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Initial Exploration of Growth of InN by Electrochemical Solution Growth

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Abstract

This report summarizes a brief and unsuccessful attempt to grow indium nitride via the electrochemical solution growth method and a modification thereof.

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The author gratefully acknowledges the work of Prof.Czeslaw Skierbiszewski of Unipress, also known as the Institute for High Pressure Physics in Warsaw, Poland, for his generous assistance with x-ray diffraction.

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NOMENCLATURE

DOE	Department of Energy
ESG	electrochemical solution growth
GaN	gallium nitride
HEMT	high electron mobility transistor
InN	indium nitride
LDRD	laboratory-directed research and development
LED	light emitting diode
MOCVD	metal-organic chemical vapor deposition
SSL	solid-state lighting
SNL	Sandia National Laboratories
XRD	x-ray diffraction

1. INTRODUCTION

Described in this report is a brief effort using a \$50,000 LDRD award to explore the possibilities of applying the Electrochemical Solution Growth (ESG) technique to the growth of indium nitride (InN). The ability to grow bulk InN would be exciting from a scientific perspective, and a commercial incentive lies in the potential of extending the ESG technique to grow homogeneous, bulk alloys of $\text{In}_x\text{Ga}_{1-x}\text{N}$ for light emitting diodes (LEDs) operating in the green region of the spectrum.

Indium nitride is the most difficult of the III-nitrides to grow due to its very high equilibrium vapor pressure of nitrogen¹. It is several orders of magnitude higher than for gallium nitride or aluminum nitride. InN has a bandgap energy of 0.7eV, and achieving its growth in bulk for large area, high quality substrates would permit the fabrication of LEDs operating in the infrared. By alloying with GaN and AlN, the bulk material used as substrates would enable high efficiency emission wavelengths that could be tailored all the way through the deep ultraviolet. In addition, InN has been shown to have very high electronic mobilities ($2700 \text{ cm}^2/\text{V s}$),² making it a promising material for transistors and even terahertz emitters.

Several attempts at synthesizing InN have been made by several groups.¹ It was shown that metallic indium does not interact with unactivated nitrogen even at very high temperatures. Thus sets up an incompatibility between the precursors in all growth methods: a tradeoff between thermally activating the nitrogen-containing precursor and the low decomposition temperature of solid InN.

We have been working to develop a novel growth technique 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, we have found that 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. Literature reports indicate measured nitride ion concentrations in LiCl at 650°C as high as 10 mol%³—a sufficient concentration to yield growth rates on the order of 0.1 to ~1 mm/hr under diffusion-limited growth conditions. Also, molten salts are compatible with the 400-1200°C temperatures likely to be necessary for growth of high-quality single-crystal III-nitrides. Since they can be worked with at (or close to) atmospheric pressure, scalability is not a problem 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 before growth begins. Finally, the molten salts offer a number of pathways to improve the solubility and control the growth of the III-nitrides by functioning as an electrolyte in electrochemical processes. We have already demonstrated growth of wurtzite GaN particles ranging from 0.2 to 0.9 mm in two hours in our laboratory using these techniques⁴.

It was the goal of this work to extend this ESG approach to the growth of indium nitride. The hope was that the abundance of the activated form of nitrogen, namely the triply-charged nitride ion (N^{3-}) would enable the facile growth of InN in solution at low temperatures.

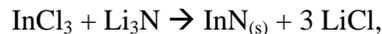
2. APPROACH

The possible permutations of the conceived Electrochemical Solution Growth method have been described in detail elsewhere⁴. The sections most pertinent to this work have been repeated and adapted here. A full description follows of the experiments performed in this work.

2.1 Dissolution and Precipitation

In this embodiment of the growth method, both precursors are created through dissolution, and the growth method is more aptly named simply “Solution Growth.” The simplest solution-growth 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. This is straightforward and this concept has been applied to growth of crystals of all kinds. However, the solubility of InN and GaN in molten salts has been shown to be negligible for the purposes of a high throughput manufacturing technique for commodities such as substrates for lighting applications. This was demonstrated in a 2006 LDRD activity⁴.

Another dissolution and precipitation approach is to separately dissolve InCl₃ and Li₃N precursors into the molten halide salt, and then allow them to react through a so-called metathesis reaction. For our example, the reaction is thus



for which the Gibbs Free Energy of the reaction is highly exothermic at room temperature, and continues to become increasingly exothermic as the temperature is increased (-10³ kcal/mol at 450°C). In fact, without the LiCl solvent the reaction is explosive^{5,6}. Equilibrium conditions for this reaction require concentrations of InCl₃ and Li₃N on the nanomolar scale, thus yielding slow growth rates in a diffusion-limited regime. However, recent experiments using gallium metal oxidation in the molten salt indicate that the formation of the tetrachlorogallate or tetrachloroindate species (LiGaCl₄ or LiInCl₄, respectively) in the molten salt tends to kinetically inhibit the reaction of the group III species with nitride, thereby possibly enabling more controlled growth at higher concentrations.

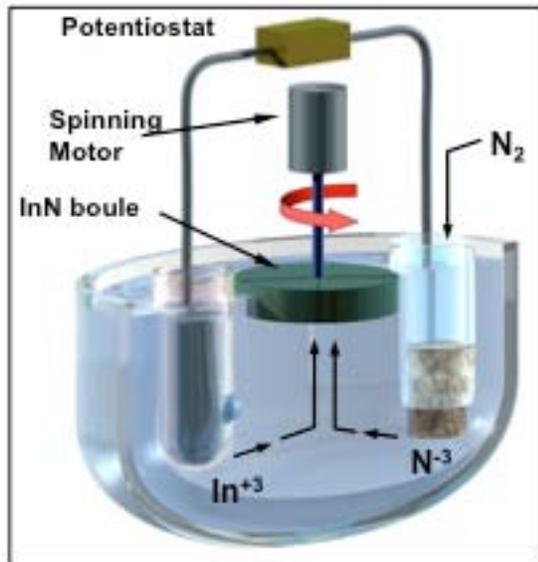


Figure 1. Schematic of Electrochemical Solution Growth Technique applied to indium nitride.

2.2 Electrochemical Solution Growth (ESG)

Another, different approach to dissolving the precursors in a solvent is to create them both electrochemically. Rather than dissolving the compound straight into the solution and precipitating it out, the cationic (In³⁺) and anionic (N³⁻) components may be electrochemically formed in solution at locations separated by a relatively large distance in the melt to prevent premature reaction (see Figure 1). This alleviates the typical difficulties of solution growth associated with constitutional supercooling by continuously generating precursors in solution in a controlled manner. This could be

accomplished by using multiple potentiostats or power supplies or through the use of a single potentiostat or power supply, as shown in the figure. In this case, nitrogen is reduced at one electrode while the indium is oxidized at the other electrode—these initial experiments have already been demonstrated in our laboratory for GaN. 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 must be maintained below the solubility limit of InN in the salt to prevent instantaneous precipitation in the solution; however, as mentioned in the previous subsection, kinetics appears to assist in slowing down the reaction so this becomes less of a concern. The slow growth rate resulting from the low concentration of precursors could be improved by controlling the rate at which ions are transported to the growth surface via forced salt flow; in this case, rotating the seed crystal analogously to rotating disk reactor MOCVD. A temperature gradient at the growth surface would allow precipitation due to supersaturation of the indium nitride.

2.3 Description of Specific Experiments

Three experiments were performed under this \$50K Late Start LDRD. Two attempted to grow InN from electrochemical solution growth and one attempt was made to grow InN from solution growth.

Experiment #1—Electrochemical Solution Growth at 400C:

Experiments were performed in an inert-atmosphere argon glove box, with an oxygen content maintained at or below 1ppm and water concentration < 0.5ppm. An alumina high form crucible (AdValueTek, 99.5%) was used to melt approximately 100g of LiCl-KCl eutectic (Aldrich, 99.9%, anhydrous beads). An indium electrode was made by inserting indium shot (Alfa, 99.9999%) into a closed-end alumina tube with a 3mm² hole drilled in it near (just below) the height of the surface of the indium (m.p. 143C), which was molten after being immersed in the molten salt at 480C. The indium was held inside the tube via surface tension. Electrical contact was made using molybdenum wire. The reference electrode was a 0.1M Ag/AgCl in LiCl-KCl pyrex tube, and nitrogen gas bubbled over a nickel wire was used as the cathode. Nitrogen gas was purified over an Aeronex nickel catalyst prior to bubbling into the melt. No seed crystal was used; the experiment was simply autonucleation in the bulk of the molten salt. Electrochemical analysis in the form of potentiodynamic sweeps, potentiostatic holds, and open circuit monitoring were performed using a Princeton Applied Research Model 273A potentiostat. An example of a cyclic voltammogram (first cycle only) is shown in Figure 2, with indium metal used as the working electrode. The sign convention employed here is that oxidation currents are positive and reduction currents are negative. In this voltage sweep, the indium oxidizes at a potential of approximately -0.55V with respect to Ag/AgCl. The electrochemical techniques employed were identical to those used to successfully grow GaN. The temperature was monitored using a Type K thermocouple encased in a one-end closed round quartz tube to protect the thermocouple and molten salt from interacting.

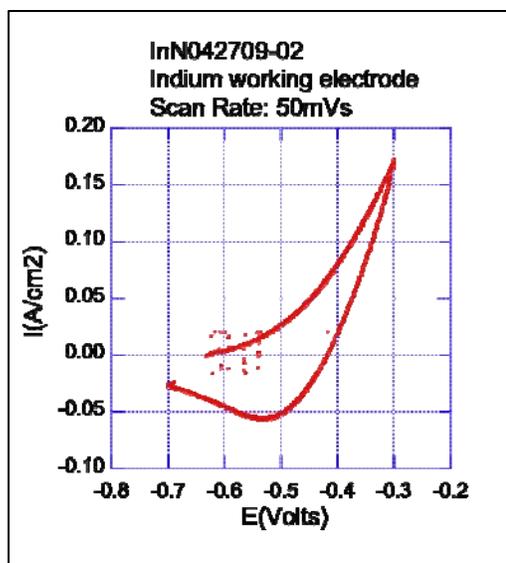


Figure 2. An example of a cyclic voltammogram obtained from using a metallic indium working electrode

Experiment #2—*Electrochemical Solution Growth at 480C*: The conditions employed for this second experiment were identical to the first, with the exception that the temperature of the molten salt was 480C.

Experiment #3—*Solution Growth at 420C*: In this case, indium chloride was dissolved in LiCl-KCl at 420C, followed by slow addition of Li_3N by hand. The vessel used was a 7/8" round test tube, 6" long, and the amount of salt used was decreased to about 10g.

In all three experiments, after the electrochemistry or addition of reactants, the salt was allowed to cool to room temperature by turning off the heat source. The salt plug containing the reaction products was rinsed with deionized water and filtered with 0.020-micron filter paper. The results were analyzed by x-ray diffraction.

3. RESULTS AND DISCUSSION

After drying the insoluble product on filter paper, samples were sent to collaborator Prof. Czeslaw Skierbizewski of Unipress in Warsaw, Poland for analysis by x-ray diffraction. Professor Skierbizewski is a collaborator on other nitride projects and offered to run the samples for us out of his own budget. Since this was such a small budget project, that was the logical choice. Unfortunately the diffractometer broke shortly after the samples were mailed to him and several delays in its repair resulted in a lengthy turnaround for data collection. Hence, the few experiments performed. Once the diffractometer was up and running, several samples from each experiment were scanned based on the different product morphologies that were observed. In all cases, the results showed the presence of indium metal (In) and potassium chloride (KCl). These initial experiments were unsuccessful in producing indium nitride by this technique.

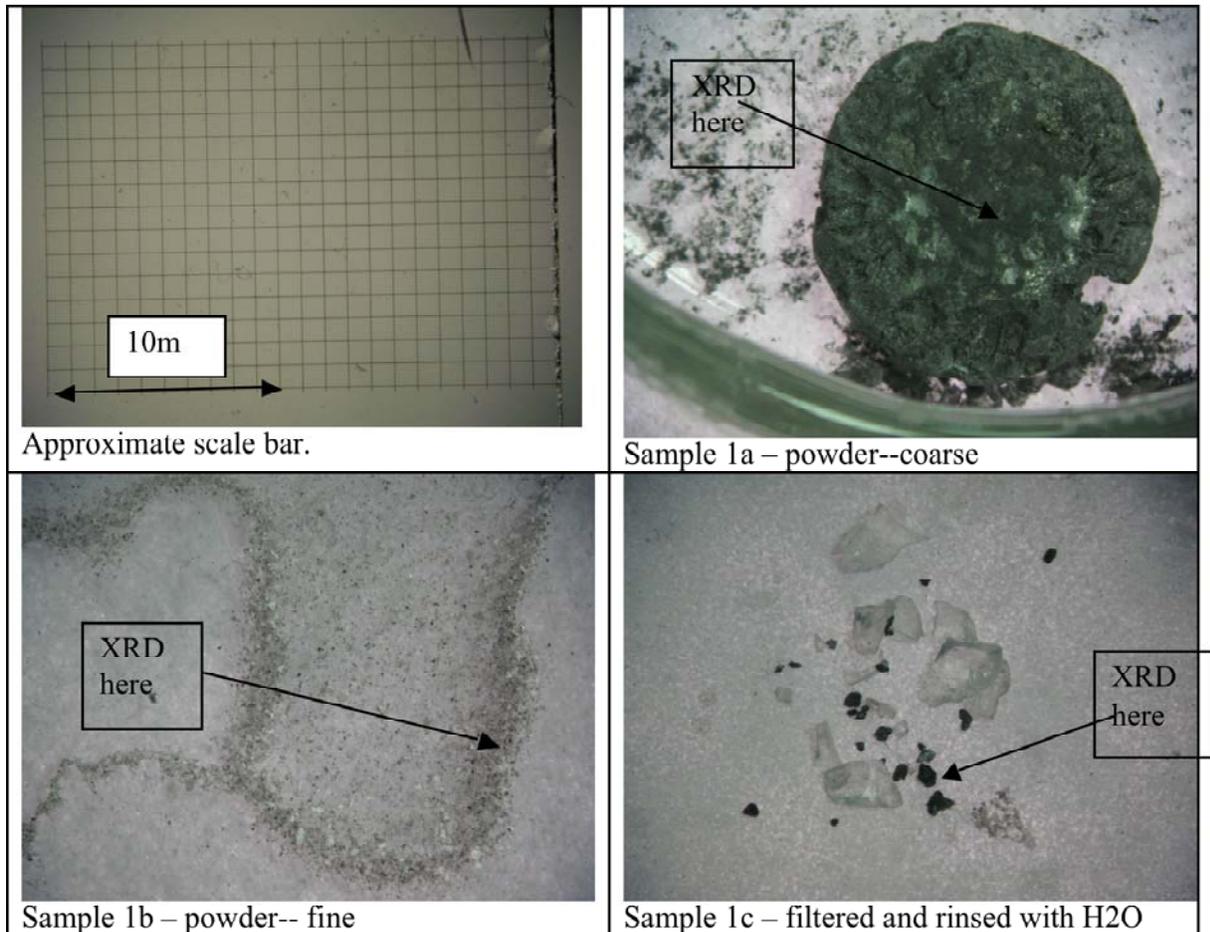


Figure 3. Photomicrographs of product from Experiment #1

One possible explanation for why the experiment failed is that the temperature was too high for successful growth of InN at atmospheric pressure. Of all the III-nitrides, InN dissociates at very low temperature—typically around 600C in vacuum. It was hoped that 400C in solution would be a sufficient thermodynamic environment to produce solid crystals. Another, more likely explanation is that the indium ions or indium chloride species complexed with the molten salt environment and the temperature was too low to both liberate the In from the precursor complex. Further exploration is required to better understand the indium chemistry in the molten salt, and its interactions with nitride ions. Literature reports on the electrochemistry of InCl and InCl₃ in LiCl-KCl at 450C^{7,8}, but little is available on the electrochemistry of indium metal in the salt. An alternative approach would be to conduct these electrochemical and chemical experiments in an ionic liquid solvent with a wide enough electrochemical window to stabilize the very reactive nitride ion, which would also influence the reactivity of the activated indium species.

4. SUMMARY AND CONCLUSIONS

The very limited survey of possible experimental approaches to atmospheric-pressure growth of bulk indium nitride explored in this work was unsuccessful in yielding InN. It is not a foregone conclusion, however, that indium nitride cannot be grown by a modified version of this technique; perhaps in a room temperature ionic liquid, or by altering the indium chemistry to make the indium ion more reactive in the high temperature molten salt. Further experiments are necessary to fully understand the chemistry and effectively adapt the growth method.

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