasonable precipitate can be achieved in the future, this result might be used to obtain funding for continued work in this direction, given that the rest of the project ideas deal with identifying ways of increasing the

solubility and controlling the growth. We are energized by the possibilities and are now highly motivated to continue to explore this approach. These early results are particularly exciting given that this part of the approach was considered by the inventor to be the weakest part of the project at the outset.

4.3 Construction of Electrochemical Apparatus

The electrochemical cell that was used for the initial experiments was a) designed with a very different experiment geometry in mind than that which will ultimately be used, and b) designed for the barest minimum cost. These two factors resulted in there being insufficient room inside the cell to make reliable electrochemical measurements. Examples of the problems encountered are: the probes often short out (because their position cannot be controlled and it is crowded in the cell; the effective electrode area is uncertain (making current densities impossible to measure accurately); and the spacing between the electrodes is always changing (which affects the IR drop between the electrodes and changes the measured voltage). Therefore, the third milestone for FY04 was to construct a new electrochemical cell so that electrochemical reactions of the oxidation of Ga or other group III metals and the reduction of nitrogen gas could be studied in the future.

A glove box was loaned to the project by Department 2521, but it needed modification before it could be used for molten salt electrochemistry experiments. The numbered list of modifications below refers to call-outs in Figure 4.2:

1. Additional AC power was added (another junction box) to drive the furnace(s) used to heat the molten salt. Specifically, additional current was required for these experiments.
2. Four hermetically sealed coaxial cable bulkhead feedthrus were added for impedance spectroscopy measurements. Feedthrus that were both hermetically sealed and isolated were not available from any vendors; therefore, these feedthrus were isolated using ceramic standoff rings and custom Viton gaskets wrapped around the shaft of the connector.
3. A hermetically sealed thermocouple bulkhead feedthru was installed. This connector will connect to eight type K thermocouples inside the box.
4. Quarter-inch Swagelok® bulkhead feedthrus were added—two for cooling water supply and return, and four for gas supplies and gas returns (two each) for process gas and backfill or purge gases. It is anticipated that the glove box will have a tendency to overheat given the heat load that will be introduced during the molten salt experiments; therefore, the option for installing a heat exchanger was considered but not implemented.
5. A half-inch Swagelok® bulkhead feedthru vacuum port was installed.
6. BNC feedthrus previously existed, and will be used for controlling electrochemical processes.

In addition, the glove box was cleaned from previous, unrelated experiments and the purification columns were regenerated.

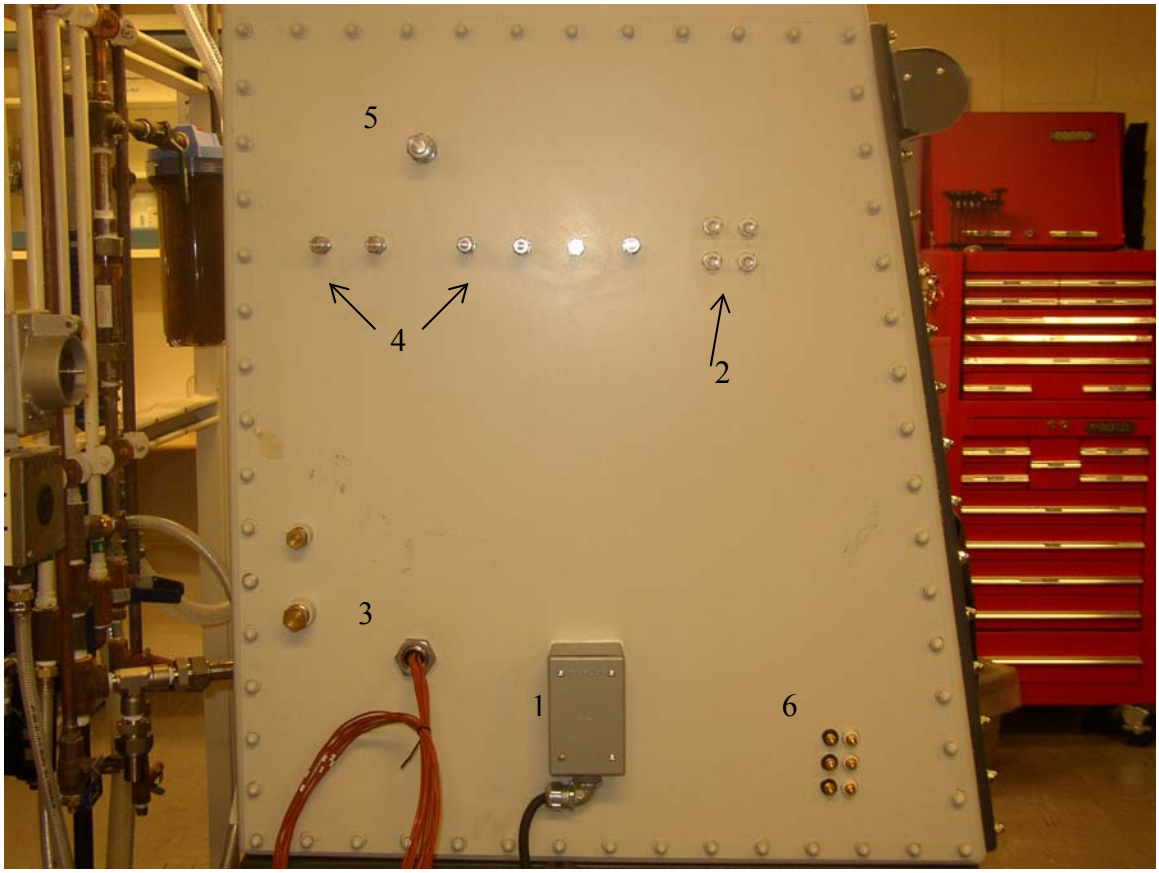


Figure 4.2 Modifications made to glove box side panel in preparation for electrochemical experiments.

Two different commercial furnaces were obtained for the experiment; one contains a window for viewing the process (if a quartz reaction vessel is used), while the other does not. Two cells were constructed of similar design but with differing dimensions and crucibles (Figures 4.3 and 4.4). Alumina crucibles (99.998%) were purchased from CoorsTek, Inc. for the furnace without a window, and quartz was used for the furnace with the window. Headpieces were made to fit each cell and are shown in Figures 7 and 8. The Swagelok® fittings were welded from the inside of the can to prevent the occurrence of a virtual leak should we later decide to have these cans form a sealing surface. There are nine ports in each headpiece; three are for the anode, cathode, and reference electrodes; two are for the impedance spectroscopy measurements; two more are for a purge gas supply and return; one is for additional chemical fill, and one port is for vacuum. The ports are shown using stainless steel fittings, but those that will support glass rods and tubes are now equipped with Teflon® fittings to prevent glass breakage. These fittings may require cooling.

All parts were assembled and a leak in the glove box was located and repaired.

**Figure 4.3 Quartz reactor for lower temperature experiments.
Tube diameter is 2.25".**

**Figure 4.4 Alumina reactor for higher temperature experiments (>1000^{o}C).
Tube diameter is ~2 3/8".**

5. SUMMARY AND CONCLUSIONS

Concepts for a technique for growing large single crystals of GaN and related III-nitrides have been presented. The approach is novel in that ionic and/or molecular precursors are created in situ and delivered to the growth front, thereby allowing for the possibility of continuous, steady state, or isothermal solution growth. The process may allow a boule to be pulled directly from the fused salt.

Solubility measurements of GaN in LiCl have begun. While there are a few issues to resolve regarding the analytical methodology, the initial results are promising enough to continue to move forward with as much speed as possible. Initial results indicate that the solubility of GaN in LiCl will be close to or higher than the ideal, entropic solubility. The greatest challenge to measuring the solubility with great precision at this time is getting the GaN that was once dissolved in the LiCl to dissolve in DI water for analysis, and one approach for accomplishing this may be a photoelectrochemical technique that has recently appeared in the literature.

Two electrochemical cells have been constructed and a glove box has been modified to provide the service feedthrus required for this project. A second glove box has been acquired as a permanent resource for the project and is undergoing the required modifications.

Intellectual property for these concepts was secured via submission of a patent application to the U.S. Patent Office (SD7721, April 10, 2005).

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