

SANDIA REPORT

SAND2007-5210

Unlimited Release

Printed August 2007

Molten Salt-Based Growth of Bulk GaN and InN for Substrates

Karen E. Waldrip

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation,
a Lockheed Martin Company, for the United States Department of Energy's
National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.



Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: <http://www.osti.gov/bridge>

Available to the public from

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd.
Springfield, VA 22161

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: <http://www.ntis.gov/help/ordermethods.asp?loc=7-4-0#online>



SAND2007-5210
Unlimited Release
Printed August 2007

Molten Salt-Based Growth of Bulk GaN and InN for Substrates

Karen E. Waldrip
Advanced Power Sources Technology, Department 02546
Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185

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 novel techniques described herein rely 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 (February 2006-September 2006) focused on establishing that mass transport of GaN occurs in molten LiCl, the construction of a larger diameter electrochemical cell, the design, modification, and installation of a made-to-order glove box (required for handling very hygroscopic LiCl), and the feasibility of using room temperature molten salts to perform nitride chemistry experiments.

ACKNOWLEDGMENTS

The author gratefully acknowledges the assistance of Bertha Montoya (2546), Whitney Bender (2546), and Mark Lord (2546) with the mass transport experiments. The author also gratefully acknowledges program management assistance from Dan Doughty (formerly of 2546) and Tom Wunsch (2546), Mark Rodriguez (1822) for characterization of materials; and the following individuals for stimulating a fruitful technical discussion: J.Y. Tsao (1130), Dr. George Antypas and David F. Smith of GNOEM Systems, Inc.; Stephen R. Lee (1123), W. G. Breiland (5526), David Ingersoll (2546), Frank Delnick (2546), and Paul Butler (5400).

CONTENTS

1. Introduction.....	7
2. Background.....	9
3. Detailed discussion of approach	11
3.1 Dissolution and Precipitation.....	11
3.2 Electrochemically Assisted Growth.....	12
3.3 Combined Dissolution and Electrochemically Assisted Deposition	12
4. Present work.....	15
4.1 Mass Transport of GaN in LiCl	15
4.2 Exploration of Alternative Solvents.....	18
4.3 Electrochemistry in Large Area, High Pressure Crystal Puller	19
5. Summary	25
6. References.....	27
Distribution	29

FIGURES

Figure 3.1 Schematic of electrochemically assisted deposition approach. Error! Bookmark not defined.	
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.	13
Figure 3.3 Powder XRD of GaN crystals grown from electrolysis of Ga metal and Li_3N	14
Figure 4.1 XRD results from mass transport experiment	17
Figure 4.2 High pressure Czochralski (HPCZ) crystal puller..... Error! Bookmark not defined.	
Figure 4.3 First generation of elevator modification for electrodes and gas feedthrus	21
Figure 4.4 Second generation of feedthrus on elevator	21
Figure 4.5 Slag on walls of crucible after melting and freezing reagent-grade LiCl-KCl.....	22
Figure 4.6 Voltammogram in as-received molten LiCl-KCl: Li_3N using a nickel wire as the working electrode.....	23
Figure 4.7 Optical image of crystals formed in electrochemical experiment in HPCZ reactor....	23

NOMENCLATURE

Ag/AgCl	silver/silver chloride
AlN	aluminum nitride
DI	deionized water
DMPI-Im	dimethylpropylimidazolium imide
DOE	Department of Energy
EDS	energy dispersive spectrometer
EERE	Energy Efficiency and Renewable Energy
ES&H	environment, safety, and health
GaCl ₃	gallium chloride
GaN	gallium nitride
H ₂ O	water
HCl	hydrochloric acid
HEMT	high electron mobility transistors
HNPSG	high nitrogen pressure solution growth
HPCZ	high pressure Czochralski (crystal puller)
HRXRD	high resolution x-ray diffraction
HVPE	hydride vapor phase epitaxy
IR	internal resistance
K ₃ N	potassium nitride
KCl	potassium chloride
LED	light emitting diode
LDRD	laboratory directed research and development
LiCl	lithium chloride
Li ⁺ (GaCl ₄) ⁻	lithium tetrachlorogallate
Li ₃ N	lithium nitride
ICP-MS	inductively coupled plasma-mass spectroscopy
InN	indium nitride
MgO	magnesium oxide
MOCVD	metal organic chemical vapor deposition
N ₂	nitrogen gas
NaCl	sodium chloride
NaN ₃	sodium azide
Na ₃ N	sodium nitride
NETL	National Energy Technology Laboratory
NH ₃	ammonia
O ₂	oxygen
PI	principal investigator
ppm	parts per million
SAR	synthetic aperture radar
SEM	scanning electron microscopy
scm	standard cubic centimeters per minute
SiO ₂	silicon dioxide
SNL	Sandia National Laboratories
SSL	solid-state lighting
US	United States
WFO	work for others
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 needs of 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 for 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 compared to many of the other processes currently being investigated.

The needs for superior material quality as well as lower product 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 high equilibrium vapor pressure of nitrogen problem, thus making the technique easily adapted to growth of InN and AlN, and possibly even their alloys.

This report describes the efforts from February to mid-September 2006 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. The work describes several background experiments, including demonstration of mass transport of GaN in molten LiCl, the investigation of other molten salts as solvents besides the hygroscopic LiCl-KCl, and initial work performed in collaboration with an industrial partner that began the path toward technology transfer to industry as the growth technique is proven to be successful.

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 ($\sim 2500^{\circ}\text{C}$). These properties also make 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 melt¹ (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 $\mu\text{m}/\text{day}$ 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 coefficient 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°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°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 University⁶ that uses molten sodium or sodium azide (NaN_3) 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 be grown to 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 have tended 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 thick⁸ by mixing $\text{Li}_3\text{N} + \text{Ga} + \text{N}_2$ at 740-800°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

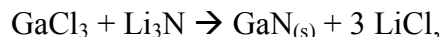
Growth of bulk single crystal nitrides of any kind is hindered by the difficulties of controlling the nitrogen precursor and delivering large quantities of active nitrogen species to a growth front, either in a melt or in solution. Fast, but controllable kinetics is desirable. This report describes a 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 approach is straightforward and the 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, GaCl₃ and Li₃N precursors are dissolved separately in the molten halide salt, and then allowed to react through a metathesis reaction. For our example, the reaction is thus



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 GaCl₃ and Li₃N 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 GaCl₃ precursor from reacting with (in this case) LiCl. It is well known that GaCl₃ + LiCl → Li⁺(GaCl₄)⁻ is a very stable compound that in our laboratory experiments has been inert with respect to Li₃N 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 GaCl₃ 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 crystal growth from solution 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 may also 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 , Na_3N or 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

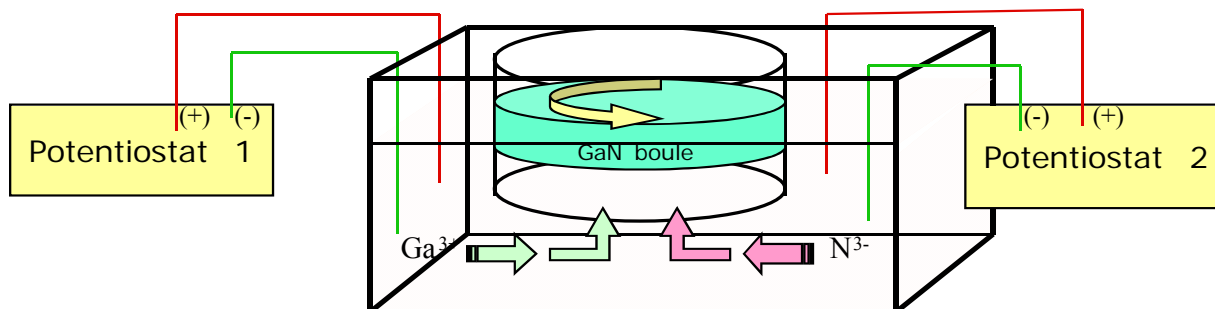
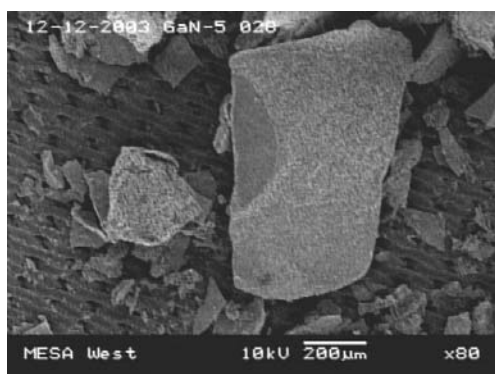
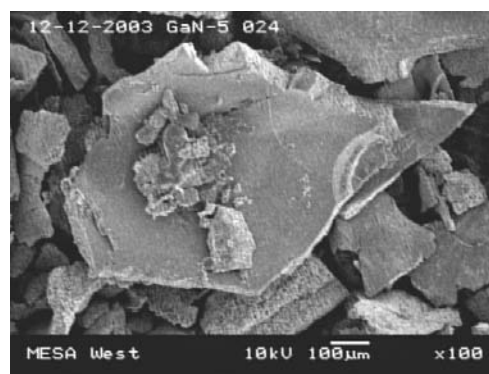


Figure 3.1 Schematic of electrochemically assisted deposition approach. A mechanism for salt (and thus precursor) transport to the growth surface is not explicitly shown.

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 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 ($\sim 3.5V$), current densities ranged from microamperes/cm² to several amperes/cm², 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 3.1 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.

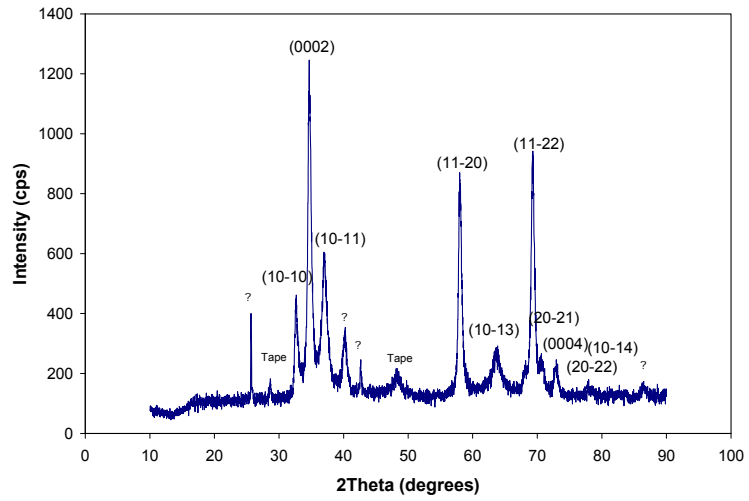


Figure 3.2 Powder XRD of GaN crystals grown from electrolysis of Ga metal and Li_3N .

4. PRESENT WORK

This section describes the work under the late-start LDRD project that was completed between February and September, 2006. It describes several background experiments, including demonstration of mass transport of GaN in molten LiCl, the investigation of other molten salts as solvents besides the hygroscopic LiCl-KCl, and initial work performed in collaboration with an industrial partner.

4.1 Mass Transport of GaN in LiCl

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. The temperature was then increased to melt the salt (m.p = 610°C). After achieving a stable melt (~650°C), an amount of GaN powder (approximately 0.5g, Alfa Aesar, 99.5%, -10 mesh) sufficient to achieve saturation was added to the melt and stirred using a quartz rod. The temperature was brought to 900°C for 30 minutes to attempt to dissolve as much GaN in solution as possible. During the time at 900°C, the solution was stirred several times using a quartz rod. After 30 minutes, the temperature of the salt was reduced to the experiment working temperature (typically 750 or 850°C). The reactor height was adjusted in the furnace to ensure that the hottest part of the melt was at the bottom, where the excess powder GaN was located, and the coolest part was near the surface, where the substrate was to be located. The temperature was measured using a type K thermocouple encased in a quartz sheath, i.e., one end closed round, to protect both the thermocouple from attack by the salt, and the salt from the decomposition products of the thermocouple.

Next, a sapphire or a metal organic chemical vapor deposition (MOCVD)-grown GaN/sapphire substrate was suspended just below the surface of the melt and the substrate was rotated. Rotation speeds were 50, 100, or 150 rpm. These speeds were chosen based on a visual evaluation of the particle and fluid flow in a mock experiment using water and MgO in one of the reactor vessels. Rates were chosen to be fast enough to observe particle movement toward the substrate surface, while slow enough not to cause visible turbulence at the reactor walls. Substrates were rotated between three and four hours in the melt. After the experiment, the substrate was slowly raised out of the melt, and the reactor was cooled to room temperature. The substrate was rinsed with DI water to remove the salt, and inspected by optical and scanning electron microscopy. In one case, the deposit was analyzed by x-ray diffraction.

Experiments were conducted with two different powders (GaN and InN), at two temperatures (750°C and 850°C), and three different rotation speeds (50, 100, and 150 rpm). However, it was discovered that the factor that had the largest impact was the material(s) used to suspend the sapphire or GaN/sapphire substrate. At first, a susceptor was constructed from a nickel plate (0.5 mm thick, 99.99% pure, Aldrich Chemicals) onto which small nickel wire loops, also >99.9% pure, were spot-welded at the corners of the plate. The loops were folded over the corners of the substrate to form little tabs to attach the substrate. This way, the susceptors could be fabricated in the lab, inexpensively and as needed. On the backside of the plate, two more nickel wires were spot welded and threaded up through a ¼" diameter quartz

tube, which was attached through a coupling to the spin motor. Mechanically, this approach was quite successful. However, 850°C is >2/3 the melting temperature of nickel (1410°C), and consequently substantial nickel diffusion took place onto the surface of the sapphire or GaN/sapphire template.

The results of one experiment in particular, performed at the highest rotation speed and at 850°C for four hours using a GaN/sapphire template, produced a thick film that delaminated upon removal from the melt. This film had a shiny, metallic appearance, but was also translucent, and appeared to be approximately 100 microns thick (judging from the optical microscope). The film was sufficiently thick to be mechanically robust enough to transfer from the surface of the original substrate onto a microscope slide for XRD analysis. XRD confirmed the presence of the original GaN layer on the sapphire substrate, and the presence of a thick film of Ni-Ga alloy (Figure 4.1). Powder XRD data were collected from the thick alloy film and analyzed by Mark Rodriguez (1822), and HRXRD data of the GaN/sapphire template were collected and analyzed by Stephen R. Lee (1123). The fact that the original, 3-micron-thick GaN film remained on the sapphire substrate suggests that the gallium in the thick Ni-Ga alloy deposit must have come from the dissolved GaN in the molten chloride salt, as there was not enough gallium present in the original GaN layer to account for all of the gallium found in the alloy film, even if the entire MOCVD film had been consumed. This suggests that mass transport of GaN in the melt did take place.

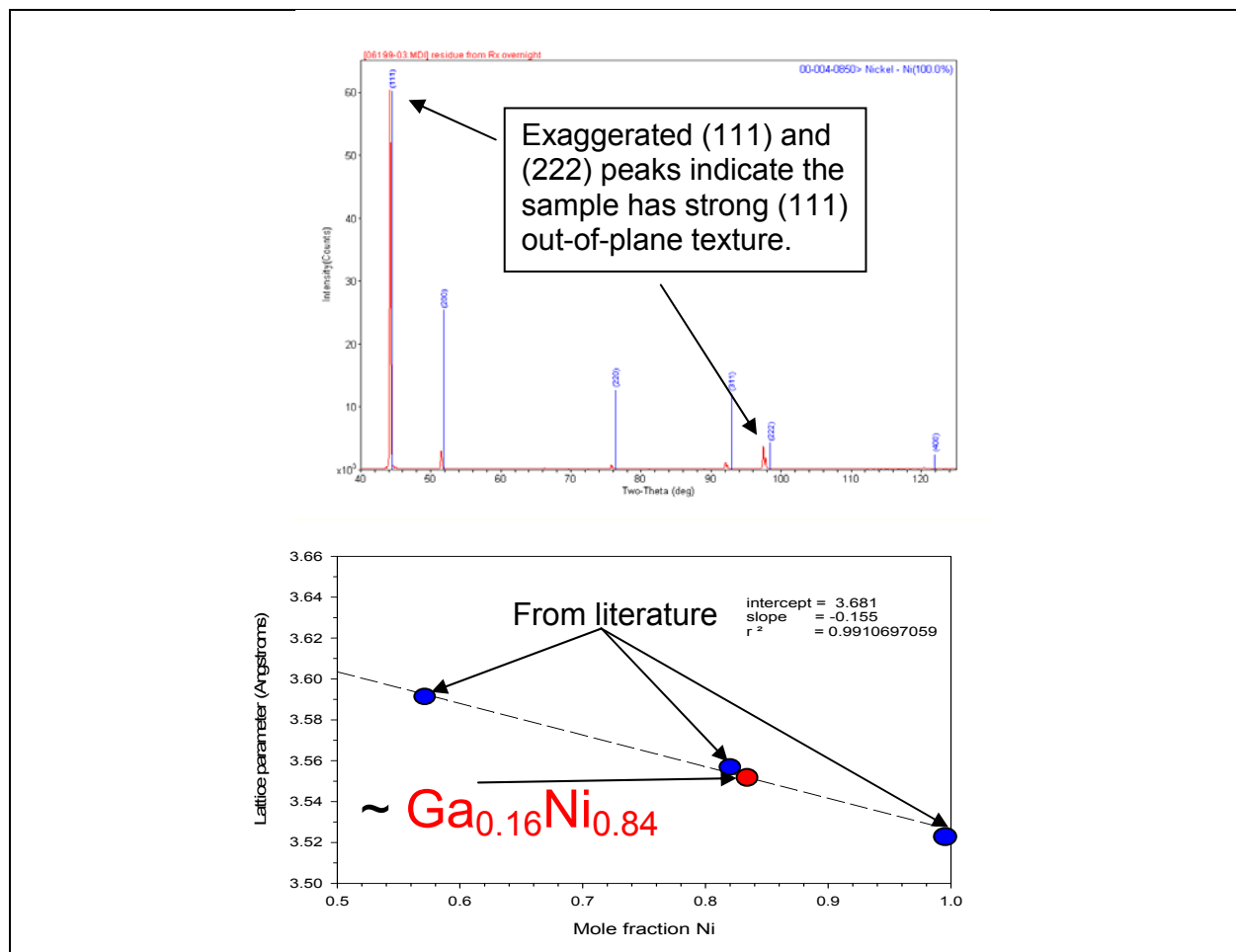


Figure 3.1 XRD results from mass transport experiment

The nickel contamination problem was addressed by using an alumina-, zirconia-, or silica- filled epoxy to cement the substrate to the quartz rod. The vendor claimed that the epoxy would be compatible with the temperatures and molten salts without contaminating the melt. From the limited experiments conducted in this funding period, this appears to be true. Three different high temperature epoxies were tested, and one was selected based on mechanical success. A methodology for repeatably lowering the substrate into the melt without causing thermal shock and subsequent substrate separation was developed. An experiment similar to the one that produced the Ni-Ga alloy film was conducted using an epoxy-mounted sapphire substrate. SEM and EDS analysis showed that nothing was deposited upon the sapphire substrate in the absence of the nickel.

Colleagues at GNOEM Systems, Inc. have suggested that these results may be consistent with those found in literature published in the late 1950's or early '60's from scientists at Stanford University, who were exploring the increased solubility of solutes in molten salts with the addition of metals. At the present time, the search for these papers continues. A set of experiments was designed to explore the effects of nickel, titanium, and gallium on the solubility of GaN in LiCl. During the first one of these experiments, however, the furnace suffered a broken heater element, and we plan to continue these experiments at a future date.

4.2 Exploration of Alternative Solvents

Lithium chloride-potassium chloride eutectic mixture has a melting point of 352°C. Its optimum working temperature range at atmospheric pressure is between 450 and 550°C, which is a fairly limited temperature window. It was chosen because the nitrogen reduction potential is only 200-300 millivolts positive of lithium reduction, and few solvents have such a wide electrochemical window. The higher the growth temperature, the more thermal energy is available to assist adatoms on the growth surface of the crystal in their movement about to find the ideal lattice site, which in turn improves the crystallinity of the crystal. Therefore, higher temperatures are typically desired in crystal growth. At high temperatures, however, and in harsh environments such as a molten salt, the more difficult it becomes to eliminate impurities from the system, e.g., from the crucible or from the electrodes, etc. Lithium chloride-potassium chloride may be used at higher temperatures than 550°C provided there is some overpressure of inert gas that will lower the vapor pressure of the KCl. This was not possible in the apparatus available at SNL, but was available through collaboration with GNOEM Systems, Inc. in their high pressure Czochralski (HPCZ) crystal puller. In addition, their reactor could easily attain temperatures in excess of 1000°C and overpressures >1600 psi.

Galvanostatic nitrogen reduction experiments were performed in NaCl at 1000°C. It was found that the voltage required to reduce sodium ions to metallic sodium was more positive than that required to reduce nitrogen gas, as a stream of liquid sodium was observed dripping off the electrode. Therefore, NaCl could be ruled out as a candidate solvent.

Ionic liquids (molten salts with melting points <100°C) are beginning to gain attention in electrochemistry for their attractive properties. They have wide electrochemical windows (~4V), they are liquid at or near room temperature, they are non-toxic, are biologically-friendly, have close to zero vapor pressure, and in some cases can be used at temperatures exceeding 250°C. Ionic liquids could enable the ability to mass produce, for example, indium nitride-based photovoltaics very inexpensively. Also, the ability to conduct the nitride electrochemistry could lead to new advances in chemical synthesis. The advantage of such solvents for crystal growth at low temperatures is that in lieu of thermal energy, additives might be employed to assist in enhancing crystal quality.

Lithium nitride was dissolved in electrochemical grade dimethylpropylimidazolium imide (DMPI-Im, Covalent, Inc.) over the course of three days at room temperature, or overnight at 60°C. In a separate vial, gallium(III) chloride was dissolved in DMPI-Im, which went easily into solution. In a third vial, a small amount of the two solutions was mixed. The lithium nitride-containing solution was brick red, consistent with the color of lithium nitride, while the GaCl₃ solution remained clear. At first nothing happened when the solutions were mixed, but then over the course of a week the solution turned a transparent light yellow and a light yellow precipitate was observed. Attempts to isolate the precipitate were unsuccessful in yielding a large enough amount for XRD analysis. Although qualitatively encouraging, project priorities dictated that these experiments be put on hold in favor of performing electrochemical experiments.

4.3 Electrochemistry in Large Area, High Pressure Crystal Puller

The electrochemical cell that was used for the initial experiments was: a) designed with a different experimental 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). Modifications had been made to a glove box during FY04; however, that glove box was no longer available to the project due to other project requirements.

A new Vacuum Atmospheres glove box was designed, specified, ordered, delivered, and installed during this project. The glove box was ordered to fulfill needs of thermal battery and other related projects, and this LDRD was a beneficiary of that investment. The new glove box is equipped with an oxygen monitor and a hygrometer, and its atmosphere is maintained below 1 ppm O₂ and H₂O.

However, a suitable electrochemical cell was not available. A terrific opportunity arose to conduct experiments in a large-area crucible when the PI was contacted by a small company (GNOEM Systems) located in Silicon Valley that expressed interest in collaborating on the crystal growth. A high pressure Czochralski (HPCZ) crystal puller with 4" crystal pulling capability was made available for use by the project (Figure 4.2), and was modified to allow for electrical feedthrus, thermocouples, and gas injection. The PI spent four weeks on location to assist with the hardware modifications and first electrochemical experiments.

The HPCZ puller was originally equipped with the capability to spin a seed crystal with fine motor control in the melt, as well as the ability to control the temperature of the melt with high reproducibility. The crystal puller hardware had to be modified to include a stage on which electrodes were mounted (see Figure 4.3). The stage could be raised and lowered using external motor control while the bell jar was closed, allowing electrodes to be lowered into the crucible after the salt was melted under inert atmosphere. The stage includes electrical mounting blocks for the electrical connections and a connection for the gas electrode. The first design took advantage of a spare optical port in the top of the bell jar and employed a coiled-spring tube to deliver the gas to the electrode. However, all electrodes had to be electrically isolated from each other and from the chamber, and the coiled spring approach proved unreliable in maintaining its electrical isolation upon lowering the bell jar. A second generation design used the feedthru available for raising and lowering the stage as a conduit for the gas (Figure 4.4), which resulted in a much cleaner and robust design. A hole in the center of the stage allowed room for the seed crystal to be lowered from the top of the chamber into the melt.

Numerous problems needed to be solved before the basic N₂ reduction electrochemistry could be demonstrated. The major efforts focused on finding or making a robust reference electrode, salt purification, and atmospheric purity, in addition to the hardware modifications described above. Ultimately, these problems were not completely resolved prior to the end of the funding period; however, a positive path forward was determined, as will be described below.

The reference electrode that had been used in previous experiments inside the small electrochemical cell consisted of a silver wire immersed in a 0.1M AgCl:LiCl-KCl solution encased in a 1/8" outer diameter Pyrex tube. Pyrex was chosen because it conducts ions at high temperatures (~450°C) and can therefore contain the molten AgCl:LiCl-KCl and maintain electrical contact with the molten salt. Pyrex softens at ~550°C, and is therefore limited to this temperature for extended use. The problem was that stress was placed on that small, fragile tube every time the elevator was lowered, causing the tube to break and contaminating the solution with silver chloride. Wires or ribbons of silver, tungsten, molybdenum, and nickel were used in an attempt to obtain a stable, quasi-reference electrode without success; all were found to dissolve over the course of the experiment. Ultimately we returned to the Ag/AgCl reference in a Pyrex tube; this time however the Pyrex tube was 1/4" in diameter and therefore much more robust. Tubes were sealed on one end with a propane torch and blown into a small bulb at the end in order to decrease the wall thickness. The original concern was that the thicker wall would cause a voltage drop across the reference electrode, but this was found to not be the case.

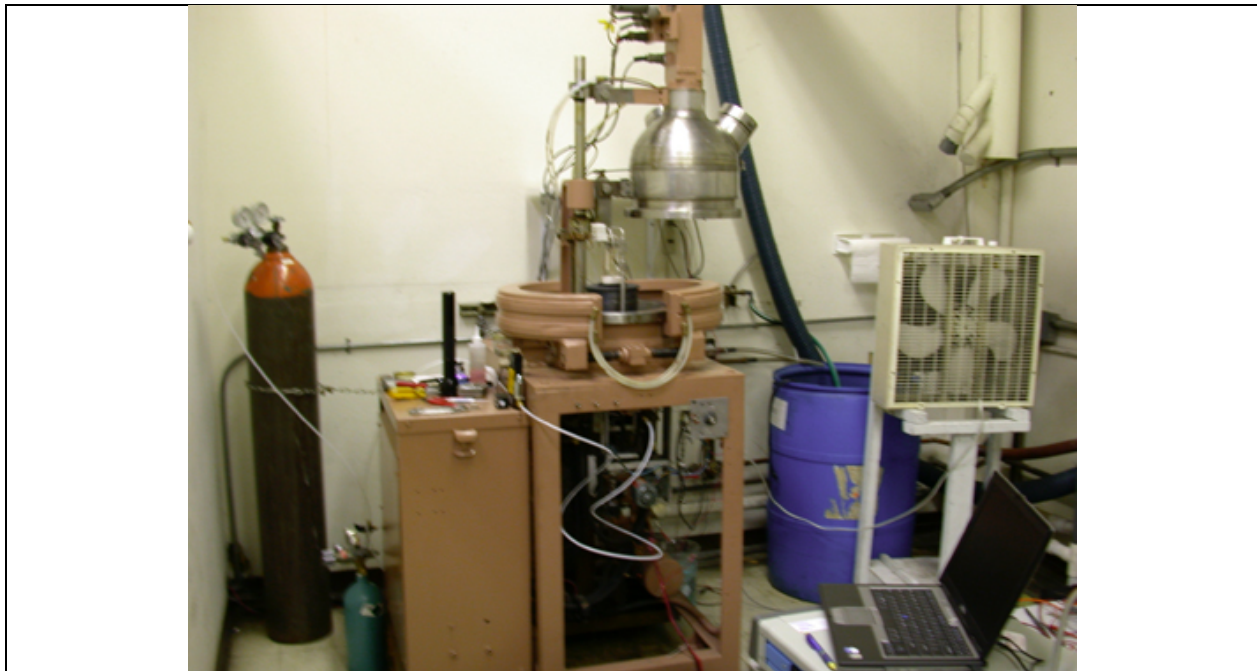


Figure 4.2 High pressure Czochralski (HPCZ) crystal puller

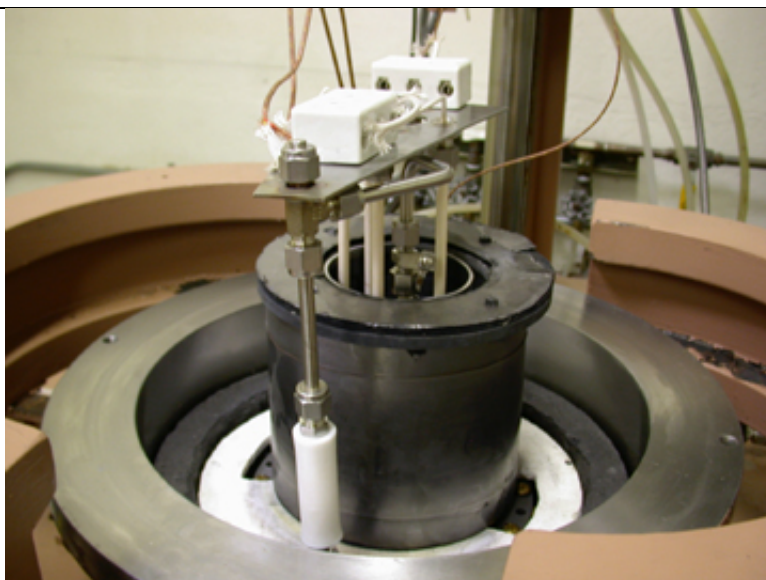


Figure 4.3 First generation of elevator modification for electrodes and gas feedthrus



Figure 4.4 Second generation of feedthrus on elevator

The next major difficulty concerned the purity of the salt and atmosphere. Reagent grade salt (Fisher Scientific) was used without purification. Approximately 200g of salt were used in each experiment. After the experiment, the salt was cooled to room temperature. A photograph of the slag that had coagulated at the surface of the melt and solidified is shown in Figure 4.5. The identity of the impurity or impurities was unknown, but was present in the reagent grade material. Using a nickel wire as the working electrode and a molybdenum wire for the counter electrode, a cyclic voltammogram was recorded against an Ag/AgCl reference electrode (Figure 4.6). In pure salt, no current above a small background signal (a few milliamps) should be observed until the voltage reaches -2.5V vs. Ag/AgCl. However, impurities present in the salt limited the voltage to approximately -1.5V . Nitrogen gas reduces at approximately -2.2V vs. Ag/AgCl at 550°C . Thus we were unable to sweep to voltages more negative than -1.5V and perform the intended experiments.

A salt purification procedure was developed with the assistance of David Ingersoll (org 2546). The procedure was based on a suspicion that the impurities present in the as-received materials originated from oil in the vacuum pumps used by the manufacturer to dry the salt. The procedure involves an aqueous extraction with organics such as hexanes and xylenes to remove organic and silicone-based oil residues, respectively, followed by filtration to remove the surprisingly large amount of solid particulates present in the salt, then recrystallization, reduction using HCl vapor to reduce any oxides that had formed while the salt was dissolved in the water, and vacuum drying in a dry room. This procedure was found to be successful in removing most and sometimes all of the black “slag” and particulate matter, and electrochemical experiments could resume in the glove box back at SNL.

A growth experiment using a nickel gas electrode and a gallium counter electrode was performed in molten LiCl-KCl at 550°C by sweeping the potential of the nickel gas electrode (in the presence of 10 sccm of N₂) negative relative to the counter electrode for two hours. Upon cooling, the salt was dissolved in deionized water and filtered to isolate the insoluble product. An optical image of the crystals that were formed is shown in Figure 4.7. X-ray diffraction data collected on these crystals showed them to be LiGa₅O₈, consistent with the hypothesis that the reduction wave observed in the electrochemical data was due to oxygen in the system.



Figure 4.5 Slag on walls of crucible after melting and freezing reagent-grade LiCl-KCl

Unfortunately, the inability to control the atmosphere in the HPCZ apparatus ultimately limited the potential window for using the salt. It is speculated that this was due to the presence of oxygen and atmospheric moisture. Currently there is no easy way to remove background moisture from the chamber, which has been used to grow some of the highest quality indium phosphide in the world. Indium phosphide is considerably less sensitive to the presence of background moisture and oxygen than is molten salt electrochemistry.

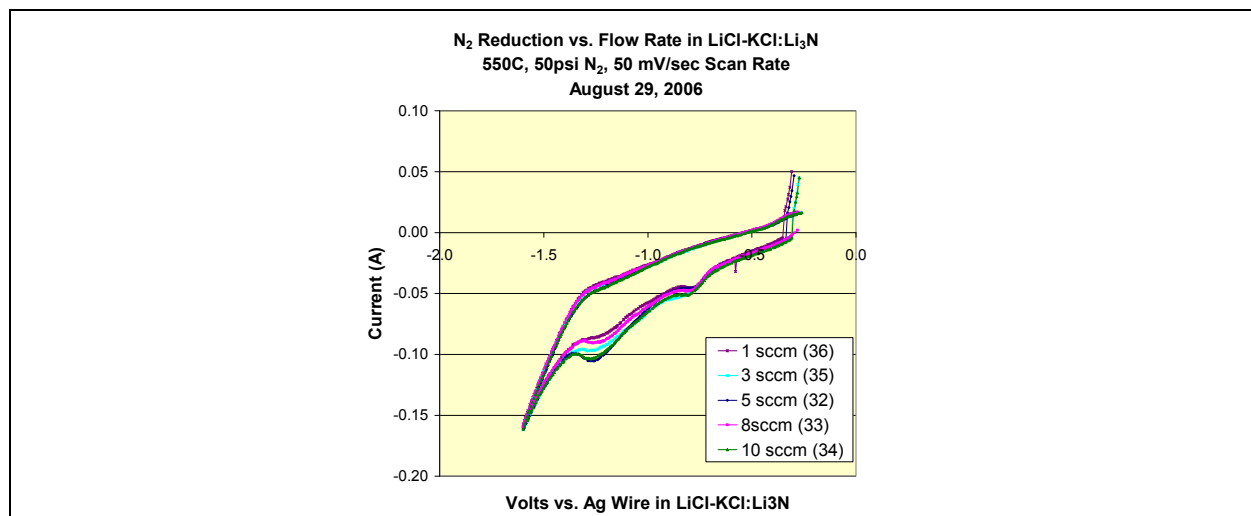


Figure 4.6 Voltammogram of as-received molten LiCl-KCl:Li₃N, using a nickel wire as the working electrode

Control of the atmosphere around the HPCZ will require the installation of a large enclosure around the reactor and was beyond the scope of the collaboration embarked upon during this LDRD. However, an enclosure was designed and a cost estimate was obtained. Many of the remaining hardware difficulties were overcome and electrochemical experiments are now possible in this modified reactor. This ability will be leveraged to obtain resources to pursue this work further. In the meantime, GNOEM has purchased a glove box and is installing a reactor at the time of writing.

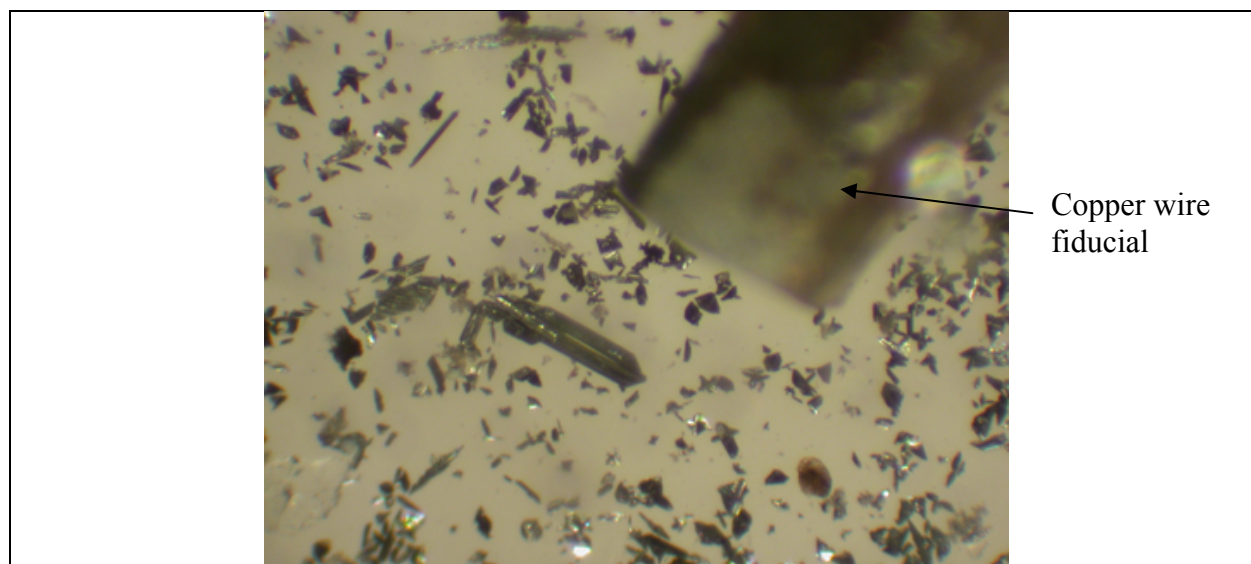


Figure 4.7 Optical image of crystals formed in electrochemical experiment in HPCZ reactor

5. SUMMARY

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.

Dissolution and precipitation experiments were attempted in order to determine whether GaN crystals could be grown through this very simple approach. Some of the experiments were not entirely successful; however, it was determined that mass transport of GaN was taking place in the molten salt, which is a critical result for the success of the ionic precursor creation growth technique development.

An opportunity arose to work with a small company that has the facilities and equipment required for manufacturing bulk gallium nitride boules. This collaboration has been very beneficial in that many of the problems that would be encountered when transferring technology from the laboratory to a manufacturing setting have already been identified and partially or fully addressed. The path forward is to demonstrate the growth of GaN (of any quality) on a substrate by producing the ionic precursors independently by electrochemical means, and then use those results to pursue the resources needed to construct the enclosure for the HPCZ and continue with the development of the technique.

Several issues were overcome, such as purification of the salt in a cost-effective manner that minimizes ES&H concerns, choice of reference electrode, and identification of the signature of oxygen contamination in the melt. While growth of single crystal gallium nitride would have been the most desirable outcome of this short-duration project, the information, knowledge, and experience obtained in this work will be invaluable in advancing the growth technique, particularly as technology transfer becomes more important.

The seed money provided by this late-start LDRD led to the award of a Work For Others (WFO) project in the area of providing native substrates for gallium nitride-based LEDs for Solid-State Lighting (SSL) from the National Energy Technology Laboratory's (NETL's) Energy Efficiency and Renewable Energy (EERE) office, in the amount of \$498,600 over two years.

6. REFERENCES

1. I. Grzegory, J. Jun, M. Bockowski, St. Krukowski, M. Wroblewski, B. Lucznik, and S. Porowski, "III-V Nitrides—Thermodynamics and Crystal Growth at High N₂ Pressure," *J. Phys. Chem. Solids* **56**, 639-647, 1995.
2. W. Utsumi, H. Saitoh, H. Kaneko, T. Watanuki, K. Aoki, and O. Shimomura, "Congruent melting of gallium nitride at 6 GPa and its application to single-crystal growth," *Nature Materials* **2**, 735-738, 2003.
3. B. Wang, "Ammonothermal growth of GaN crystals in alkaline solutions", *Journal of Crystal Growth* **287**, 376-380, 2006.
4. M. Callahan et al., "GaN single crystals grown on HVPE seeds in alkaline supercritical ammonia", *Journal of Material Science* **41**, 1399-1407, 2006.
5. C.M. Balkas, Z. Sitar, L. Bergman, I.K. Shmagin, J.F. Muth, R. Kolbas, R.J. Nemanich, R.F. Davis, "Growth and characterization of GaN single crystals," *Journal of Crystal Growth* **208**, 100-106, 2000.
6. H. Yamane, M. Shimada, T. Endo, F.J. Disalvo, "Polarity of GaN single crystals prepared with a Na flux," *Jpn. J. Appl. Phys. Part 1* **37**(6), 3436, 1998.
7. A. Denis, G. Goglio, and G. Demazeau, "Gallium nitride bulk crystal growth processes: A review," *Materials Science and Engineering R* **50**, 167-194, 2006.
8. Y. Song, W. Wang, W. Yuan, X. Wu, X.L. Chen, "Bulk GaN Single Crystal: Growth Conditions by Flux Method," *Mater. Res. Bull.* **247**, 275-278, 2003.
9. K.E. Waldrip and F.M. Delnick, Personal laboratory observation, May 2003.
10. R.W. Cumberland, R.G. Blair, C.H. Wallace, T.K. Reynolds, and R.B. Kaner, "Thermal control of metathesis reactions producing GaN and InN," *J. Phys. Chem. B* **105**, 11922-11927, 2001.
11. T. Goto and Y. Ito, "Electrochemical reduction of nitrogen gas in a molten chloride system," *Electrochimica Acta* **43** (21-22) 3379-3384, 1998.

DISTRIBUTION

1	MS0123	Henry R. Westrich	1011
1	MS0601	Jeffrey Y. Tsao	1130
1	MS0601	Robert M. Biefeld	1126
1	MS0601	Thomas M. Kerley	1126
1	MS0614	Cara Johnson	2540
1	MS0614	Thomas F. Wunsch	2546
5	MS0614	Karen E. Waldrip	2546
1	MS1164	Paul C. Butler	5400
1	MS1421	Jerry A. Simmons	1130
2	MS9018	Central Technical Files	8944
2	MS0899	Technical Library	9536
1	MS0123	D. Chavez, LDRD Office	01010
1	MS0161	Patent and Licensing Office	11500