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Atmospheric Pressure Growth of Bulk GaN for Substrates for High Temperature Electronics and Optoelectronics

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Abstract

Gallium nitride is a promising material for numerous optoelectronic and high power, high frequency, and high temperature applications (e.g., synthetic aperture radar, chem.-bio sensing, utility power switching, down-hole sensors, water purification, solar-blind detectors, etc.). While many GaN-based opto/electronic devices have been demonstrated, all applications that require high power operation suffer in performance and reliability from the lack of native substrates. The advent of a scalable, manufacturable, and affordable process for growth of bulk GaN for substrates would greatly advance these technologies. Melt growth is impractical as it requires temperatures >1600˚C and pressures >45,000 atmospheres, and is kinetically slow. A novel materials synthesis technique is described that takes place in a molten salt at atmospheric pressure. The salt is a relatively good solvent for molecular GaN and an excellent solvent for its ionic precursors, which can be continuously created electrochemically, thus enabling boule growth. This flexible, unique, and interdisciplinary approach solves the kinetic, thermodynamic, scalability, cost, and manufacturability issues inherent in alternative methods. Electrochemical growth of gallium nitride crystals at atmospheric pressure at 450°C has been demonstrated, and options are discussed for improving and extending the technique to production of large area boules.

Key words: bulk nitride growth, molten salt, nitrogen gas reduction

1.0 Introduction

Gallium nitride is a wide bandgap semiconductor (E_g =3.45 eV) that has the potential to provide robust, reliable high power, high frequency electronic devices in high temperature and/or chemically aggressive environments, such as down-hole power applications, hybrid and electric vehicles, synthetic aperture radar. GaN is also an important optoelectronic material for solid-state lighting and ultraviolet photodetectors. Its wider bandgap results in high electric field breakdown strength (3.3 MV/cm vs. 2.0 MV/cm for SiC), which may make it useful for power switching applications.[1]

However, widespread implementation of gallium nitride-based devices is stifled by, amongst other things, poor material quality due to the lack of native substrate. Current technology employs silicon carbide or sapphire as the substrates on which to grow GaN device layers heteroepitaxially, resulting in high dislocation densities (10^8 -10^9 cm^{-2}). Various dislocation filtering schemes are employed to reduce the dislocation densities in the highest-quality devices, but are limited to about 10^7 cm^{-2}. Dislocation densities are required to be below 10^5 cm^{-2} for robust, efficient, long-lived devices.

The best way to improve the material quality is to grow epitaxial layers on high quality native GaN 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 points and high equilibrium vapor pressures of nitrogen over the solid phase at the high temperatures encountered in this materials system. In conjunction with slow kinetics, both the manufacturability and scalability of these existing processes may ultimately be limited, and the cost of such processes is potentially prohibitive when one considers the impact on a high-volume, low-cost commodity such as LEDs for the purpose of reducing the amount of energy used for lighting in the United States and the world.

Described herein is an approach to growing bulk GaN 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 is liquid at atmospheric pressure at the temperatures under consideration, which provides an excellent host environment for the gallium nitride ionic precursors. Although the technique is in its infancy, we have demonstrated individually the pieces of the technique, and have demonstrated growth of millimeter-sized GaN wurtzite crystals at 450-500^{o}C at atmospheric pressure in under two to three hours in unoptimized conditions.

2.0 Background

2.1 Other Bulk GaN Growth Techniques

Gallium nitride has a congruent melting point of about 2500^{o}C, but dissociates into gallium metal and nitrogen gas at 800^{o}C at 1 atm pressure. Melt-based approaches have been performed in the laboratory, and have shown that the equilibrium vapor pressure of nitrogen over the solid near the melting point is 60,000 atmospheres,[2] placing melt growth of GaN at the extremes of experimental physics.

2.1-1 High Nitrogen Pressure Solution Growth

The best bulk GaN material is currently produced by the UNIPRESS group in Warsaw, Poland using the High Nitrogen Pressure Solution Growth technique (HNPSG). Transparent GaN platelets measuring 1.5cm x 1.5cm x ~100 μm can be grown in several weeks.[3] In this approach, gallium nitride is grown at 1600-1800K by dissolving nitrogen gas in molten gallium metal. The nitrogen gas dissociates to atomic nitrogen in the gallium. The high temperatures are required to obtain the solubility of atomic nitrogen to increase the growth rate; however, at those temperatures, the vapor pressure of nitrogen in equilibrium with solid GaN is in excess of 20 kbar. Typical operating pressures are in the range of 45,000 atmospheres. It is unlikely that this approach can be scaled up or become a manufacturable technique.

2.1-2 Ammonothermal Growth

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. Gallium nitride feedstock is dissolved in ammonia using either acidic or basic mineralizers and precipitated using a thermal gradient.[4,5] This technique is in its early stages of development; however, in principle, it should be capable of producing high quality crystals. However, because the chosen solvent, ammonia (NH_3), is volatile even at room temperature, it requires high overpressure (4,000 to 5,000 atmospheres) to maintain it in a liquid state at the growth temperature (500-800^{o}C). It may become very difficult to scale this process.

2.1-3 Modified Sandwich Sublimation Technique

Bulk GaN growth can be accomplished through sublimation of either the powder or by reaction of gallium vapor with ammonia at a hot substrate.[6] Growth via sublimation of the powder is difficult due to decomposition into Ga and N_2 at temperatures >800C. Therefore, vapor phase Ga is typically reacted with cracked NH_3 at a seed crystal. The driving force for the mass transfer of Ga to the substrate is a thermal gradient. This technique has the benefit of operating near atmospheric pressure, but the temperatures are high (~1200^{o}C is required to decompose the GaN powder or vaporize molten Ga, and to crack the ammonia). The growth rates are high but persistent control issues remain due to the difficulty associated with delivering reactive nitrogen species to the growth front: ammonia decomposes into N_2 and H_2 at temperatures as low as 300C, and there are many opportunities for this to occur prior to reaching the substrate surface.

2.1-4 Alkali Flux Methods

The Sodium Flux technique is a technique that is being developed by the Cornell University group[7] that uses molten sodium or sodium azide (Na_3N) as the nitride source. They found that the 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[3]. Crystals have yet to reach millimeter size on a regular basis, despite long growth times (~200 hrs). Sodium azide is an explosive material and is therefore difficult to handle, and care must be taken when working with sodium metal. While these issues are resolvable, they tend to impede rapid development. Song et al. are investigating the use of a lithium flux to synthesize GaN platelets with lateral dimensions of 1-4mm and 20-300 μm thick[8] by mixing Li_3N + Ga + N_2 at 740-800^{o}C and cooling over 2-3 days. The crystals are transparent and of high microstructural quality.

2.2 Molten Salt-Based Growth of Gallium Nitride

The root cause of the difficulty in producing high growth rates in the above techniques stems from the kinetic difficulty in liberating nitrogen from its precursor molecules to react with gallium in a controlled manner. The technique described below is similar to the flux techniques described above in that it uses the nitride ion (N^{-3}) as the nitrogen precursor species, which is an extremely reactive intermediate. Possibly the only environment in which this species can exist is a molten halide salt, such as LiCl. Goto and Ito[9] have reported the ability to produce nitride ions continuously and nearly quantitatively in a molten chloride salt be electrochemically reducing nitrogen gas at 450C. The ability to produce and use nitride ions in solution to grow III-nitrides is the premise behind this approach. There are multiple ways that this can be accomplished, and here we report initial data from these explorations.

3.0 Experimental

Nitrogen gas is the ideal nitrogen precursor in that it is abundantly available, easily purified, inexpensive, and its delivery to the growth chamber can be readily controlled. However, nitride salts (e.g., Li_3N) are also available and are easy to implement experimentally. Both precursors have been explored in this initial work.

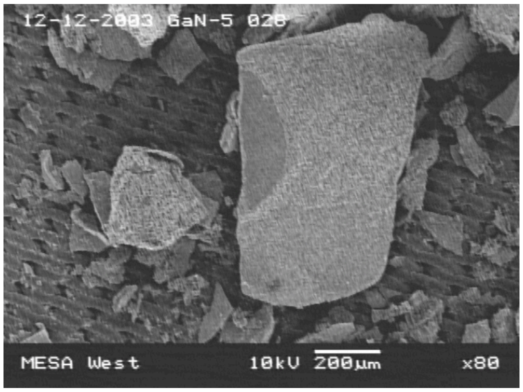

Figure 2 GaN crystal formed by galvanodynamic reaction of Li_3N and molten gallium at 450C and atmospheric pressure. The crystal measures 0.9mm lengthwise by 0.6mm across.

Approximately 15g of lithium chloride-potassium chloride eutectic (m.p. 352^{o}C) mixture was melted using a resistive heater under a base pressure of 1x 10^{-6} Torr in a quartz test tube and brought up to atmosphere in a controlled atmosphere nitrogen glove box. The melt temperature was brought to between 450 and 500C. A gallium electrode was formed by dropping gallium pellets (Alfa Aesar, 99.99999%) into the bottom of the tube after first having been etched in hydrofluoric acid for three hours and dried under nitrogen. Electrical contact was made to the gallium electrode via either platinum or molybdenum wire. Nickel was used as a counter electrode, and Ag/AgCl was the reference electrode during the experiments in which a reference electrode was used. Background scans of current vs. voltage were taken prior to the addition of Li_3N (Alfa Aesar, 99.99%) to the salt. The amount of Li_3N added was in the range of 100-300 mg. In the cases in which a reference electrode was not used, the current was stepped from 0 to 5 mA and returned to 0 mA in 50μV steps at 3 sec/step. When a reference electrode was used, the voltage was swept from the open circuit voltage (OCV) to +0.6V and back to OCV at scan speeds between 10 and 200 mV/sec. This was repeated for the duration of the growth experiments which lasted two to four hours. Solartron 1286 and 1287 potentiostats were used, as well as a Princeton Applied Research Model 271 potentiostat. The salt was cooled either by slowly reducing the power to the heater until the

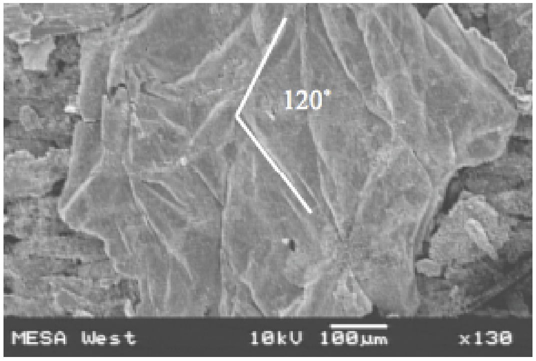

Figure 1 GaN crystal formed by potentiodynamic reaction of Li_3N and molten gallium at 450C and atmospheric pressure. The crystal measures about 1.25 mm lengthwise (not entirely shown) and 0.8 mm across at its widest.

salt solidified (to avoid cracking the quartz test tube), or by pouring the molten salt and reaction product into a steel beaker. The product was separated from the salt by rinsing with deionized water and filtering using a stainless steel mesh.

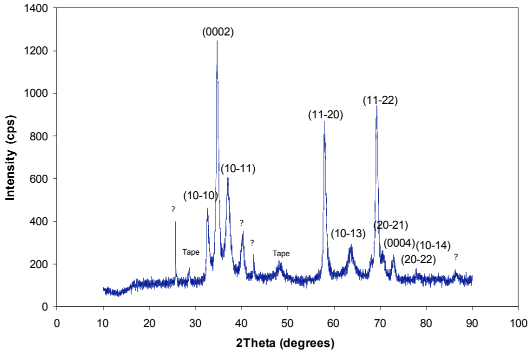

Figure 3 Powder x-ray diffraction spectrum of reaction product. All major wurtzite GaN peaks are represented.

The reaction products were analyzed by x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and photoluminescence (PL). Scanning electron micrographs from separate growth runs are shown in Figures 1 and 2. The crystal in Figure 1 was formed from the current-swept (no reference electrode) approach, with a total experiment time of 127 minutes. It is not known during which part of the current sweep that the growth mechanism was active. The crystal shown in Figure 2 was formed during potentiodynamic sweeping of the system, and the total growth time was just under three hours. The entire crystal measures over 1 mm in length, and 0.8 mm across. The facets on the surface of the crystal are 120°, which is consistent with the hexagonal crystal structure. Multiple crystals were formed during each of these experiments. The presence of nitrogen was confirmed using EDS under a 5kV accelerating voltage. Oxygen was also present. Powder XRD was performed at the University of Florida's MAIC (Major Analytical Instrumentation Center) using Cu K_α radiation. A sample diffraction pattern is shown in Figure 3. All of the major wurtzite GaN peaks are present. The crystals were non-luminescent under 266 nm excitation.

Experiments were performed to confirm that the reaction would proceed using nitrogen gas as the precursor. Electrochemical reduction of nitrogen gas was first verified in our system (Figure 4). The red line is the background current vs. voltage scan of the salt without nitrogen flowing, and the blue line is with N_2 gas flowing at 5 sccm. When the gallium electrode was used as the counter electrode, wurtzite GaN powder was formed and confirmed by powder XRD. No attempt was made to control the generation of bubbles during this experiment. Larger grains would be possible with proper engineering of the gas electrode to prevent turbulence at the growth surface.

4.0 Discussion

The above experiments demonstrate the ability to produce and use the nitride ion for growth of bulk nitride materials, and verify that the chemical reaction will proceed at a rate that is neither too fast and therefore uncontrollable, or too slow and therefore undesirable. Lithium nitride, while convenient for quick experiments, has certain drawbacks to its use as the nitride precursor. Li_3N dissociates into 3 Li^+ and N^{-3} in LiCl-KCl. At the gallium electrode nitride oxidizes the surface of the molten gallium metal, and at the cathode or counterelectrode the lithium is reduced to lithium metal. At the temperatures used in these experiments, the lithium is molten and drips off the nickel cathode into the molten gallium pool, thus contaminating the metal. It is speculated that lithium contamination is responsible for the lack of PL response, although other defects, such as nitrogen or gallium vacancies, could certainly be responsible. Other experimental geometries could be considered; however, lithium metal has a fairly high solubility in the molten salt and it is likely that in excess, it would continue to be a contaminant in the process. Nitrogen gas,

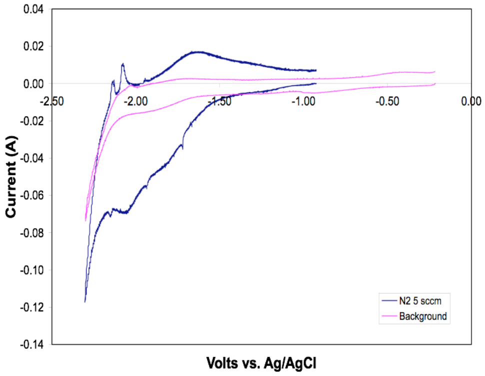

Figure 4 Voltammogram of nitrogen reduction in molten LiCl-KCl eutectic at 450C.

however, appears to be ideal for this process. Using the properly selected potentials, nitrogen gas can be reduced at one electrode and gallium can be oxidized at the other. Follow on work includes electrode design to prevent disruption of the growth surface by gas bubbles.

Electroplating is not expected to be capable of producing thick deposits of high quality, insulating gallium nitride, although large area stress-free seed crystals may potentially be grown on the surface of the molten Ga pool. Nevertheless, the principles demonstrated by these experiments might be used to create a technique capable of continuous, scalable growth of bulk GaN boules. Alternatively, the precursors can be formed electrochemically in the solution and delivered via forced salt flow to a seed crystal (Figure 5). Molten halide salts can solubilize both gallium (Ga^{3+}) and nitride (N^{3-}) ions 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%[10]—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. The apparatus is simple and does not require extensive modeling to build. 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. Because the solvent system is also an electrolyte, electroactive impurities may be removed prior to growth by doing a pre-electrolysis to remove oxygen and other species. Furthermore, the approach could be adapted to grow many other bulk nitride materials, such as InN, AlN, possibly C_3N_4, or other magnetic metal nitrides for power applications.

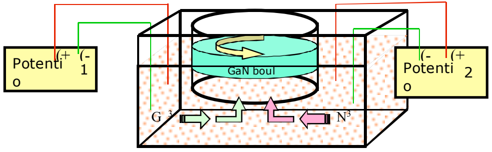

Figure 5 Schematic of bulk growth via continuous in situ electrochemical generation of ionic precursors. A mechanism for salt (and thus precursor) flow is not explicitly shown.

5.0 Summary

A novel approach to growth of III-nitrides is described and aspects of the technique have been demonstrated. Millimeter-sized wurtzite GaN crystals have been grown at atmospheric pressure in unoptimized conditions in two to four hours' growth time at 450-500C using the ability to electrochemically create and solubilize nitride ions in a molten chloride salt. The nitride ion may be the key to overcoming the thermodynamic and kinetic barriers that have plagued the ability to produce large area, high quality bulk III-nitrides. Because it is essentially an atmospheric-pressure solution-based growth technique, it has the potential to become a scalable and commercially viable process for the production of large area, low cost bulk GaN for substrates for high temperature electronics and optoelectronics applications.

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