Final Technical Report

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Acknowledgment, Disclaimer and Proprietary Data Notice

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List of Acronyms

GaN = Gallium Nitride
ESG = Electrochemical Solution Growth
TEM = Transmission Electron Microscopy
SEM = Scanning Electron Microscopy
XPS = X-ray Photoelectron Spectroscopy
XRD = X-ray Diffraction
EDS = Electron Dispersive Spectroscopy
PL = Photoluminescence
UV = Ultraviolet
SIMS = Secondary Ion Mass Spectroscopy

A: Executive Summary

The objective of this project was to develop the Electrochemical Solution Growth (ESG) method conceived / patented at Sandia National Laboratory into a commercially viable bulk gallium nitride (GaN) growth process that can be scaled to low cost, high quality, and large area GaN wafer substrate manufacturing. The goal was to advance the ESG growth technology by demonstrating rotating seed growth at the lab scale and then transitioning process to prototype commercial system, while validating the GaN material and electronic / optical device quality. The desired outcome of the project is a prototype commercial process for US-based manufacturing of high quality, large area, and lower cost GaN substrates that can drive widespread deployment of energy efficient GaN-based power electronic and optical devices.

In year 1 of the project (Sept 2012 – Dec 2013) the overall objective was to demonstrate crystalline GaN growth > 100um on a GaN seed crystal. The development plan included tasks to demonstrate and implement a method for purifying reagent grade salts, develop the reactor 1 process for rotating seed Electrochemical Solution Growth (ESG) of GaN, grow and characterize ESG GaN films, develop a fluid flow and reaction chemistry model for GaN film growth, and design / build an improved growth reactor capable of scaling to 50mm seed diameter. The first year's project objectives were met in some task areas including salt purification, film characterization, modeling, and reactor 2 design / fabrication. However, the key project objective of the growth of a crystalline GaN film on the seed template was not achieved. Amorphous film growth on the order of a few tenths of a micron has been detected with a film composition including Ga and N, plus several other impurities originating from the process solution and hardware. The presence of these impurities, particularly the oxygen, has inhibited the demonstration of crystalline GaN film growth on the seed template. However, the presence of both Ga and N at the growth surface indicates that the reactor hardware physics is all functioning properly; achieving film growth is a matter of controlling the chemistry at the interface. The impurities originating from the hardware are expected to be straightforward to eliminate. Activities were defined for an extension of budget period 1 to eliminate the undesired impurities originating from the reactor hardware and interfering with crystalline GaN film growth. The budget period 1 extension was negotiated during the 1st half of 2014. The budget period 1 extension spanned approximately from August 2014 to August 2015. The project objective for this extension period was to demonstrate at least 0.5um crystalline GaN film on a GaN seed in the lab scale reactor.

The focus of the budget 1 extension period from August 2014 to August 2015 was to eliminate oxygen contamination interference with GaN film growth. The team procured the highest purity lowest oxygen salt for testing. Low oxygen crucible materials such as silicon carbide were installed and evaluated in the laboratory reactor. Growth experiments were performed with high purity salt, high purity hardware, and optimized oxide removal from the seed surface. Experiments were characterized with methods including UV inspection, profilometry, x-ray diffraction (XRD) to determine crystalline structure, optical and scanning electron microscopy, photoluminescence, x-ray photon spectroscopy (XPS), transmission electron microscopy (TEM), and secondary ion mass spectroscopy (SIMS). Despite successfully integrating the low oxygen materials in the laboratory reactor, the goal of depositing 0.5um of crystalline GaN on the MOCVD GaN seed was not met. Very thin (ca. 10nm) cubic phase GaN deposition was observed on the hexagonal MOCVD GaN seeds. But there was a competing etching reaction which was also observed and thought to be related to the presence of metallic lithium, a

byproduct of the LiCl-KCl salt used as the process medium. The etching reaction could potentially be addressed by alternate salts not containing lithium, but would necessitate starting all over on the reactor and process design. Further, controlling the reaction of Ga and N in the bulk salt to favor deposition on the seed has proved to be very difficult and unlikely to be solved within the scope of this project in a manner consistent with the original objective for wafer or crystal scale thickness for GaN deposition on a GaN seed. Upon completion of the budget 1 extension period in August 2015 the project partners and DOE agreed to stop work on the project.

During the period of September 2015 through July 2016 a bulk GaN project proposal was developed to redirect the project towards SunEdison Semiconductor and Kyma Technology partnering on development and improvements in bulk GaN wafering. The proposal was in review with DOE/AMO. However, in August 2016 it was announced that GlobalWafers, a company based in Taiwan, intended to acquire SunEdison Semiconductor. At that time the proposal was put on hold pending the acquisition approval. The acquisition was closed in December 2016 and the PI informed DOE/AMO in January 2017. DOE/AMO advised that due to the foreign acquisition of SunEdison Semiconductor the redirected project proposal could not go forward and that project closeout should be executed.

B: Introduction

GaN crystal growth is a critical enabling technology that is essential for bolstering US competitiveness in high efficiency power electronics and solid state lighting. However, unlike Silicon (Si) and Gallium Arsenide (GaAs) which have well established bulk crystal growth and large area wafer manufacturing processes, manufacturing technology for the production of bulk GaN substrates does not yet exist. Traditional semiconductor bulk crystal growth techniques are not transferrable to the GaN system due to its unusual thermodynamic properties. Existing techniques for GaN wafers are limited to heteroepitaxial growth of GaN films on sapphire, silicon carbide (SiC) and Si substrates, which impose serious limitations on the size and quality of GaN substrates. Heteroepitaxial growth of GaN on sapphire based on Hydride Vapor Phase Epitaxy (HVPE) is commercially available, but is limited by lateral scalability, material quality, and prohibitively high cost, curtailing the use to niche applications. "True" bulk GaN growth techniques such as Ammonothermal growth and High Nitrogen Pressure Solution Growth (HNPSG) show promise, but require extreme pressures (>4,000 atmospheres) and tend to have very slow growth rates (<60um/day). To date, no growth technique has been proposed that provides an adequate value proposition, i.e., a desirable combination of growth rate, scalability to larger wafer sizes, electronic grade material quality, and manufacturing cost.

What is required is a fundamentally different approach for GaN growth, one which is not driven by thermodynamics or limited in quality by heteroepitaxy. Sandia National Laboratory invented a novel Electrochemical Solution Growth (ESG) process for bulk GaN growth that does not have the limitations of traditional GaN crystal growth methods. ESG is a low temperature (500^{o}C), atmospheric pressure process that has demonstrated to crystalline GaN particle growth, and in the form of seeded growth has the potential to be a scalable, low cost, high growth rate method capable of producing large area, high quality boules of GaN. ESG has the potential to be an efficient manufacturing process for growing cost effective GaN substrate crystals suited for conversion to wafer substrates that can be used in existing semiconductor and optical device manufacturing in plants.

Successful development of the ESG method for growing GaN substrates is expected to deliver significantly more than a 50% substrate cost reduction over competing technologies such as HVPE on sapphire, Ammonothermal Growth, and High Pressure Solution Growth, while meeting or exceeding their functional properties. Further, the low temperature, atmospheric pressure approach to the ESG growth will enable significantly lower energy consumption and simplify equipment design to produce bulk GaN substrates. The potential market for GaN based devices could grow to over $50B in the next several years, with power electronics and LEDs each currently representing more than $10B device market opportunities. The available market for GaN substrates will be in excess of $1B. Successful development of the ESG method for bulk GaN fully addresses these existing markets while also having the potential to accelerate GaN market adoption in power electronics and LED lighting through improved manufacturing yields, improved device performance, and lower unit cost.
Key competitive advantages for the ESG growth method are expected to be the several orders of magnitude higher growth rate and scalability to large area substrate sizes. Initial estimates have been made for ESG-produced GaN substrate costs based on raw material costs (Ga source) and typical conversion cost rates to a wafer substrate based on silicon experience. The expectation is for a potential mature wafer cost in the range of around $200 for 100mm diameter substrate and around $500 for 150mm diameter substrate. At these costs the bulk GaN substrates can be competitive on overall cost of ownership with heteroepitaxy approaches such as GaN on Sapphire and GaN on Silicon through superior material properties and the possibility to enable an overall system cost reduction through more efficient devices, reduced component counts, and smaller system size.

According to recent technical analysis by Yole Development, widespread adoption and deployment of GaN-based power electronics and lighting could lead to as much as a 25% reduction in world energy consumption by 2025. The transition to GaN-based power electronics will lead to more efficient power switching devices and more compact power systems. The most promising near term markets for cost effective bulk GaN substrates are in high voltage power electronics for motor control, power supplies, PV inverters, and other high voltage and high power switching applications. Although functional power devices are being fabricated on GaN on Silicon wafers, the device architecture is limited to a lateral device due to the breakdown voltage limitation imposed by the interface between the silicon substrate and the AlN/AlGaN/GaN epitaxial layer stack. Bulk GaN substrates may enable vertical power device structures with higher breakdown, more efficient power switching, and potential for higher yields and better reliability due to much lower defect density. Cost effective, large area bulk GaN substrates also have the potential to improve the performance and reduce the cost of LEDs for lighting and laser diodes for high density data storage. LED performance, for example, is limited by drive current induced “droop” in the light output which is sensitive to the defect density of the GaN on Sapphire substrates. Bulk GaN substrates with GaN homoepitaxy, will have lower defect density and be capable of higher drive currents resulting in more light output per chip and lead to a reduction in the LED component count at the system level. The long term environmental and energy savings impact (2020) from lower cost bulk GaN substrates are estimated to offer an energy savings potential of 12.4 billion KWh/year from LEDs and 9.8 billion kWh/year from power electronics, and potential carbon emissions reductions of 6.86 million tons/year from LEDs and 5.41 million tons/year from power electronics (sources STFC, JST, 2009).

C: Background

Bulk GaN substrate technology is a critical enabler for a wide range of energy intensive applications in solid-state lighting and high power electronics. However, unlike Si and GaAs semiconductor technologies wherein devices can be fabricated using bulk native substrates, GaN semiconductor technologies are severely limited by the lack of native substrates. So far, commercial GaN devices such as laser diodes (LD), light emitting diodes (LEDs) and power devices are fabricated on epitaxial GaN layers grown on either sapphire or SiC substrates. Lattice mismatch between the substrate and epitaxial layer leads to higher defect density, which in turn leads to increased current leakage and reduced breakdown voltage, and overall reduced efficiencies and performance of optoelectronic and electronic devices. In addition, heteroepitaxy also increases stress in GaN epitaxial layers, which severely limits size and thickness of the GaN layer. Another major challenge for heteroepitaxy is that the thermal mismatch can lead to wafer curvature during cooling, which results in GaN film cracking [2] and reduced yields. So far, these issues have limited the size of heteroepitaxial wafers to 2" to 4" in diameter.

The ideal solution would be to grow homoepitaxial layers on bulk GaN substrates. However, success in the growth of bulk GaN crystals has been limited and an economical process that is capable of manufacturing bulk GaN crystals has not yet emerged despite decades of investment in adaptations of traditional bulk crystal growth techniques to produce GaN. Table 1 summarizes the salient characteristics and challenges associated with various approaches to attain bulk GaN, and shows that substrate material is either unavailable, prohibitively expensive, and scalability is highly limited. It is to be noted that HVPE is a heteroepitaxial growth technique (i.e., not a true bulk growth technique) that has been included here because it represents the current state-of-the art in commercially available "bulk" GaN.

Unlike Si and GaAs, GaN cannot be easily grown from a melt as Ga and N do not provide adequate reactivity under normal conditions. With a high melting point and relatively low decomposition temperature, GaN cannot be grown from its stoichiometric melt using Czochralski or Bridgman methods [3]. While HVPE-grown material is technically commercially available, it is prohibitively expensive. HVPE is a thick epitaxial film growth technique that can takes advantage of the natural reduction of dislocations that occurs with thickness over MOCVD-grown thin films, but the final crystal quality suffers from curvature resulting from the strain produced by lattice and thermal mismatches between substrate materials and GaN. Efforts to grow GaN from its melt by High Pressure Nitrogen Solution Growth (HPNSG) have produced the best quality crystals in the world (10^2 dislocations/cm^2) by dissolving dinitrogen (N_2) into liquid Ga at temperatures of 1500^{o}C and 20,000 atmospheres. While remarkable progress has been made, the technique is inherently limited by its pressure to 2" wafers and will never result in a cost effective large scale, high throughput manufacturing process. An alternative method, Ammonothermal, is to dissolve GaN powder feedstock in liquid ammonia as an analogue of the process used to grow quartz by the hydrothermal method; this has been heavily invested in over the course of two decades and is the most promising of the true bulk growth techniques. Its main limitation is growth rate and subsequent cost, even if claims of scalability are eventually substantiated. Finally, the Sodium Flux technique employs molten alkali metal (sodium) to dissociate the dinitrogen precursor at modest temperatures and pressures; although it has demonstrated early success in producing a 2" wafer, it will also be limited by scalability and cost.

Also shown in Table 1 is a comparison of the characteristics of commercially available Si, GaAs, and SiC. SiC is interesting to note that although its quality and size are of commercial interest, its widespread penetration into power electronics has to date been limited by its high cost. As can be seen from Table 1, a reduction of cost of more than an order of magnitude is required to make GaN substrates commercially viable. We believe our proposed technology will make this possible.

Material	Technique Type	Growth Rate	Diameter	Thickness	TD Density	Challenges	Commercial Status
GaN	HVPE	100 μm/h	2"	5.8 mm	>10^6 cm^{-2}	Stress/Curvature Scaling, Cost Growth direction	$2000 /$cm^2$
	Ammonothermal	~ 4 μm/h	2"	> 10 mm	~ 10^4 cm^{-2}	Growth rate Purity High cost	Research quantities only
	HPNSG	< 1 μm/h	0.8"	< 1 mm	~ 10^2 cm^{-2}	Scaling Growth rate High cost	Research quantities only
	Na flux	20 μm/h	2"	3 mm	~ $10^5$$cm^{-2}$	Slow growth Low yield Scaling, Cost	Not available
SiC	CVD Sublimation	1 mm/hr	150 mm	mm	~ 10cm^{-2} (micropipes)	Scaling Growth rate High cost	Volume production $300M sales
GaAs	VGF	4 mm/hr	150 mm	any size	~ 10^3 cm^{-2}	Mature technology	Volume production, >$0.5B sales
Si	Melt Czochralski	60 mm/hr	Large 450 mm	any size	~ 0	Mature technology	Volume production >$10B sales

Table 1: Comparison of growth methods

We assembled a multi-disciplinary team of engineers and scientists with expertise in all aspects of semiconductor crystal growth, molten salt electrochemical deposition, modeling, equipment engineering, process modeling, reactor design, materials and device characterization, and pilot scale manufacturing through commercialization. MEMC has over 50 years of R&D and manufacturing excellence in crystal growth and wafer technologies. Sandia National Laboratory is a center of excellence in compound semiconductor materials and devices, electrochemistry and electrochemical storage technologies. Sandia has extensive expertise in high temperature electrochemistry, ionic liquids, and growth and characterization of compound semiconductor materials. Georgia Tech is a leading center for research in compound semiconductor electronics and photonics, and has extensive capabilities for semiconductor materials and devices, epitaxial growth by metalorganic chemical vapor deposition, and heterojunction structures in III-V compound semiconductors. We have the engineering and technical skills to develop the proposed technology, as well as the experience in manufacturing scale-up and commercialization of wafer technologies for the worldwide electronics, photonics and solar markets

In the first phase of the project, we will optimize the electrolyte chemistry and electrode type and configuration for enhanced ion production. We would further optimize the kinetics and formulate a practical electrolyte system to support rapid GaN growth. We will do extensive modeling to understand the ion mobilities in the electrolytes and develop flow models to reduce precipitation in the bulk. We will design and build crystal growth systems. This will be followed in the second stage with scale up to a larger reactor, and high quality crystals for extensive materials characterization and prototype device development.

D: Results and Discussion

D.a: Budget Period 1, September 2012 – December 2013

D.a.i: Task 1.1, Selection of molten electrolytes and supply chain for pure salts

The purpose of this task was to establish the salt purity level necessary to grow a GaN film. Because of the expense and extremely limited availability of high purity electrochemical grade salts, it is necessary to develop in-house purification of reagent grade salts. Purified reagent grade salts were tested from 20g up to the 500g scale and compared with high purity salt sourced from Aldrich. Purifications have been performed under varying conditions to determine an acceptable process window. The purification process was characterized visually, by current-voltage analysis, by luminescence of auto-nucleated GaN in the frozen salt, and by x-ray diffraction analysis of auto-nucleated GaN powder filtered from the frozen salt solution. Purified salt has been consistently produced and tested throughout the first year of the project in tasks 1.2 and 1.4. The purified salt has also been used on a separate battery related project in Sandia and has been judged to have very low oxygen which is necessary for a successful ESG process. Some oxygen contamination is expected because it is known that the molten salts will dissolve the alumina (Al_2O_3) crucibles, but the oxygen levels in the as received in-house purified electrolyte have not been high enough to interfere with battery processes. ESG growth runs with the Aldrich high purity reference salt have been deferred until the impurities added from the reactor hardware and detected in deposited films are reduced. This work is planned in task 2.1 of the next budget period.

Accomplishments:

- Simple, low cost, and high yield purification process with electrochemical background comparable to high purity salt.
- Auto-nucleation of GaN particles in purified salt.
- 90% range weight yield for salt purification process.
- Reproducibility demonstrated throughout the first year of project.

Results:

Visual quality: The as-received reagent grade salts appear dark immediately after melting as shown in figure 1a. In intermediate stages of the purification process the salt has a faint, dark gray tinged appearance. After purification the molten salt has a clear appearance as shown in figure 1b

Figure 1a: as-received Figure 1b: after purification

Current-voltage analysis: Current-voltage analysis has been routinely performed to probe the electrochemical background of the purified salts. Unpurified, reagent grade salt exhibits very large background current due to its high impurity level. This is shown in the figure 2 comparison with purified salt. Figure 3 shows an overlay of cyclic voltammograms of several purified salts tested in a standardized setup compared with high purity Aldrich salt. Significantly, the electrochemical background of the purified salts is similar to the high purity reference indicating the potential for a low level of interfering impurities.

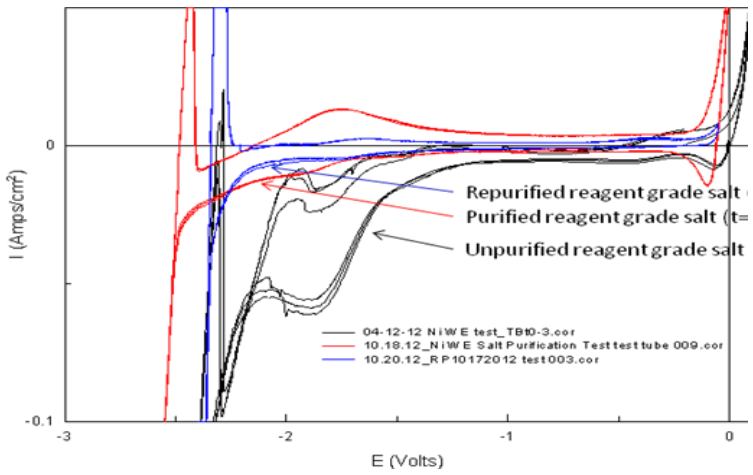

Figure 2: current-voltage plot for unpurified vs. purified salt

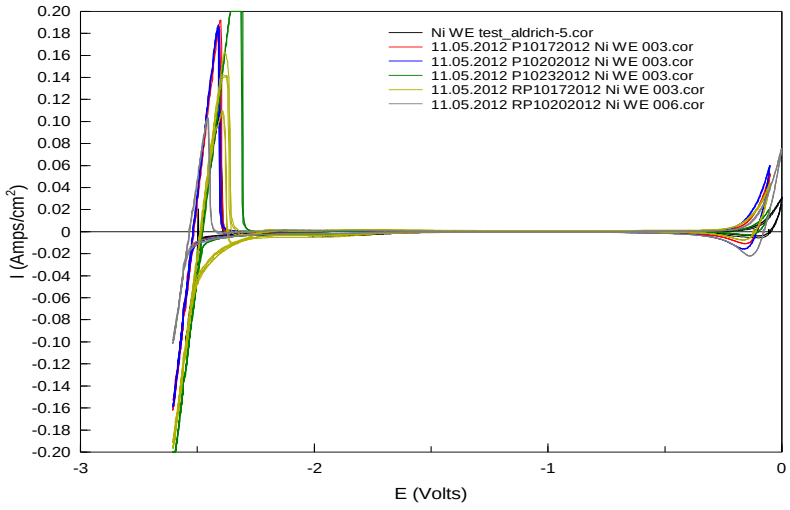

Figure 3: current-voltage plots for purified salts vs. reference

GaN auto-nucleation in purified salts: GaN auto-nucleation has been demonstrated in the purified salts described above. GaN particles have been confirmed by yellow luminescence from the frozen salt as shown in Figure 4. GaN composition has been confirmed by x-ray powder diffraction on GaN particles separated from the salt and is shown in Figure 5.

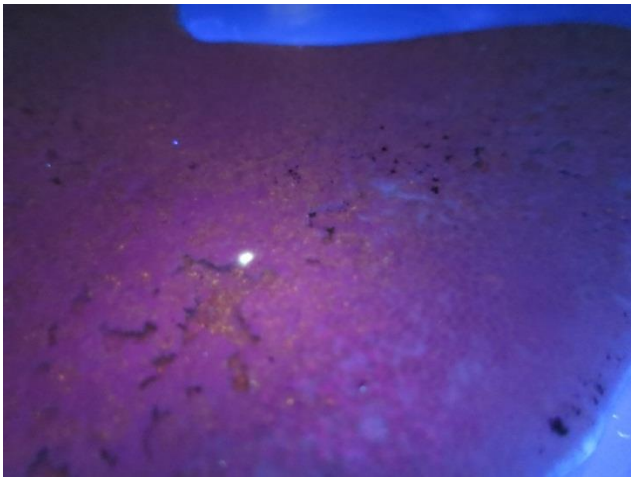

Figure 4: Luminescence following GaN auto-nucleation in purified salt

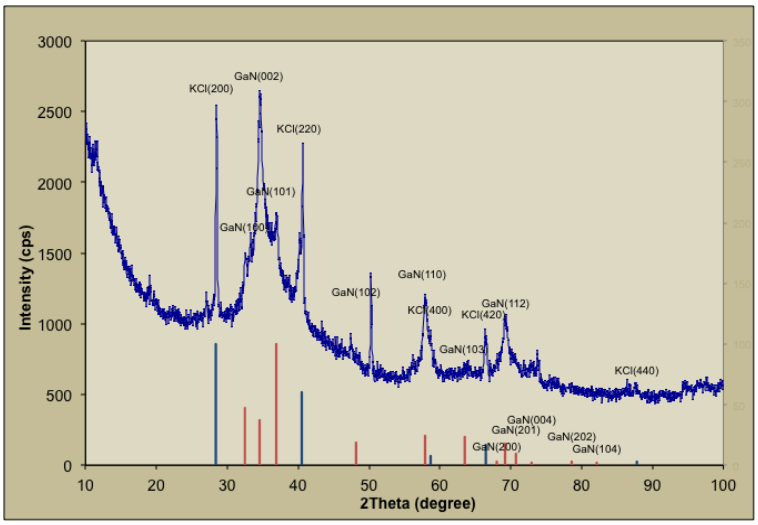

Figure 5: X-Ray powder diffraction showing GaN particles

D.a.ii: Task 1.2, Develop Reactor 1 seeded rotating disk processes to 10mm growth diameter and 100um GaN film thickness. Characterize electrochemical behavior of N and Ga ions in LiCl-KCl eutectic.

The path to developing the seeded rotating disk process included:

- Developing reproducible, robust nitrogen electrodes that operate at high current density;
- Developing a robust, reproducible, high current density gallium electrode
- Developing a reliable reference electrode
- Developing baffles that prevent the interference of one ion on the opposite electrode
- Developing a procedure for wetting the seed crystal and cleaning the surface oxide
- Understanding observed etching of the seed crystal
- Developing a seed holder that can reliably suspend the seed in solution without interfering with the fluid dynamics (causing eddy currents or excessive diffusion distances)
- Developing hardware materials that do not contribute to the impurities in the electrolyte solution

An ESG reactor concept drawing and the actual laboratory scale reactor used in this project are shown side by side below in Figure 6.

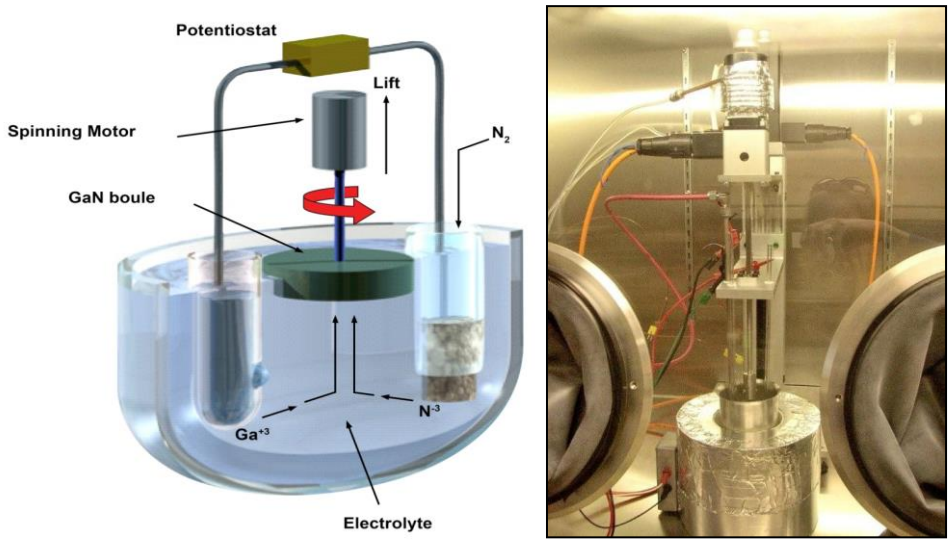

Figure 6: ESG reactor schematic and image

The original approach was to develop the hardware out of readily available, machinable materials that were relatively inexpensive to test out the hardware design. Some impurities from the hardware were expected to incorporate in the growing GaN, but those could easily be eliminated later by switching out hardware components with those made from more chemically stable materials once all the growth parameters were worked out. It turned out, however, that the impurities leaching from the hardware were at levels much higher than anticipated and actively interfered with the growing crystalline film. Therefore the film was difficult to grow and it wasn't until a layer deposited on the seed that we could determine that the interface and the excessive oxygen were preventing film deposition.

Nitrogen electrodes. The manufacturer of the nitrogen electrode active material changed the manufacturing process without informing its customers, and the effect on the ESG process was significant. The new process had a much higher impurity concentration, which interfered with the electrochemistry of interest. Furthermore the electrode bodies made from Pyrex are able to

sustain higher current densities (~300mA/cm^2) but only last anywhere from 20 minutes to 1.5 hours. At the potentials used in the experiments, ions will drive into the glass and substitute for the sodium ions, causing mechanical failure after a short time. Electrodes of a different configuration were fabricated and tested and while they typically sustained lower current densities (~30mA/cm^2), they held up for days at a time. These were found to perform well in long-duration growth experiments.

Gallium electrode bodies. Gallium electrode structures may be fabricated from any glass or ceramic material. The Pyrex bodies performed well at the potentials seen by the gallium electrode in our experiments but dissolve slowly over time in the molten salt. These will have to be replaced with alternative materials in BP2.

Reference electrodes. The reference electrode is a Ag/AgCl in LiCl-KCl in a thin wall Pyrex tube. The Pyrex tube contains the silver impurities outside the experiment, maintains constant Ag/AgCl composition, and the Pyrex is ionically conductive at the temperatures used in ESG growth experiments. However, like the gas and gallium electrodes, the Pyrex slowly dissolves over time in the molten salt and therefore will ultimately need to be replaced. The challenge in BP1 was obtaining tubes with walls that were sufficiently thin to allow good conduction between the reference electrochemical system and the molten salt in the ESG experiment. We learned to identify proper wall thickness tubes for the experiments.

Baffles. Baffles will be discussed in further detail below. As the experiment hardware became reproducible, so did the experimental results. Consistently, gallium was observed to deposit on the nitrogen electrode. After some time in the rotating seed experiments the interference from the gallium would cause the current on the nitrogen electrode to climb very high, often exceeding the capacity of the potentiostat. With the help of the modeling effort described in 1.3, baffles were fabricated to reduce this problem. Materials selection is important and ultimately fully dense alumina was chosen.

Seed crystal surface cleaning and wetting. The seed crystal is a single crystal thin film of GaN on sapphire grown by MOCVD and is described in full detail below. Once removed from the MOCVD chamber a native oxide will form on most films that must be removed prior to growth. Observations showed that the molten salt did not wet the seed crystal; this was originally thought to be due to the native oxide. Attempts to remove the oxide did not result in better wetting, however. A wetting agent was found and added to the melt to improve wetting characteristics. A methodology for separately removing the native oxide was developed and implemented. Unfortunately it was later discovered that the oxides in the hardware materials were likely re-contaminating the film surface, preventing deposition.

Seed holder design and fabrication. The seed holder must suspend the seed crystal upside down just underneath the surface of the molten salt while rotating at relatively high speeds. The seed must be as flush with the seed holder as possible to prevent disruptions in laminar flow at the seed surface. A recessed seed will result in lengthy diffusion distances for nutrients to the seed surface. It is desirable that the seed not fall out of or off of the seed holder during the run. It is also desirable to be able to quickly clean and reuse the seed holder in subsequent runs. Several designs were fabricated and tested and a design was settled upon, made out of 99.9% pure nickel. The nickel dissolves in the molten salt and was found on the seed surface. Also, the potential of the seed holder was found to drift during the experiment and must be stabilized. Several

schemes are available to eliminate these problems and will be addressed in terms of eliminating hardware-related impurities in task 2.1.

Seed crystal etching. The seed crystal was observed to etch rather than collect deposits in several of the runs. This is an encouraging initial result because etching is the opposite of growth—if the material will dissolve, it will grow, in most cases. Etching occurred in the early stages of the growth run attempt. The etching phenomenon was not well repeated in the duplicate reactor and the cause is still not well understood. There are two prevailing explanations. One is that impurities enhance the solubility of GaN in molten LiCl-KCl, while the other is that the equilibrium process from the reaction of lithium tetrachlorogallate and lithium nitride is highly favored to the left at the beginning of the growth run when the gallium and nitride ion compositions are effectively zero:

$$LiGaCl_4 + Li_3N \rightarrow GaN(s) + 4\ LiCl$$

Note that gallium ions injected into the molten salt are expected to react with the salt to form the alkali tetrachlorogallate species, and nitride ions similarly react with the salt to form the alkali nitride species. Understanding and controlling the etching will be important producing high quality growth and will continue in BP2.

Developing hardware components from materials that do not corrode in the electrolyte. As noted several places above, it became apparent that the level of corrosion of the hardware materials was a major contributing factor to growth/no growth once the first film appeared and was analyzed. In BP2, the hardware materials will be fabricated from non oxide-containing materials, and further electrolyte purification techniques will be developed.

The presence of a thin film containing both Ga and N is a significant positive accomplishment because it reveals that the hardware and solution chemistry is working—the ions are being produced and delivered to the surface. It is not surprising that the growth is inhibited by the impurities at the interface, the vast majority of which originate from the hardware. It is not difficult to change hardware components to new materials now that the design has been decided upon, although it entails some lead time in receiving the parts. In BP2, the new hardware materials will be fabricated and tested and the level of impurities in the electrolyte can be analyzed by measuring the impurity content in the growing film. Those specific impurities will be targeted for removal from the electrolyte. Once the interfering impurities (namely oxygen and nickel) are removed, gallium nitride is expected to deposit on the seed crystal surface.

Our work to date demonstrates that the gallium nitride process can be run continuously for multiple days without hardware failure, and that the process is functioning as expected from the electrochemical and mechanical perspectives. The new reactor materials are expected to be similarly robust. This capability to perform extended duration growth runs will make thick film growth possible in BP2.

<u>Accomplishments:</u>

- Timely delivery of MOCVD grown GaN, AlGaN, and AlN growth seeds from GIT.
- More than 50 runs made using the reactor 1 rotating seed process.

- Initial electrochemical measurements of N and Ga ion transport and concentrations complete.
- Implemented method for removing native oxide from seeds prior to ESG process.
- Modeled and tested improved hardware concepts such as seed holders, electrodes, and baffles.
- Demonstrated hardware configuration for rotating seed runs of long run duration (>10 hours).
- Detected film growth of ~ 0.5um layer on 10mm square GaN seed template containing Ga, N, and several other impurities originating from the reactor hardware.

Results:

Example electrochemical cyclic voltammogram (CV) data are shown below in Figure 7; a three-electrode system is typically used. The red curve is the background CV taken on the nickel working electrode (no N_2 gas flowing). The background is close to 0 mA and is considered very pure. In the absence of nitrogen gas flow, the peak on the left at ~-2.5V vs. Ag/AgCl is lithium deposition (negative current) and lithium metal re-oxidation, or stripping (positive current). Near -0.2V vs. Ag/AgCl is the oxidation and re-reduction of nickel metal from the nickel metal working electrode. Overlaid on these data are the gallium oxidation and reduction data at about -0.5V vs. Ag/AgCl, with gallium as the working electrode. The curve intersecting the x-axis at around -2.1V vs. Ag/AgCl is the nitrogen reduction (negative current) and nitride oxidation (positive current). To run an experiment, either the nitrogen or the gallium electrodes may be selected as the working electrode. The potential relative to the reference electrode is held constant at a select potential value for 2-54 hours. The seed crystal is immersed just below the melt and rotated between 60 and 400 rpm. After the experiment, the seed crystal is lifted from the melt, rinsed in DI water, and analyzed by visual inspection, optical microscopy, photoluminescence, alpha step profilometry, SEM, EDS, XPS, and/or SIMS and TEM.

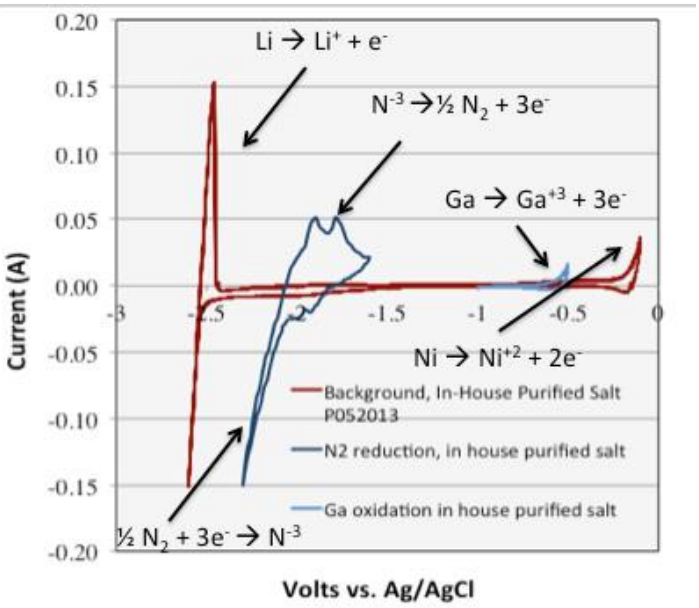

Figure 7: Cyclic Voltammogram

The following section describes results from the characterization of processed samples from reactor 1. The 10mm square growth seeds were prepared by Georgia Tech where they grow a GaN template by MOCVD on a 50mm sapphire substrate and then dice the sample into 10mm squares. A cross section of the most common template structure used in year 1 is shown in Figure 8. Additional seeds with varying top layers including AlGaN and AlN have been prepared and are in queue for testing.

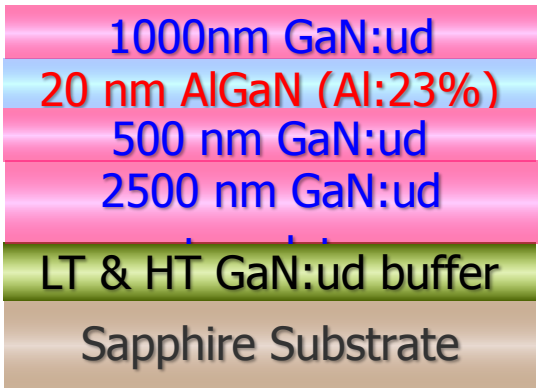

Figure 8: seed cross section

After ESG processing in reactor 1 the sample is examined visually in room light and under UV light. Under UV light there is trap in GaN layers that has yellow luminescence. In this way the sample can be quickly judged as to whether a GaN film is present on the sample. However, it does not differentiate between the GaN seed film and GaN added in ESG process, which is an advantage for the future testing planned for AlN and AlGaN seeds which do not exhibit yellow luminescence. An example image is shown below in Figure 9. Note the absence of yellow emission around the sample edge region likely indicates GaN etching.

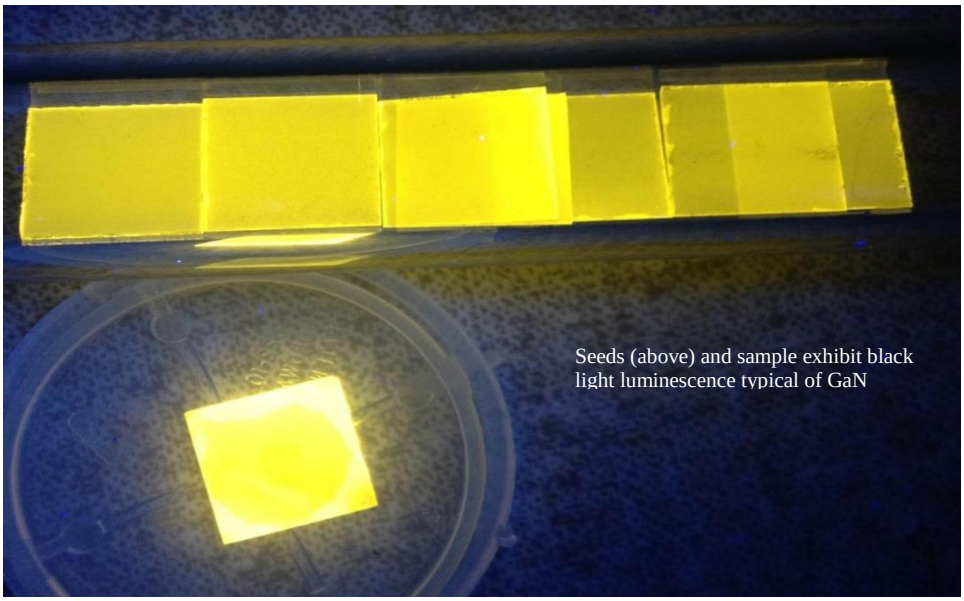

Figure 9: UV light inspection of processed sample vs seeds

A comparison of the photoluminescence of an unprocessed seed and sample from ESG processing is made to assess the GaN emission intensity and wavelength as shown in Figures 10a and 10b. Compared with the seed (10a), the PL emission wavelength for the processed sample (10b) is approximately the same, the intensity is lower, and the width of the emission is approximately the same. The results indicate that GaN is still present at the same quality and is not measurably thicker than original seed layer. If there was a significant thickness addition from the ESG process, the expectation for PL would be some changes to the GaN emission line due to different properties of the ESG film such as broadening, intensity change, and perhaps also a shift in wavelength.

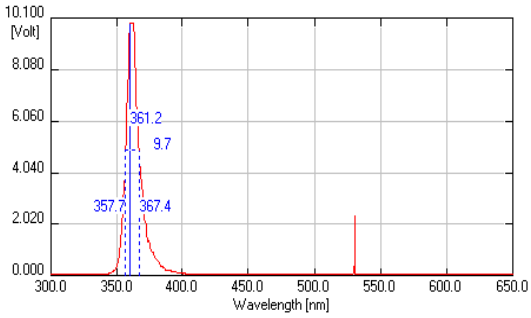

Figure 10a: PL of seed

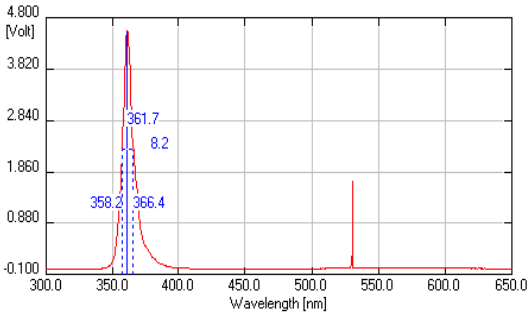

Figure 10b: PL of processed sample

In order to visualize what the ESG process has added to the seed template a cross sectional analysis was performed using focused ion beam milling (FIB) and transmission electron microscopy (TEM). The attached cross section (Figure 11) shows an amorphous film of a few tenths of a micron in thickness on the GaN seed template was added by the ESG process.

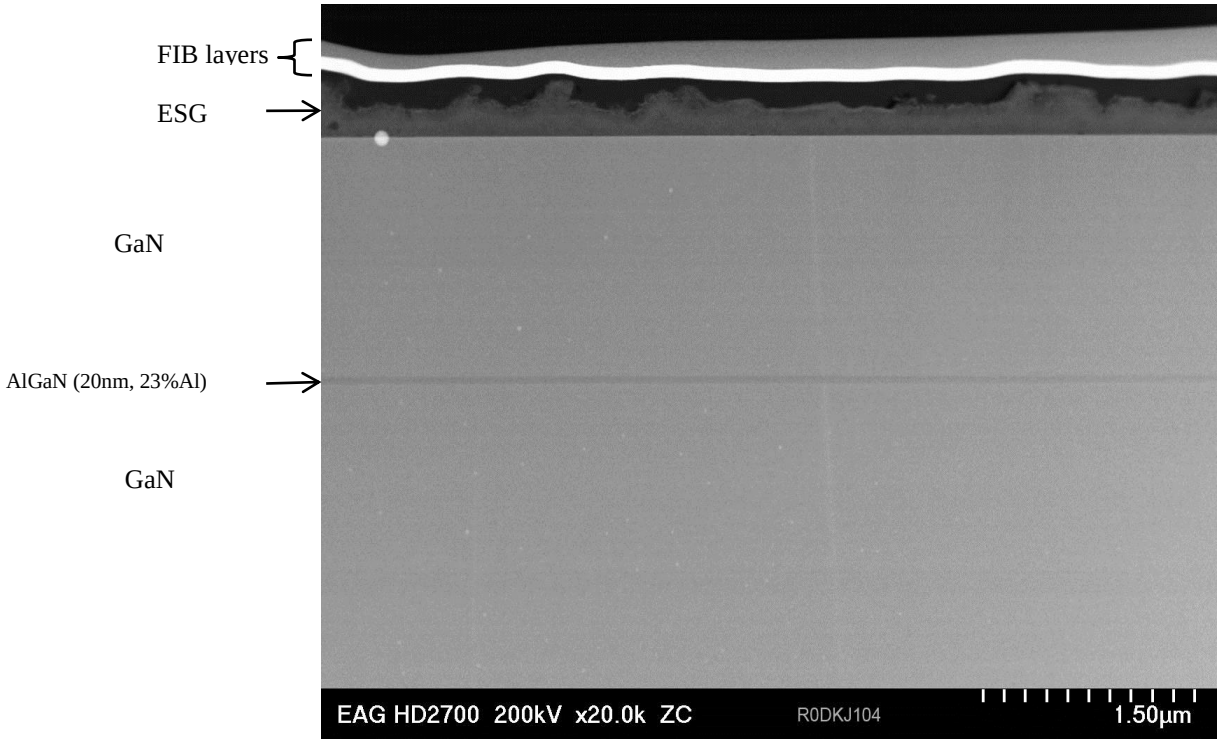

Figure 11: TEM cross section of processed sample

The composition of the ESG film has been measured by both XPS and EDS (Figure 12), and compared with the seed template. The good news is that both methods detect Ga and N in the ESG film. However, a very high level of oxygen is detected along with other impurities from the reactor hardware including Ni from the N_2 electrode, Al from the alumina parts, and Si from the silica parts. The oxygen is coming from the alumina and silica parts and is likely reacting on the seed surface to form an oxide that prevents crystalline growth of a GaN film. The sources of oxygen from the reactor will be eliminated in future experiments by changing out the materials in the hardware to oxygen-free reactor materials.

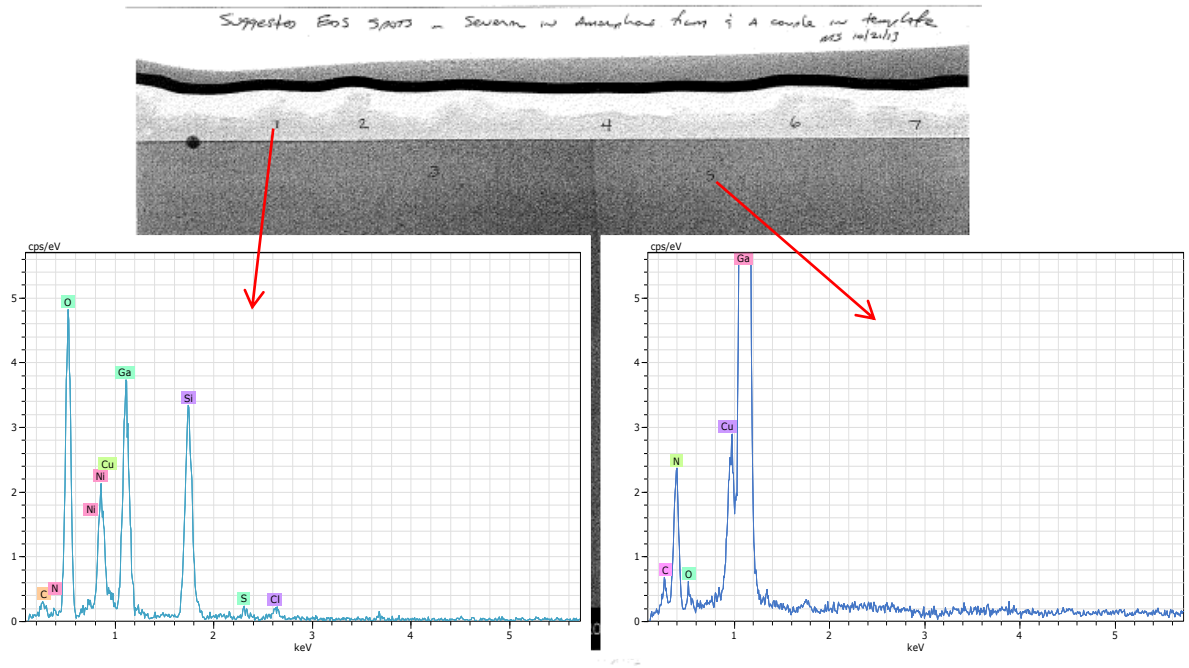

Figure 12: EDS on ESG film vs GaN template

D.a.iii: Task 1.3, Model the flow kinetics, transport of nitrogen and gallium ions, and growth of GaN film in molten salt.

The purpose of this task was to develop a model for the growth of a GaN film in molten salt. The model has been developed and includes fluid flow induced by a rotating seed in the molten salt, values for Ga and N ion diffusion and solubility, and reaction chemistry including electrode surface reaction where ions are generated, bulk reaction, bulk crystallization, and growth on seed. The output of the model is an effective deposition rate at the seed. The model has been used in the design of improved hardware configurations for reactor 1, the design of reactor 2, and for process parameter sensitivity analysis.

<u>Accomplishments:</u>

- Developed fluid flow model describing Reactor 1 configuration.
- Added reaction chemistry to Reactor 1 model and performed film growth rate sensitivity simulations to seed rotation, bulk reaction rate, and precipitation rates.

- Used model to evaluate Reactor 1 hardware improvement ideas (baffle) and to design Reactor 2 hardware configuration (funnel).

Results:

Based on the drawings and nominal process conditions for reactor 1, a fluid flow model was developed that describes the forced convection flow in the molten salt induced by the rotating seed disk. Figure 13 shows the fluid flow model cross section with rising flow from the center of the vessel induced by seed rotation (middle top), falling flow along the sides, and the influence of the Ga (left) and N_2 (right) electrodes on the flow pattern.

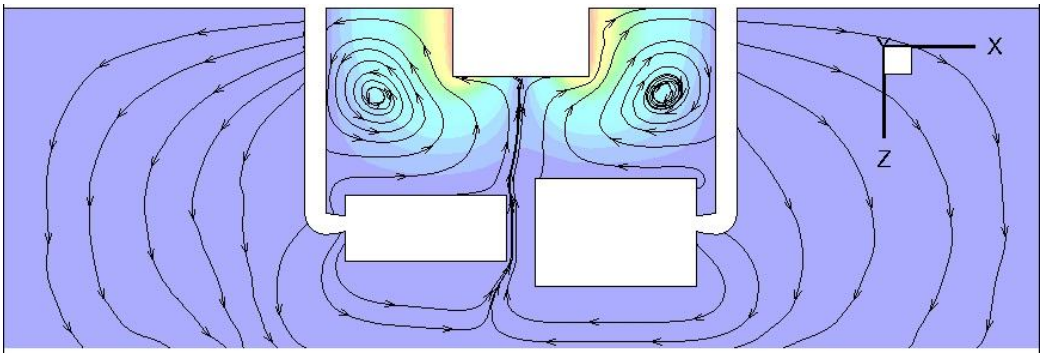

Figure 13: Cross section view of fluid flow pattern through reactor electrodes

Reaction chemistry was added to the model. It assumes ion generation at the electrodes in proportion to the applied current, a reaction rate between Ga and N, a sticking coefficient for the Ga and N at the seed surface, and a bulk precipitation parameter dependent on the supersaturation of the precursors in the salt. The reaction chemistry equations are shown in Figure 14.

$$Ga^{3+} + N^{3-} \rightarrow GaN$$
$$r = k(T)[Ga^{3+}]^1[N^{3-}]^1$$

Bulk formation

$$\frac{zF}{M_{Ga}} \int_{Ga} \left(q_{Ga^{3+}} \cdot \mathbf{n}\right) dS = I$$

z : valence $(=3)$

F : Faraday constant

$q_{Ga^{3+}}$: Mass flux of galium ions

M_{Ga} : Molar mass

I : Circuit current

Current measurement

$$[GaN]_{seed}^{surf} = (1-\beta)[GaN]_{seed}^{bulk}$$

β : Sticking coefficient

Surface precipitation

$$GaN \rightarrow GaN(p)$$
$$r = k_p(T)\left([Ga]-[Ga]_{sat}\right)$$

Bulk precipitation

Figure 14: reaction equations in model

The nominal reactor 1 rotating seed configuration model is described here. It is first simulated with zero current to obtain the fluid flow field. At time zero, an external current of 200ma is imposed on the two electrodes while everything else is kept fixed. The deposition rate of GaN on the seed is then monitored and the integral of the flux over the entire seed surface is reported in terms of an equivalent current. In this case the simulation was run with a low bulk reaction rate assumption (R=0.01), no bulk precipitation (P=0), and a sticking coefficient of one (B=1). Figure 15 shows the GaN concentration to be well mixed in the melt with a concentration gradient near the seed where the GaN is consumed into film growth. The seed rotation rate determines the reactant mixing in the bulk with higher rotation rates reaching steady state in shorter time period. Figure 16 is the simulated GaN deposition rate on the seed comparing fast and slow seed rotation rates. For the parameters chosen in this simulation the limiting phenomena is the mixing in the bulk. At longer times the solution is well mixed in the bulk and a concentration gradient is present near the seed.

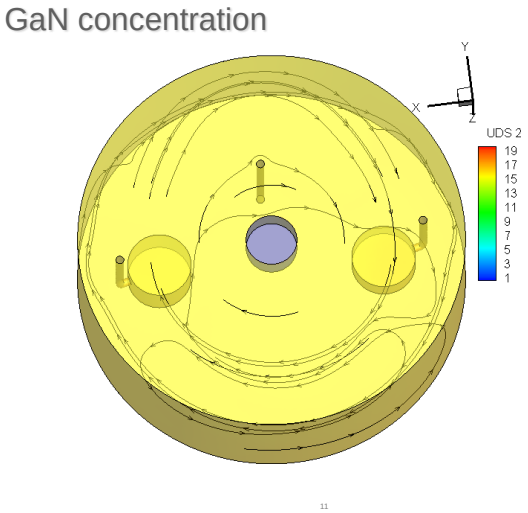

Figure 15: GaN concentration in the melt when well mixed

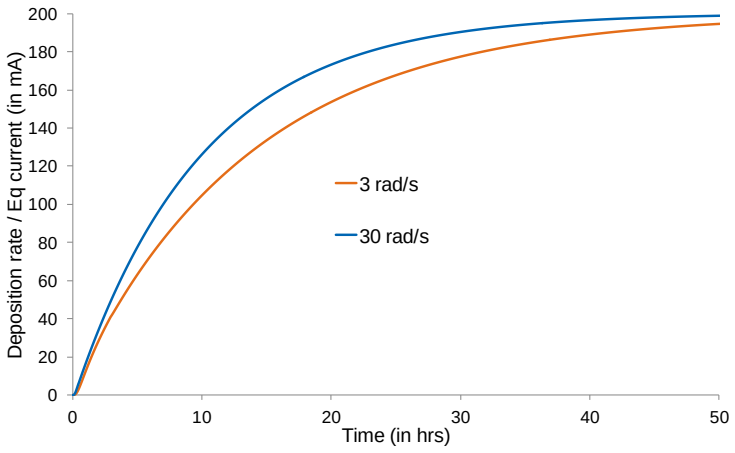

Figure 16: GaN deposition rate with seed rotation rate

One of the technical challenges with the ESG process is to limit the bulk reaction of the gallium and nitride ion precursors. Excessive bulk reaction in the form of precipitates will limit the species available for growth on the seed. An idea for reducing the bulk reaction is to use a baffle as a barrier between the gallium and nitrogen electrodes, thereby directing the flow of the ions to the seed rotating seed. Modeling was performed to determine the impact of the baffle on the flow patterns and estimated GaN deposition rate on the seed. The impact of spacing between the rotating seed and the top of the baffle was modeled for the "high" barrier case with small spacing and the "low" barrier case with large spacing. The concept is shown in figure 17 for the high barrier case.

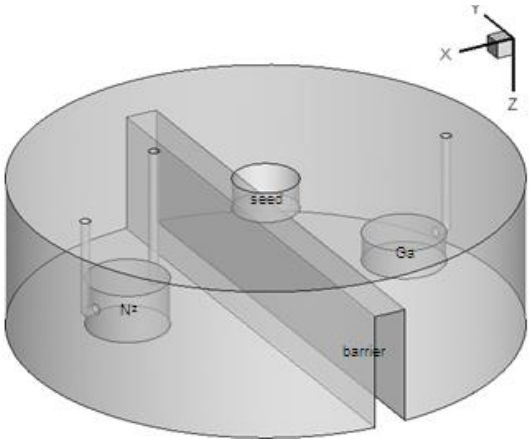

Figure 17: high barrier case

Figures 18a and 18b show the flow streamlines for the high and low barrier cases. In the case of the high barrier with small spacing to the rotating seed the reactants are drawn to the proximity of the rotating seed where it is hoped they will have a much higher probability to stick and react on the seed to form the GaN film. In the low barrier case with large spacing to the seed the flow lines are similar to having no barrier at all.

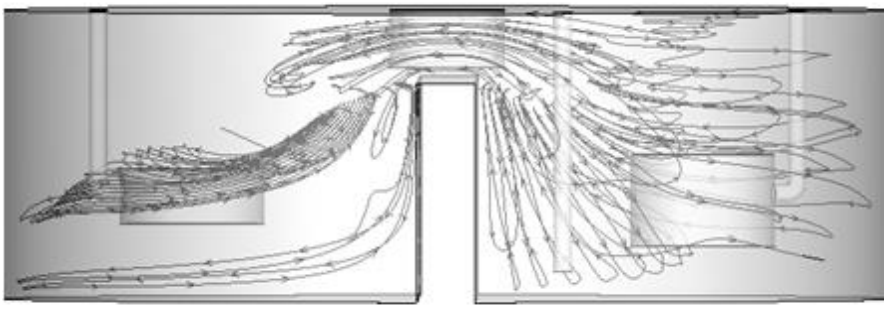

Figure 18a: high barrier case

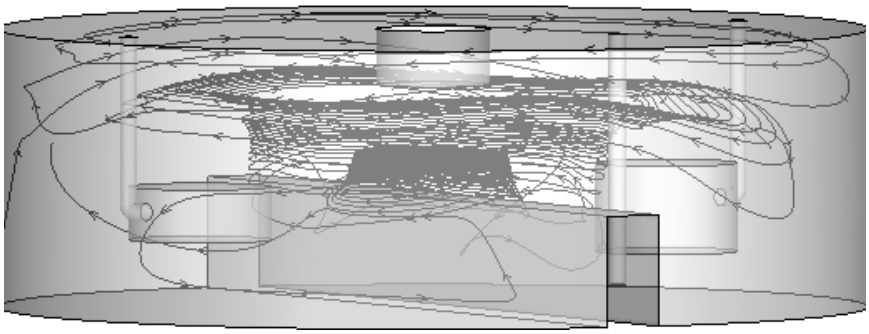

Figure 18b: low barrier case

Estimates indicate that the high barrier case should enable higher GaN deposition rate than the low barrier or no barrier cases. Comparison calculations are shown in figure 19. Based on these results the initial baffles were fabricated for reactor 1 testing from Al_2O_3 to a height that enables evaluation of the high barrier case.

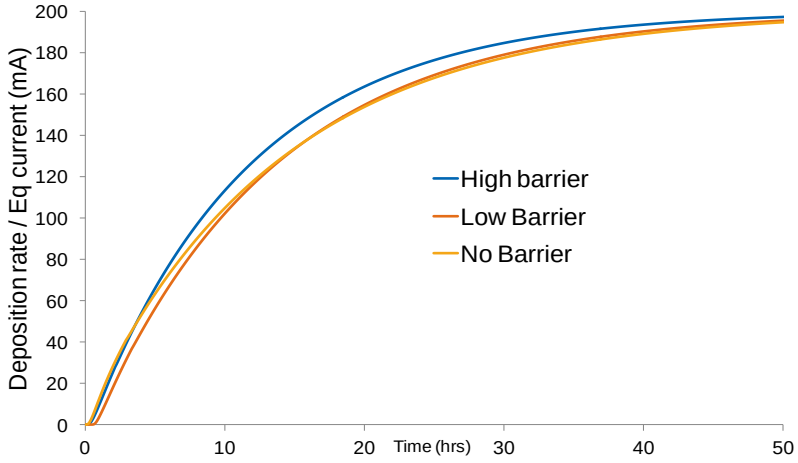

Figure 19: GaN deposition rate for barrier vs no barrier

A more elaborate design concept to optimize the zone of interaction between the gallium and nitrogen ions near the rotating seed was conceived. The concept is for an inverted funnel shaped growth chamber that directs the rotating seed induced flow of nitrogen ions, which are generated near the bottom of the chamber, up and over a gallium source cup place near the rotating seed. A conceptual illustration of the concept is shown in figure 20.

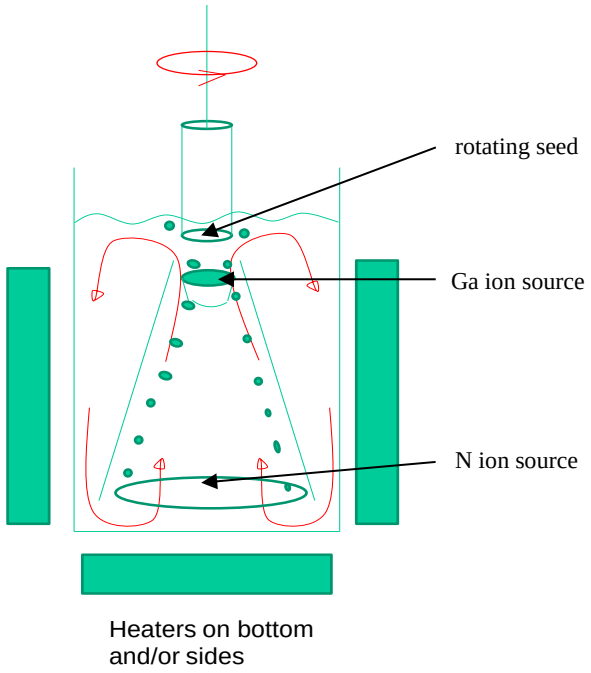

Figure 20: funnel concept

Modeling of the funnel concept shows the rotating seed drives the flow of the salt over the nitrogen electrode and then up across the surface of the gallium electrode before coming into contact with the seed. The modeled flow lines are illustrated in figure 21. The funnel hardware has been incorporated into the Reactor 2 design and fixtures have been made for testing at both the 10mm and 50mm seed size.

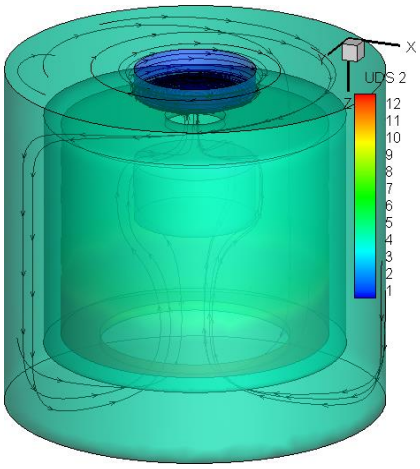

Figure 21: flow lines for funnel concept

To date, there are not sufficient experimental results to fully validate the reaction models. Sensitivity analysis has been performed using the model and will continue in order to guide the design of process experiments. An example case is shown here for the configuration of Figure 17b (low barrier case) with an electrode current of 200ma, reaction rate (R) of 0.01, bulk precipitation rate (P) of 0.01, and seed sticking coefficient (B) of 1. Rotation rate was varied to

determine the impact of mixing on the equivalent deposition rate. With this parameter combination the higher mixing induced by higher rotation rate reaches steady state deposition rate more quickly, but because of the increased mixing there is less GaN film deposition due to higher parasitic precipitation. The overall conversion efficiency from electrode current to deposition current for this parameter set is about 1%.

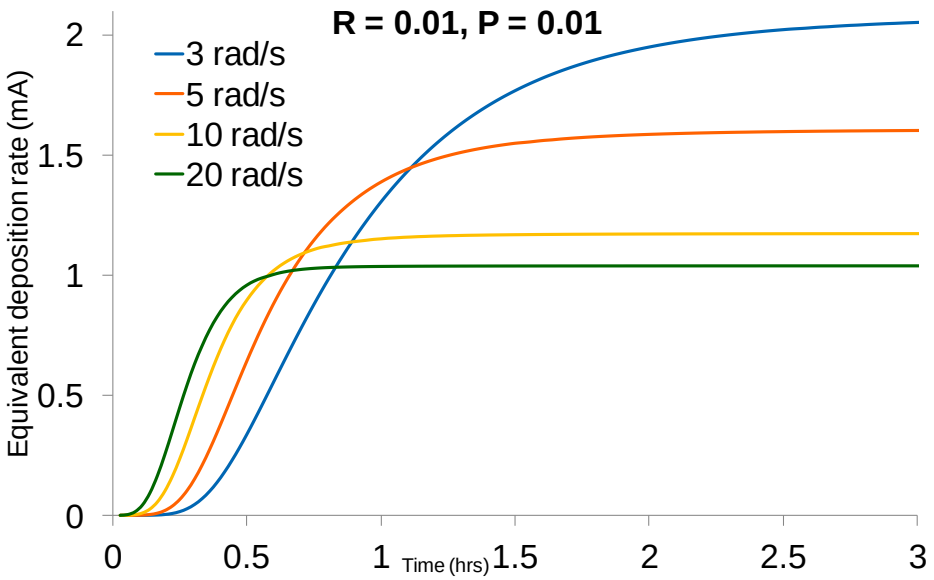

Figure 22: deposition rate sensitivity

Diffusion constants and concentrations of gallium trichloride and lithium nitride were measured by electrochemical techniques. The value of the diffusion constant for GaCl3 was 2.5E-04 cm^2/s and the value for lithium nitride was 1.8E-05 cm^2/s. The nitride value agrees well with the measurement reported in the literature by Ito and Goto (*J. Nuc. Mat.* **344** (2005) 128-135).

D.a.iv: Task 1.4, Establish rate kinetics for GaN growth to 10mm diameter.

The tasks were performed and significant experimental learning was achieved. Given the learning from task 1.2, this task will be incorporated in task 2.1. The growth kinetics will be determined once the interfering impurities at the seed crystal surface are reduced.

D.a.v: Task 1.5, Determine Reactor 1 process window for reproducible GaN growth.

Several experiments were performed during BP 1 that controlled electrode and fluid dynamics behavior. While this task is not 100% complete, much progress was made on electrode design and fabrication techniques, electrochemical techniques used during the growth experiment, and on reactor hardware that improved the run-to-run reproducibility. The confounding factor is the impurities present from the reactor hardware materials that inhibit crystalline growth at the seed surface. The work will be carried over into tasks 2.3-2.4 where we expect to achieve thick crystalline film growth with a lower impurity process solution and the expected growth efficiency improvements from reactor 2 hardware.

D.a.vi: Task 1.6, Design and build Reactor 2 for 50mm diameter GaN film growth.

The reactor 2 design approach was to produce a scaled up version of reactor 1 with a larger crucible / heater that will have the capability to use 50mm diameter growth seeds. The reactor 2 design drawings were finalized around May 15, 2013 and part requisitions were released. Parts started arriving in June and the reactor completed assembly in early September. Two reactor 2 units were fabricated, one with 10mm seed capability was delivered to Sandia during a visit on September 17-19. The other unit with 50mm seed size capability is being installed in the glove box at SunEdison. The hardware assembly includes motors to drive the up/down translation and the rotating seed. The assembly that is lowered into the molten salt will provide reproducible positioning of the seed and electrodes, and will permit a variety of electrode configurations to be tested.

Accomplishments:

- Completed SunEdison lab renovation on schedule and under budget.
- Completed Reactor 2 design, assembly, and installation.
- Fabricated two Reactor 2 configurations within year 1 budget to enable parallel testing of hardware at Sandia and SunEdison in year 2 project tasks 2.3 and 2.4.

Figure 23 shows the design drawing of reactor 2 as viewed from the front of the SunEdison glove box and Figure 24 shows the parts prior to installation in glove box. The heater / crucible assembly hangs below the glove box table reducing the temperature rise in the glove box and providing additional vertical clearance.

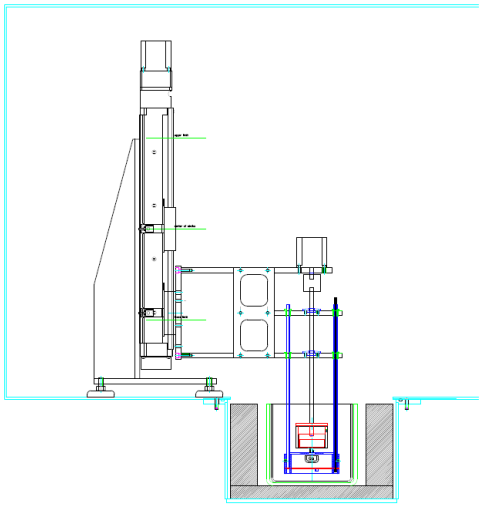

Figure 23: Reactor 2 drawing

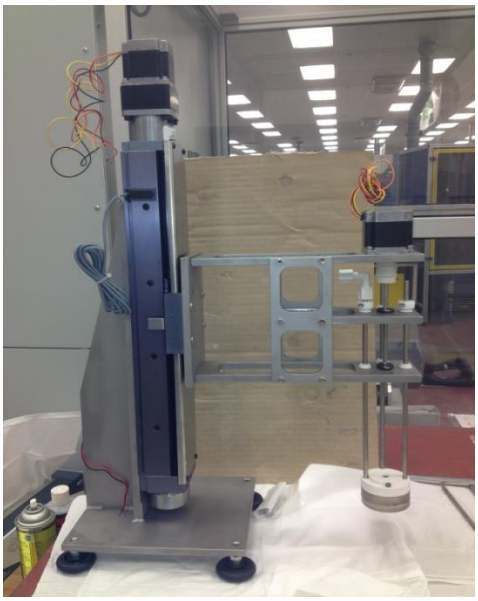

Figure 24: Reactor 2 components outside glove box

D.a.vii: Task 1.7, Project Management and Reporting

Accomplishments:

- Met the project reporting and invoicing requirements.
- Project conducted within original lead company negotiated budget and cost share commitment.
- Team members presented the project at Spring MRS 2013 (April), ICNS 2013 (August), and International Bulk Nitride Semiconductor Workshop 2013 (September).

D.a.viii: Progress towards BP1 go / no go decision criteria

- Demonstrate reproducible (3 runs of same process with same results) seeded GaN film growth in reactor 1 to a diameter of 10mm and a thickness of at least 100um.

As discussed in progress report section this criteria has not been met in the first budget period. Film growth of < 1um has been detected. The film is high in unintended impurities that are interfering with templated crystalline film growth in the ESG process, particularly oxygen coming from alumina and silica parts. The project team needs the opportunity to execute task 2.1 to significantly reduce impurity levels added from the process. When combined with the expected improvement in the efficiency of reactor 2 hardware in tasks 2.3 & 2.4, significant barriers will have been removed towards the 100um templated film growth. The project team proposes to make 100um film growth at 50mm substrate diameter the BP2 criteria.

The original approach at the outset of the project was to use readily available, inexpensive hardware component materials for development purposes with full knowledge that they would contribute some contamination to the growing crystal. It was not believed at the outset that those impurities would actually prevent growth from occurring. However, toward the end of BP1, as the experiments became much more reproducible and the duration was extended to days, the impurities introduced into the electrolyte as a result of the dissolution of these hardware materials over the course of the long experiments does in fact substantially interfere with the growth. The oxygen impurity levels in the as-received in house purified electrolyte are expected to be negligible compared to the observed impurity levels in the grown films as evidenced in other parallel battery development efforts using this electrolyte. The high levels of nickel present indicate a substantial amount of dissolution of the seed holder. The nickel dissolution is straightforward to eliminate (we can bias the nickel seed holder negative so that it is anodically protected), but the alumina and Pyrex require purchasing and testing of new hardware materials. Experiments are planned with at least two candidate materials in the early part of BP2.

- Demonstrate GaN films with dislocation density matched to the seed template and background carrier concentration less than $10^{19}cm^{-3}$.

For the same reasons cited above this criteria has not been met in the first budget period. The project team needs the opportunity to execute task 2.1 to significantly reduce impurity levels added from the process. When combined with the expected improved efficiency of reactor 2 hardware in tasks 2.3 & 2.4 it is expected that the project team will have removed significant barriers to the templated film growth and the background carrier concentration target.

- Complete the design and assembly of reactor 2.

Complete.

D.b: Budget Period 1 Extension, August 2014 – August 2015

D.b.i: Task 1.8, Demonstrate crystalline GaN film growth on GaN seed crystal

The Go / No Go requirement for the budget period 1 extension was to grow at least 0.5um of crystalline GaN film on a GaN seed in the laboratory scale reactor. Results for the first budget period showed that is necessary to eliminate oxygen contamination and oxide interferences with crystalline GaN film growth. The sub-tasks in this budget period extension were; 1) procure the highest available purity, lowest oxygen salt for testing, 2) install and evaluate low oxygen crucible material in reactor, 3) perform growth experiments combining the low oxygen system and optimized seed oxide removal, and 4) characterize the GaN films using UV inspection, profilometry, XRD, optical microscopy and SEM, photoluminescence, XPS, SIMS, and TEM.

A series of process experiments were performed from September 2014 through March 2015. The sequence started with confirmation of the prior baseline process / results using in-house purified salt and the existing reactor hardware configuration. Process experiments were then

performed with incremental changes to high purity salt, SiC hardware, and alternate electrode configurations. A table summarizing the experimental conditions is attached below.

Sample IDs	Process Conditions Salt/crucible/electrode/reference IHP= in-house purified salt UHP= ultra high purity from Aldrich
090914, 091214, 091814	IHP/Al2O3/Al2O3/glass (baseline tests)
110414	UHP/Al2O3/Al2O3/LiSb
111814	IHP/Al2O3/Al2O3/LiSb
122614	UHP/SiC/Ni wire/LiSb
010515	UHP/SiC/Ni tube+wire/LiSb
011615	UHP/SiC/Ni tube+foam/LiSb
021015	UHP/SiC/Ni foam/LiSb
021315	UHP/SiC/double Ga/Li3N/LiSb
021715	UHP/SiC/double Ga/Li3N/LiSb
021915	UHP/SiC/double Ga/Li3N/LiSb
022715 (repeat 021715)	UHP/SiC/double Ga/Li3N/LiSb

Table 2: Process condition summary

In these experiments a GaN seed crystal grown by MOCVD was used. Figure 25 below shows a drawing of the cross section of the layer stack for the seed crystal and the processed sample.

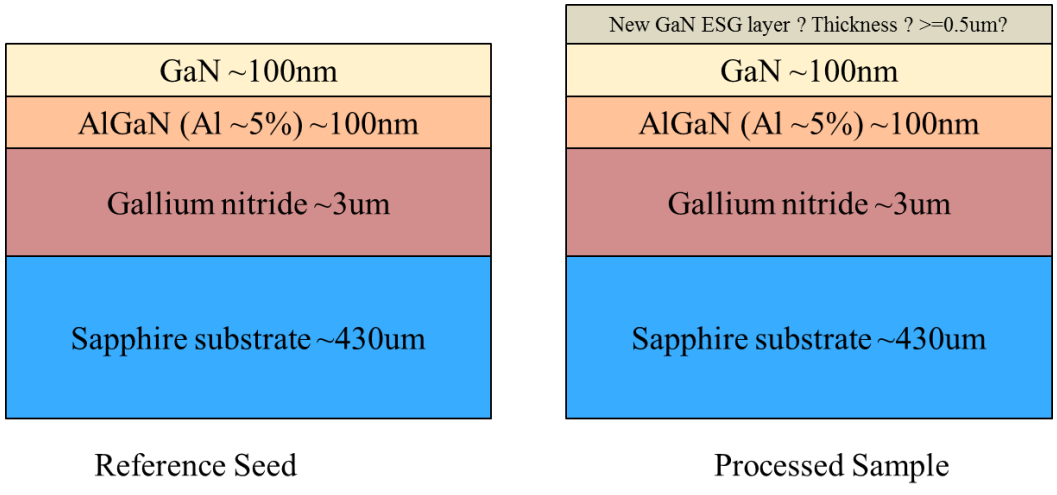

Figure 25: cross section schematics

All experimental samples were examined under UV light for GaN's characteristic yellow luminescence, which confirmed the surface composition after growth to be GaN, either the original seed layer or new growth. Optical microscopy and SEM were used to examine the

sample surface after ESG processing. Example comparison SEM images in Figure 26 show that the relatively smooth sample surface of the seed is changed by the ESG processing. The images do not confirm whether this change is due to GaN film growth or etching of the GaN seed. The lower right image from 150217 has a surface morphology that could be characteristic of either growth or etching.

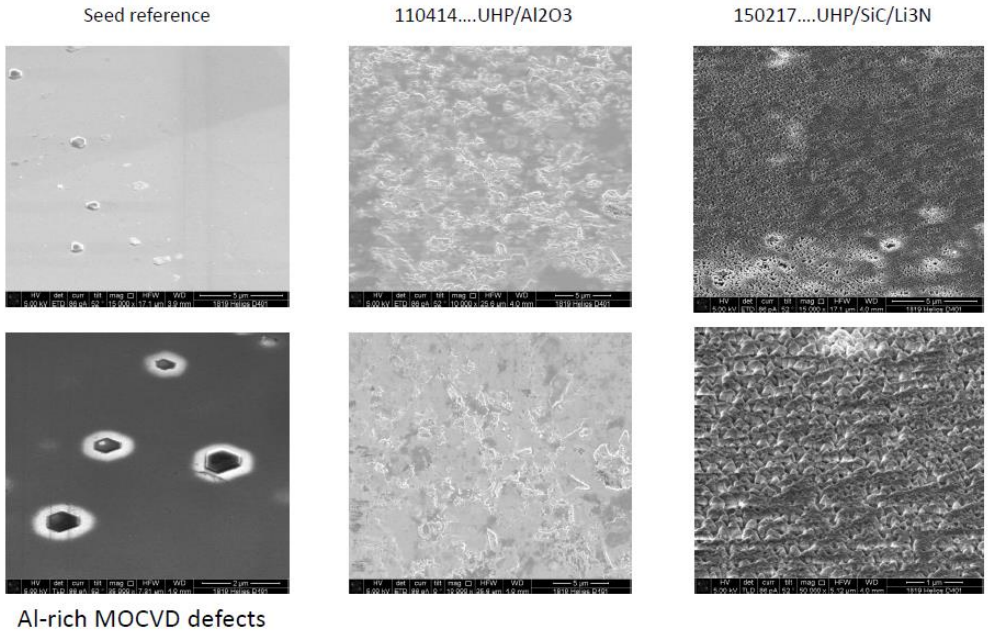

Figure 26

All the experimental samples were measured by XPS to determine the elemental composition of the sample surface in comparison with the seed reference. Figure 27 is a line graph showing the atomic percentage of Ga, N, and O for each experimental sample versus the seed reference is shown below. Although XPS confirms the presence of Ga and N on all experimental samples, none matches the result for the non-processed seed sample. XPS also shows 2-3X higher oxygen composition on all processed samples versus the seed reference. The XPS does not provide confirmation that a new layer has been grown.

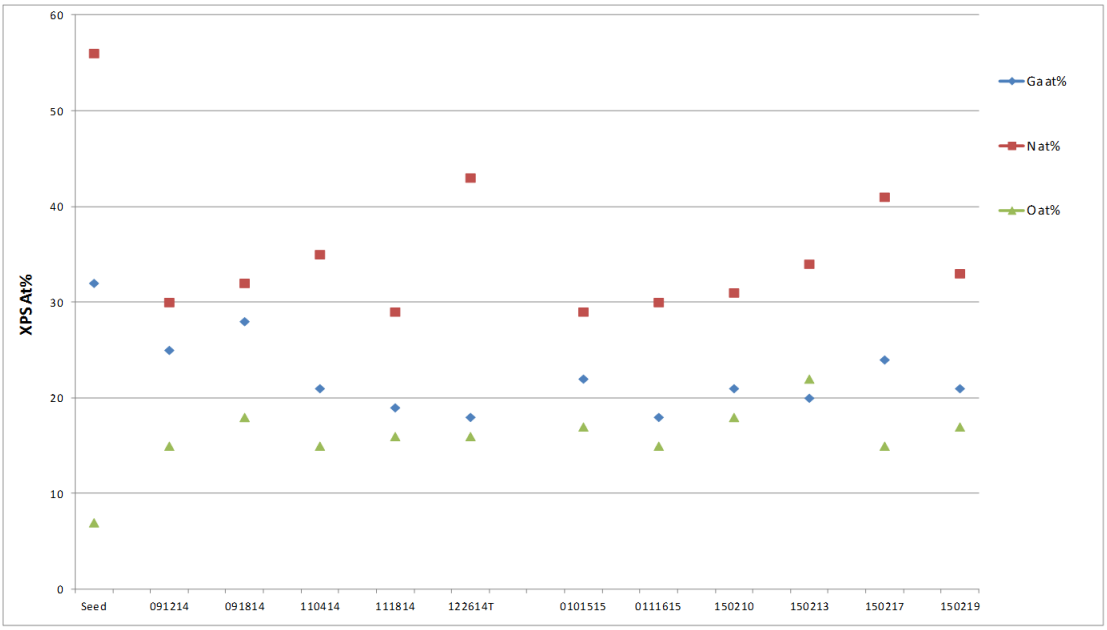

Figure 27: line graph of XPS compositions

XRD measurements were made to determine the GaN crystalline film structure. Comparisons were made between the (002) GaN peak from the seed and the processed samples. An overlay plot is shown in Figure 28 below. Shoulders were detected in the processed samples which could indicate that an additional crystalline layer of varying thickness between the samples has been added, possibly with a slight change in lattice constant or elemental composition of an additional layer. To further confirm whether a new layer had been added the most promising samples were chosen for SEM and TEM cross sections.

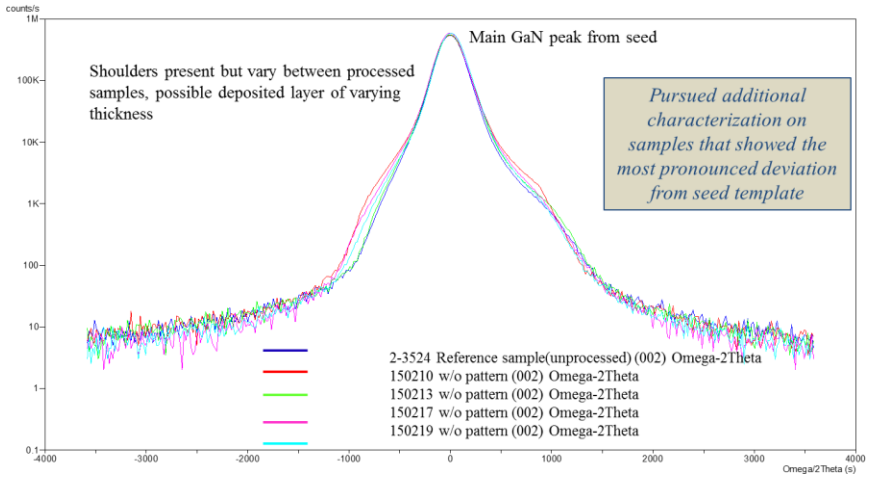

Figure 28: XRD seed vs processed sample

SEM cross sections were prepared on two samples, 150217 and 110414, using focused ion beam etching. The total thickness of the layer stack was then measured as shown in the images below in Figure 29. This includes the original seed layer stack plus whatever additional film was added. As shown in the earlier cross sectional diagram, the original MOCVD layer stack on sapphire substrate was estimated to be approximately 3.2um by the seed provider. The SEM cross section for the reference sample showed thickness of

approximately 3.6um. The processed samples have total thicknesses comparable to the seed reference sample. Can conclude from this measurement that the processing did not remove the entire seed layer stack through etching nor did it add measurable additional GaN thickness. The magnification of the SEM cross section is not sufficient to detect whether a very thin layer (ca. nanometers) has been grown.

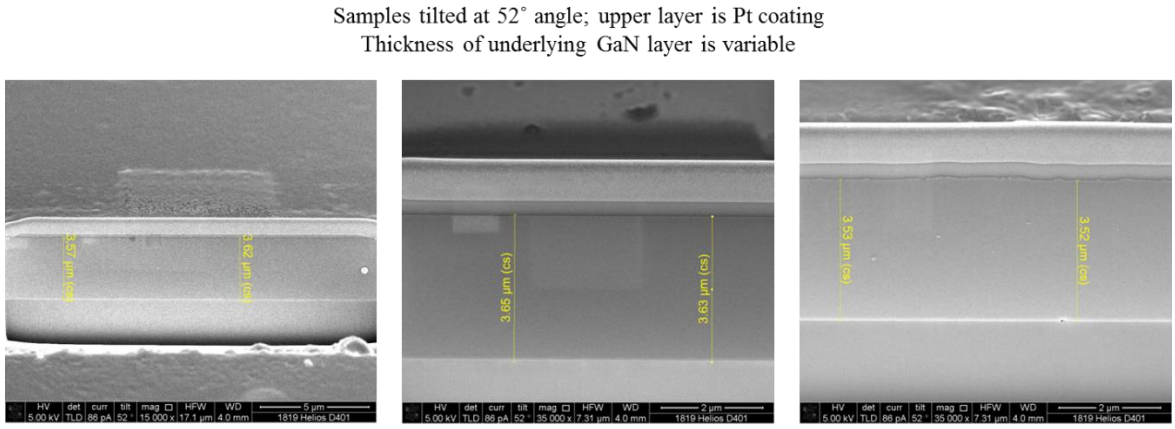

Figure 29: SEM cross sections

TEM cross sections were prepared on two samples, 150217 and 110414, to increase the resolution at the sample surface. The TEM on sample 150217 (Figure 30) shows that the top 100nm GaN layer on the seed has been partially etched away, possibly by metallic lithium. No new growth was detected on this sample.

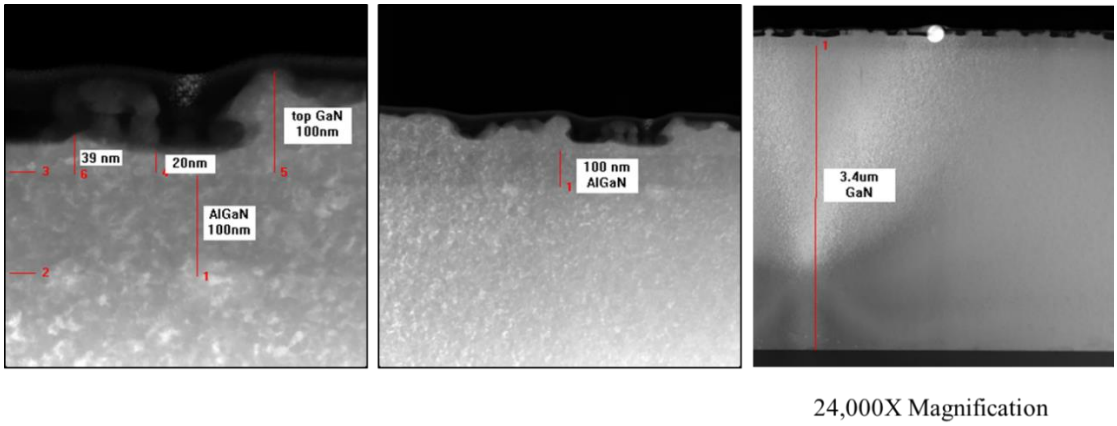

Figure 30: TEM cross sections

The TEM of sample 1101414 in Figure 31 shows some evidence of cubic GaN deposition from the ESG process on the hexagonal GaN seed. The thickness of ESG deposition is less than 10nm. The high resolution TEM image in Figure 32 further shows the layer stacking in the top few atomic layers, illustrating the difference between the cubic structure of the ESG GaN and the underlying hexagonal MOCVD GaN. We speculate that the difference in crystal structure could be related to the much lower GaN growth temperature (400-500C) in

ESG process as compared with the MOCVD process (1000C). It's possible that growing the ESG film at higher temperature may change the crystalline structure from cubic to hexagonal.

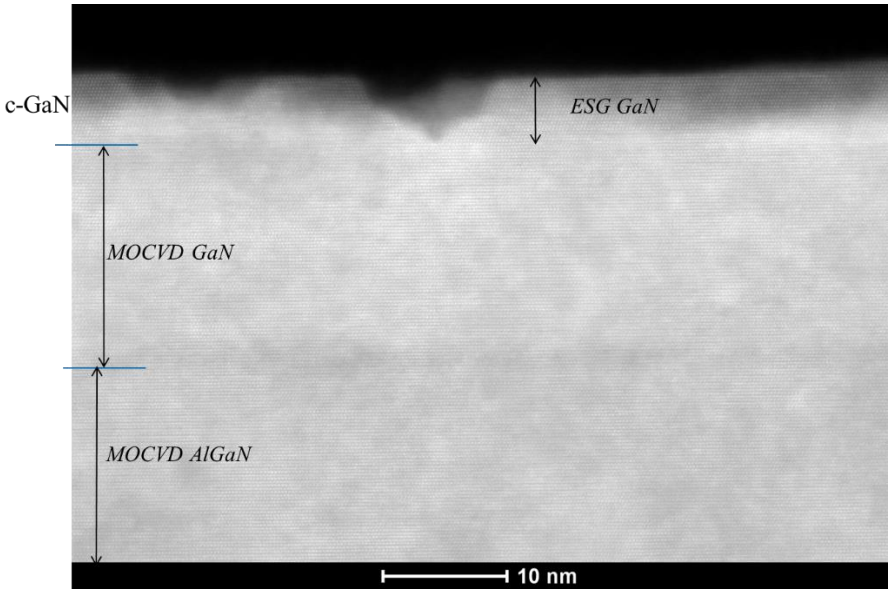

Figure 31: TEM cross section

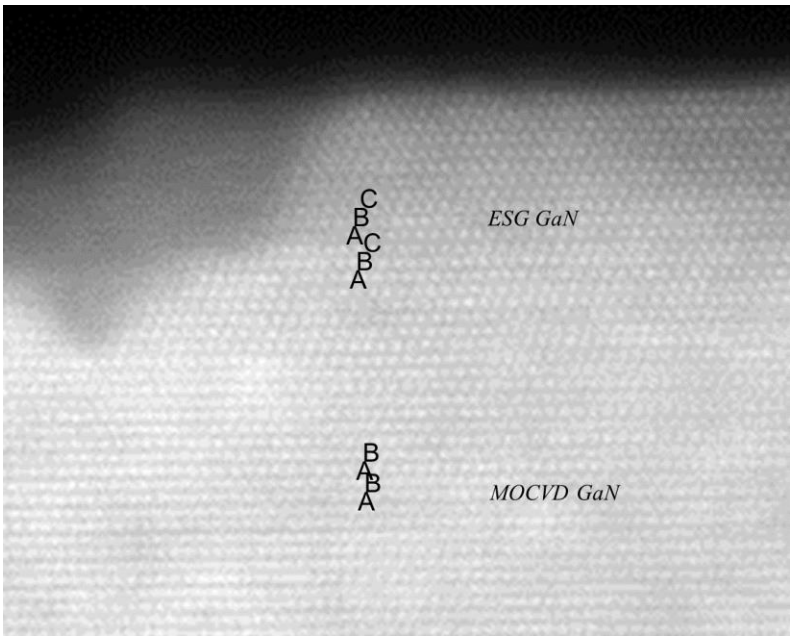

Figure 32: TEM cross section

D.b.ii: Progress towards BP1 extension go / no go decision criteria

The budget period 1 extension Go / No Go of > 0.5um crystalline GaN growth was not met. The project team concluded that there was not a clear path to meeting the original project goal of thick, high quality GaN layers at high growth rate over large surface areas. The

project team held a detailed project review on July 21, 2015 and informed DOE/AMO project managers of the intent to stop the project.

E: Benefits Assessment

The project did not result in a path to commercialization of Electrochemical Solution Growth of GaN. No benefits compared to existing GaN growth technologies can be claimed or reported.

F: Commercialization

The barriers to thick, high quality GaN growth on a seed have been discussed in the results section. These prevent commercialization of the process in its present form.

G: Accomplishments

The project did not deliver on the main objective of thick, high quality GaN growth on a seed. However, several successes can be reported related to the project tasks including the demonstration of long-term reduction of nitrogen gas in the electrochemical solution, successful implementation of hardware capable of long duration process cycles resistant to high temperature and corrosive salt, and the deposition of a very thin cubic-GaN film on the seed crystal. Models were developed to describe the process and to support process / equipment design concepts and experimental evaluations. The ESG technology concept was presented at the Materials Research Society Spring 2013 meeting, the International Conference on Nitride Semiconductors in August 2013, and at the International Bulk Nitride Semiconductor Workshop in September 2013.

H: Conclusions

GaN growth by the ESG method was limited by competing reactions including etching of the seed crystal and the strong reaction of Ga and N species in the salt solution prior to reaching the seed surface. Significant effort was spent on reducing the unwanted impurities such as oxygen from the hardware and process system. In retrospect, the project should have been started with the highest purity salt instead of in-house purified salt, and with the highest purity hardware. Significant process and equipment development are needed to overcome the competing bulk nucleation and surface etching reactions preventing commercially viable film growth. The underpotential deposition of lithium metal (from the KCl-LiCl salt) in the presence of gallium is likely responsible for the competing etching mechanism. It's possible to eliminate lithium from the system by moving to a KCl-CsCl eutectic which would also operate at a higher temperature (~ 650C) and could change the film crystal structure from cubic to hexagonal. The change in salt would necessitate a new starting point for the hardware configuration and process development.

I: Recommendations

Future efforts to develop ESG growth of GaN should be conducted at the basic science level instead of as a manufacturing development project.

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