# II.C.6 Photoelectrochemical Material Synthesis at LANL

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Project End Date: Project continuation and direction determined annually by DOE

## Overall Objective

The overall objective of this project is to evaluate the InGaN ternary alloy system for use as a photoelectrode for photoelectrochemical (PEC) hydrogen generation. In the past, problems with the material quality of InGaN have led to an incomplete picture for this material as a PEC photoelectrode. This project utilizes a novel molecular beam epitaxy (MBE)-type film synthesis based on a high flux beam of energetic nitrogen atoms to improve InGaN material quality.

## Fiscal Year (FY) 2013 Objectives

- Improve electrical properties of n-type InGaN
- Improve electrical properties and crystallographic quality of p-type InGaN
- Determine mechanisms causing corrosion of p- and n-type InGaN and seek to find solutions to problem

## Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(AE) Materials Efficiency – Bulk and Interface

(AF) Materials Durability – Bulk and Interface

(AG) Integrated Device Configurations

## Technical Targets

This project is conducting fundamental studies on the synthesis of InGaN films for use as PEC electrodes for hydrogen generation. Insight gained from this work will determine if wide band-gap nitride based semiconductors are suitable materials for PEC photoelectrodes. While this work is at an early stage, it has the long-term goal of addressing the ultimate, long-term DOE technical targets for hydrogen production identified in the 2012 Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan, Table 3.1.8:

- PEC hydrogen cost: $2.10/kg
- Energy conversion ratio (efficiency): 25%
- 1-sun hydrogen production rate: $2.0 \times 10^{-6}$ kg/s∗m$^2$

## FY 2013 Accomplishments

- InGaN films show photocurrent at 0 V applied bias, suggesting the interfacial energetics are favorable for spontaneous photoelectrolysis.
- Have improved mobility and carrier concentration levels in n-type and p-type InGaN.
- Have improved surface morphology of n-type InGaN films, which will lead to improved stability and corrosion resistance.

## INTRODUCTION

The overall purpose of this work is to provide an economic solar-based technology for creating hydrogen. The bulk of hydrogen reformation currently is done using fossil fuel sources. To move away from the current fossil fuel model for hydrogen production, new technologies must be developed or made more efficient and cost effective. One proven method for hydrogen production is PEC hydrogen production, also known as photoelectrolysis.

The photoelectrolysis of water is the process whereby light, illuminating a semiconductor, is used to split water into hydrogen and oxygen. The incident light, absorbed in a semiconductor electrode, splits water directly. These water splitting systems consist of three main components, a light harvesting system (the semiconductor) and two gas evolving electrodes, one for hydrogen and one for oxygen. Combining the light harvesting electrode and the electrolyzer into a single monolithic device simplifies device design. This is accomplished by putting the semiconductor material into an aqueous solution, illuminating it with sunlight, and driving the water splitting reaction directly. With one of the gases, either hydrogen or oxygen, evolved directly off the surface of the semiconductor, the other electrode is spatially separated so that the two gasses do not mix. The result of this configuration is that sunlight is the only energy input and that

hydrogen is evolved with no external electron flow. Critical to this design is having a semiconductor material that is corrosion resistant under operating conditions.

## APPROACH

Among the technical barriers limiting PEC hydrogen production, becoming widespread and economically viable are efficiency and cost. Closely related to these challenges are material quality of photoelectrodes and the stability of these materials under operating conditions.

To improve the material quality, we use a unique MBE-type growth platform called energetic neutral atom beam lithography/epitaxy (ENABLE) to grow InGaN films. ENABLE utilizes a semi-collimated beam of energetic nitrogen atoms (energies spanning 1.0 to 5.0 eV) as the reactive nitrogen source for InGaN film growth. The metals are evaporated from standard thermal sources. The advantage of ENABLE is that the reactive nitrogen atoms have sufficient energy to overcome reaction barriers involved in film growth, which reduces the need for high substrate temperatures that are required for conventional growth. High substrate temperatures are a recognized problem for high quality InGaN growth, as they lead to In phase and compositional segregation and clustering within films.

## RESULTS

In previous years, we have demonstrated n-type InGaN growth on c-axis sapphire, and these films have shown non-zero current at zero bias under illumination, which may be indicative of PEC water splitting. An example of one such film can be seen in Figure 1. While this film does show non-zero current of 25 μA/cm$^2$, this value is well below the theoretical limit for this material under experimental conditions, ~5 mA/cm$^2$. Additionally, the performance of the materials degraded over time, and it appears that the material is corroding or etching under operating conditions. To address these two challenges, lower than expected efficiency and corrosion/stability of material under operating conditions, we have pursued three directions. These are improved material quality (including surface morphology), p-type doping, and growth on conductive substrates.

In previous years we demonstrated the target compositions believed to be ideal for InGaN as a PEC photoelectrode, but material quality, while state-of-the-art, was still not sufficient for use in a working PEC cell. Additionally, the electrical properties (conductivity) of the films were too low and likely limiting performance. Over this year, we have achieved a noticeable improvement in InGaN film crystallinity and surface morphology and an approximate factor of 2 increase in carrier mobility.

P-type films are desirable from a stability standpoint because they force electrons to the semiconductor/electrolyte

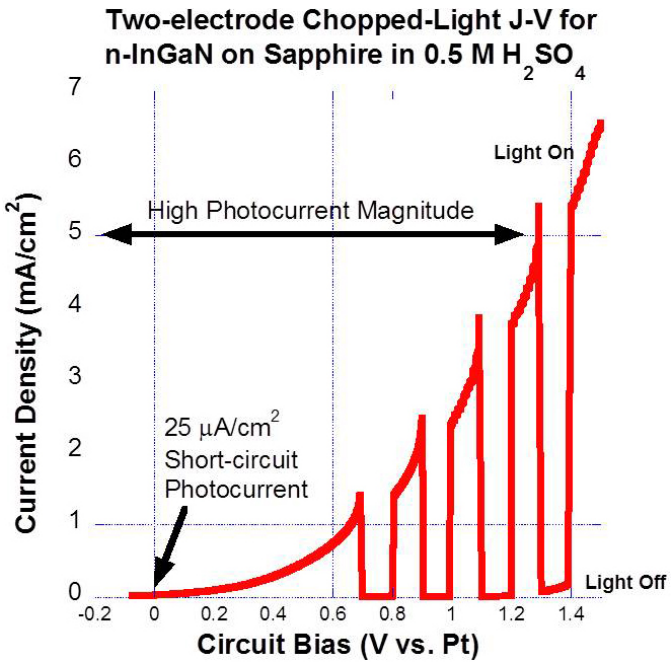


**FIGURE 1.** Current-voltage plot of InGaN photoelectrode showing non-zero current at zero applied volts.

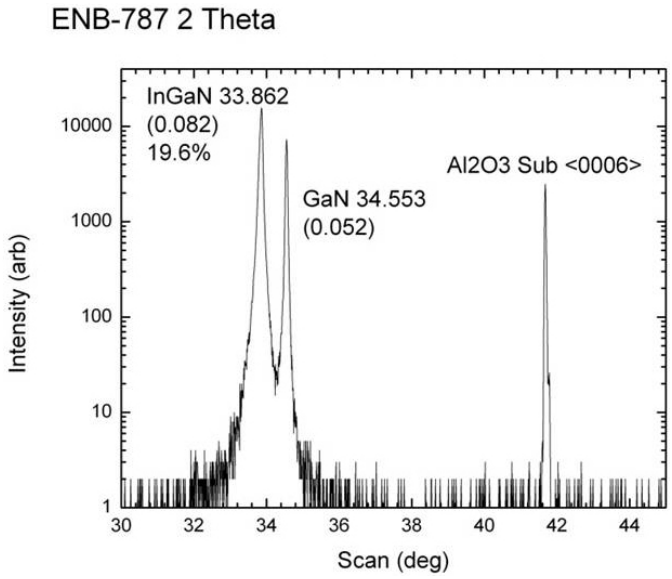


**FIGURE 2.** XRD pattern of InGaN film. Numbers next to peak markers are observed diffraction angles, numbers in parentheses are full width at half maximum. The InGaN film was 19.6% In

interface offering cathodic protection. This could solve the corrosion problem that is observed. Figure 2 shows an X-ray diffraction (XRD) pattern of an ~20% InGaN film that has been p-type doped. Figure 3 shows an electrochemical capacitance voltage (ECV) measurement of the same film, showing a p-type acceptor concentration of ~6x10$^{20}$ cm$^{-3}$. According to hall measurements, the film measures p-type

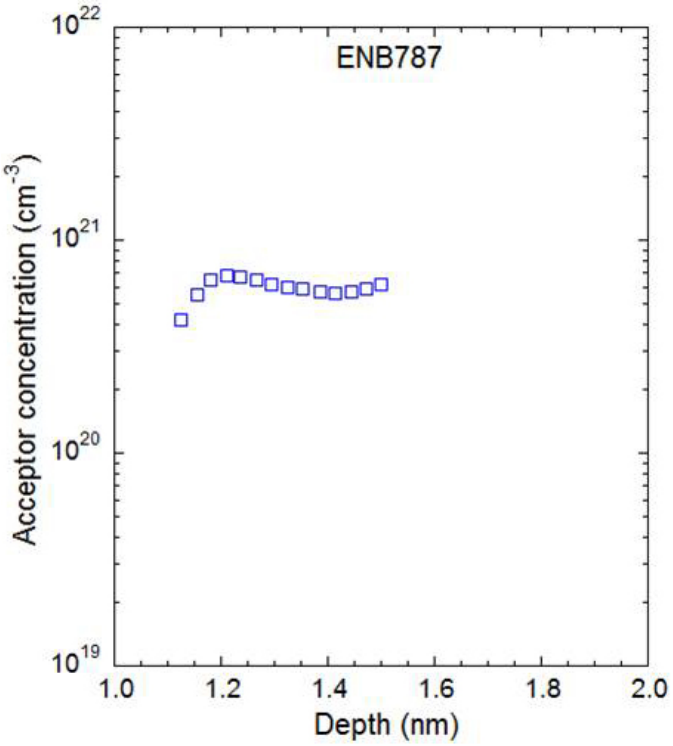


**FIGURE 3.** ECV plot showing acceptor concentration (p-type carriers) near the surface of the InGaN film from Figure 2.

with a carrier concentration of $2.2x10^{19}$ $cm^{-3}$ with a acceptor mobility of 2.75 $cm^2/V*s$. This means ~3.5% of the acceptors are active, which is a reasonable value for a p-type III-N film. Similar p-type films have been evaluated for their PEC performance, but their efficiency and stability is not markedly different from representative n-type InGaN films (Figure 1). Likely, the reason for the stability and efficiency not improving is that the p-type films tend to be of lower crystalline and surface quality, due to the defects introduced by doping the film.

While sapphire is much simpler to use for InGaN growth, due to the Si substrate being reactive and fouling the epitaxy during initial growth phases. The non-conductive substrates (sapphire) require a non-ideal front contact configuration where majority carriers have to traverse several mm laterally for collection. This contact configuration leads to a low photon to current efficiency and prevents accurate ensemble efficiency and durability assessments. InGaN films do show excellent vertical conductivity (often more than an order of magnitude larger than lateral) due to the columnar grain structure that is intrinsic to this material system. Furthermore, a back ohmic contact enables greatly reduced collection distances and should lead to enhanced utility of photogenerated electrons. Growing on conductive substrates (Si) allows one to bypass the lateral conductivity and collection problem by having the electrical transport follow a more favorable and shorter path.

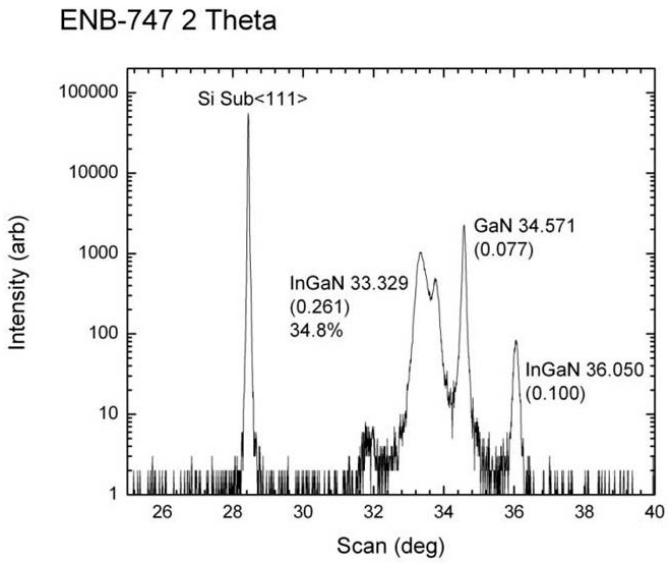


**FIGURE 4.** XRD pattern of InGaN film grown on Si <111>. Numbers next to peak markers are observed diffraction angles, numbers in parentheses are full width at half maximum. The InGaN film was 34.8% In.

Figure 4 shows an XRD pattern of ~35% n-type InGaN film grown on conductive <111> Si. Compared to the peak width of the InGaN in Figure 2, this peak is much wider, indicating poorer crystalline quality. Also, ECV showed that the film had a high carrier concentration of ~$1x10^{21}$ $cm^{-3}$; $1x10^{18}$ $cm^{-3}$ is a more typical value for films grown on sapphire. Additionally, the surface was quite rough, 30-nm root mean square as measured by atomic force microscopy, which is more than twice a typical value for a film grown on sapphire. All of these figures of merit show that the film quality on Si is far inferior to films grown on sapphire. As a result, we have not observed the enhanced performance expected by moving to a back contact and conductive substrate (Si). By improving the film quality on these substrates, a noticeable performance improvement should be observed. Most of the film quality issues are traceable to the initial buffer layer growth on the Si surface; work will focus on improving this initial phase of growth.

## CONCLUSIONS AND FUTURE DIRECTIONS

While the initial results of this work are promising, more study is needed to determine if the InGaN alloy system can be made into a useful, efficient photoelectrode for PEC water splitting. Future work will focus on the following areas:

- Improved material quality. While the demonstrated InGaN films in this work are state of the art, it appears that the material quality and electrical properties remain insufficient for use as a PEC electrode. Further work optimizing crystallinity and surface morphology, both on sapphire and conductive Si substrates, will be done.

- Improve corrosion resistance/stability. It appears that some corrosion of the InGaN photoanodes is taking place. This may be because the InGaN films are N-polar, rather than metal-polar on the surface. The N-polar face is known to be less stable and will corrode in strong acids and bases. Initially, we will evaluate the corrosion resistance of N- and metal-polar GaN to validate the relationship in a PEC environment. We will then attempt to create metal polar InGaN films.
- Further improvement of p-type InGaN. P-type films are desirable from a stability standpoint because they force electrons to the semiconductor/electrolyte interface offering cathodic protection. This could solve the corrosion problem that is observed due to the use of N-polar InGaN.

## FY 2013 PUBLICATIONS/PRESENTATIONS

**1.** 'Photoelectrochemical Material Synthesis at LANL'. Todd L. Williamson, Project # PD097. 2013 DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES PROGRAM ANNUAL MERIT REVIEW, May 15, 2013.