Photoelectrochemical Material Synthesis at LANL

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05/15/2013

Project ID #
PD097

Overview

Timeline

- Project start date: 10/01/2010
- Project end date: 9/30/2013*
- Percent complete: *75%*

Budget

- Total project funding
  - DOE share: $ 365K
  - Contractor share: $ 0K
- Funding received in FY12: $ 100K
- Funding for FY13: $ 65K

Barriers

- Barriers addressed
  - AE. Materials Efficiency – Bulk and interface
  - AF. Materials Durability – Bulk and interface
  - AG. Integrated Device Configurations

Partners

- Interactions/ collaborations
  - ➢ NREL
- Project lead
  - ➢ Todd Williamson, LANL

* Project continuation and direction determined annually by DOE

Relevance

- The objective of this work is to explore the use of Group III Nitrides, specifically InGaN, for Photoelectrochemical Hydrogen production.

- The focus of this year's work has been on creating p-type and metal-polar InGaN which should offer increased stability and higher conversion efficiency than n-type, N-polar InGaN that has been produced previously

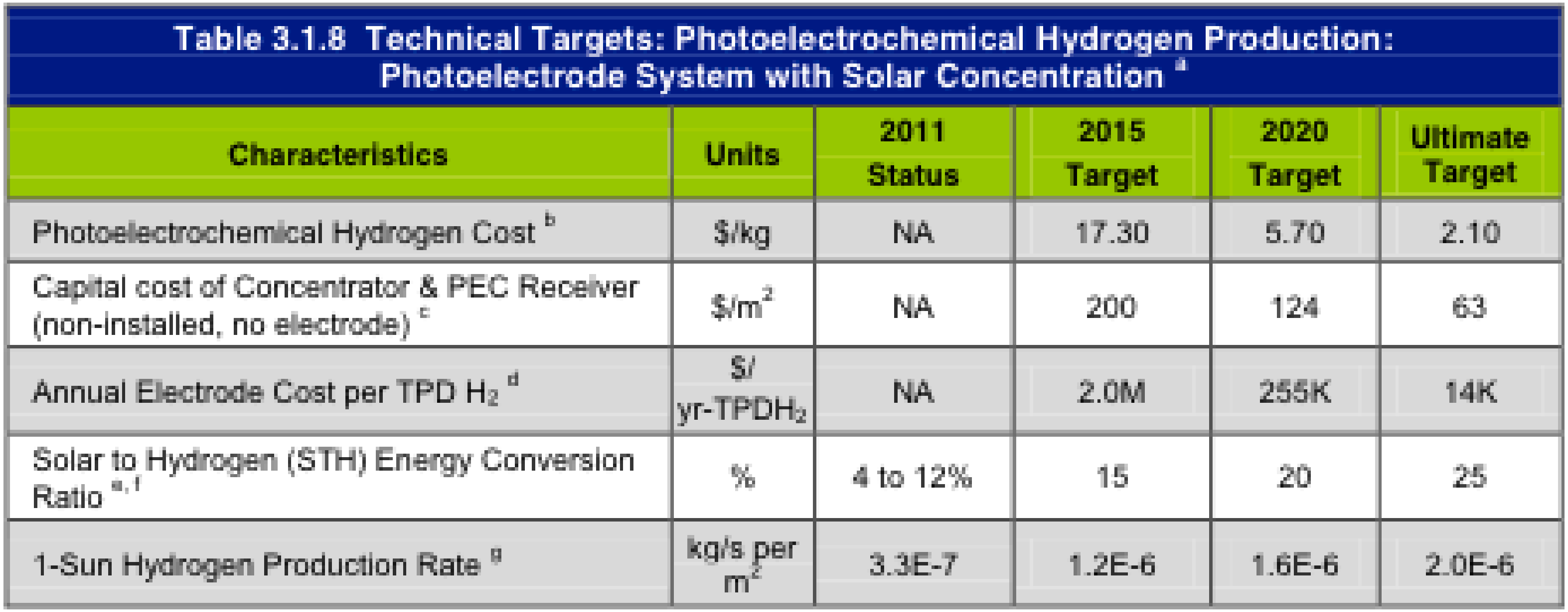


Table 3.1.8 Technical Targets: Photoelectrochemical Hydrogen Production: Photoelectrode System with Solar Concentration [a]

Characteristics	Units	2011 Status	2015 Target	2020 Target	Ultimate Target
Photoelectrochemical Hydrogen Cost [b]	$/kg	NA	17.30	5.70	2.10
Capital cost of Concentrator & PEC Receiver (non-installed, no electrode) [c]	$/m^2	NA	200	124	63
Annual Electrode Cost per TPD H_2 [d]	$/ yr-TPD$H_2$	NA	2.0M	255K	14K
Solar to Hydrogen (STH) Energy Conversion Ratio [e,f]	%	4 to 12%	15	20	25
1-Sun Hydrogen Production Rate [g]	kg/s per m^2	3.3E-7	1.2E-6	1.6E-6	2.0E-6

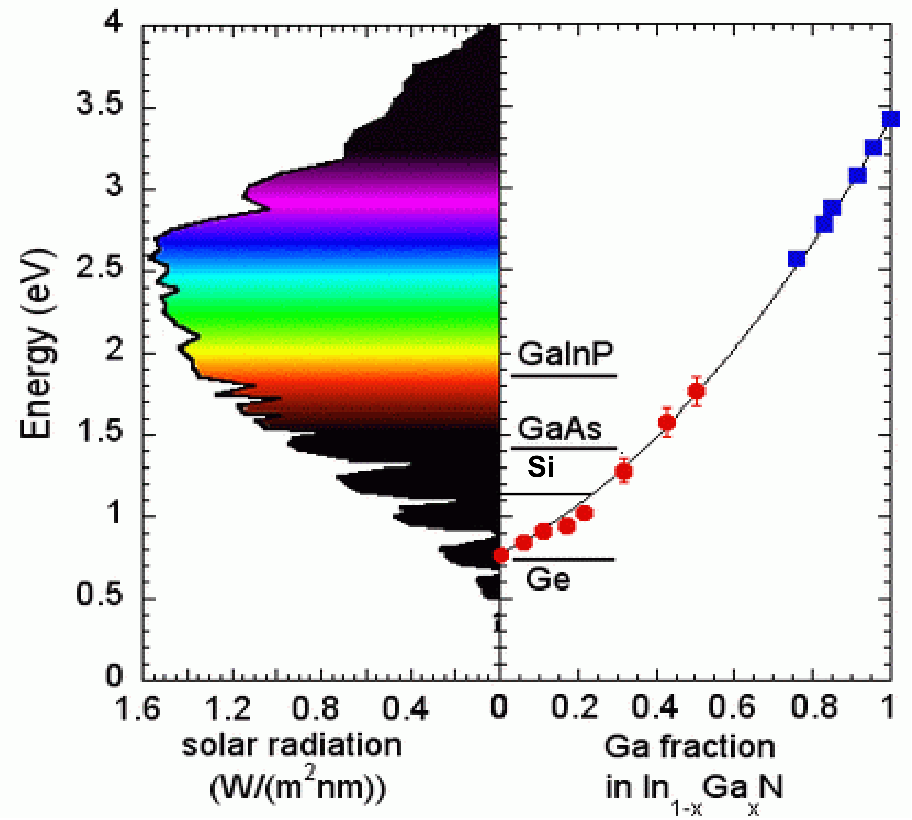
Approach

Our approach is to take utilize the InGaN ternary alloy system, a materials system whose bandgaps can span nearly the entire solar spectrum.

Pure nitride $In_xGa_{1-x}N$ has potential to be both stable and efficient PEC electrode

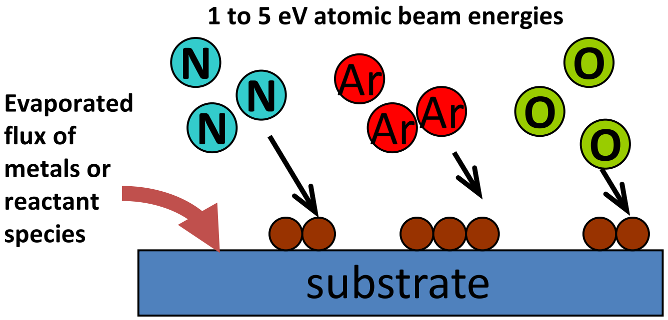
InGaN materials are grown at Los Alamos National Lab (LANL) and their PEC H_2 production performance is characterized at the National Renewable Energy Lab (NREL)

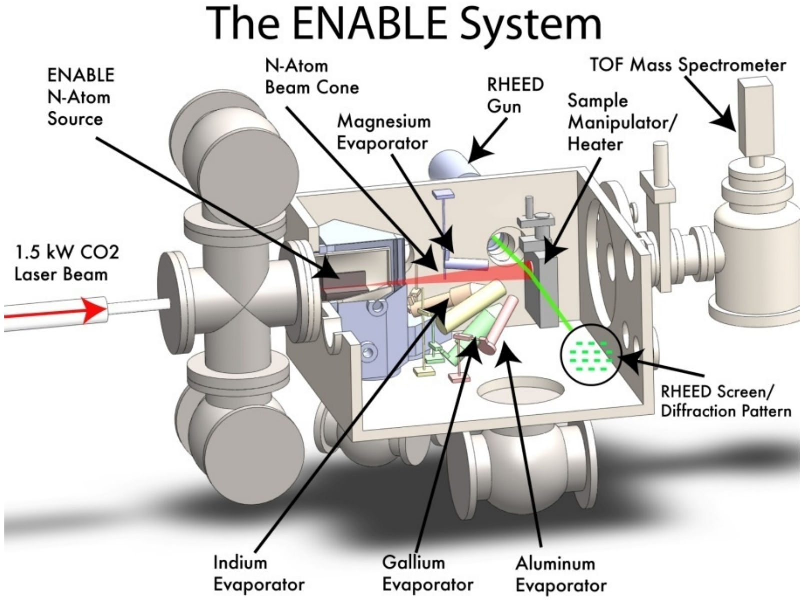
Walukiewicz et al, J. Appl. Phys 94, 6477(2003)



Approach – Film Synthesis

Energetic neutral atom beam assisted surface chemistry





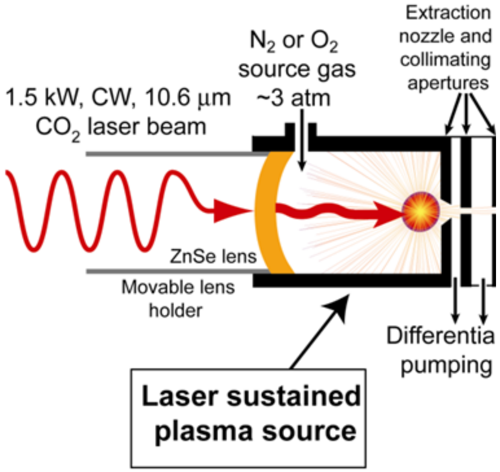
What is ENABLE:

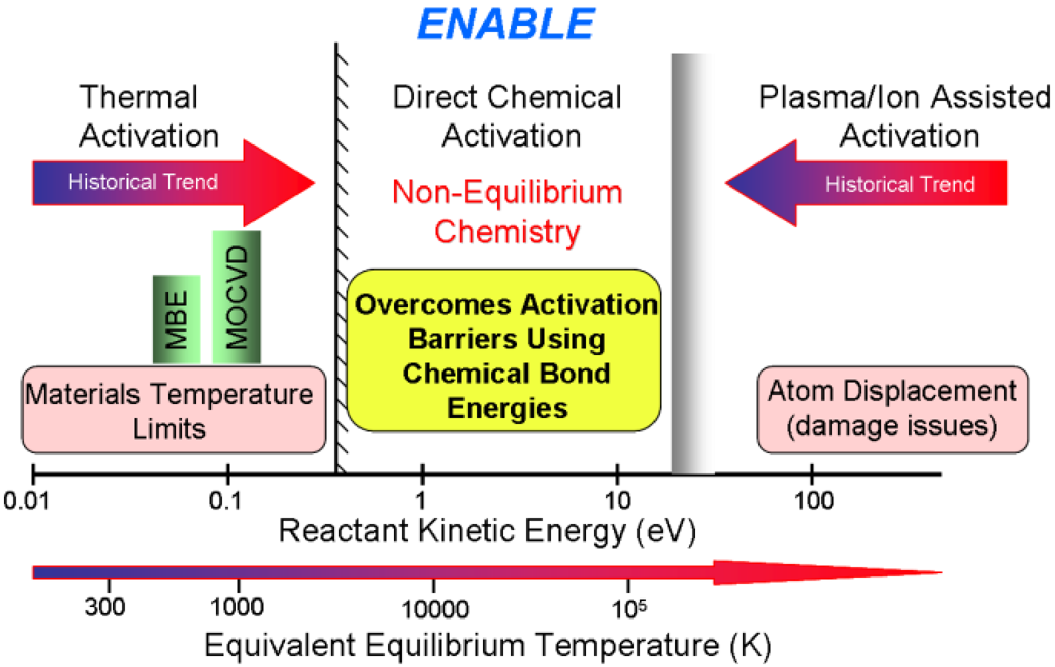
ENABLE is a unique MBE-type film growth technology that uses a *high-flux* beam of *energetic* neutral nitrogen (or oxygen) atoms with kinetic energies of 1 to 5 eV for overcoming reaction barriers. Conventional thermal sources are used for metals.

Advantages:

- With ENABLE, the *kinetic energy* of *neutral atoms* provides the reactant energy required to grow thin films via *direct chemical activation* (not high T or charge)
- The atom's kinetic energy also *promotes surface diffusion* and byproduct removal
- ENABLE provides a *high flux* of reactive species facilitating *high film growth rates* (>5 microns/hr) and *non-equilibrium* growth conditions allowing thermodynamic limits to be overcome
- No toxic chemical precursors or hazardous waste stream

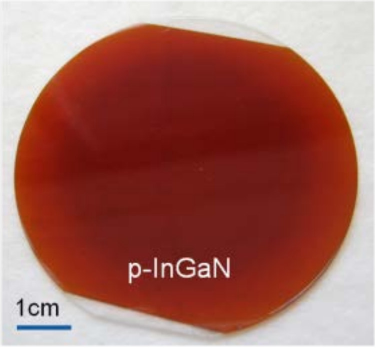
Approach – Film Synthesis





ENABLE advantages for Group-III Nitride films:

- InGaN films can be grown over the full alloy composition range with good epitaxy & crystallinity
- Excellent compositional uniformity with no phase segregation
- Permits compositional grading for complex device architectures



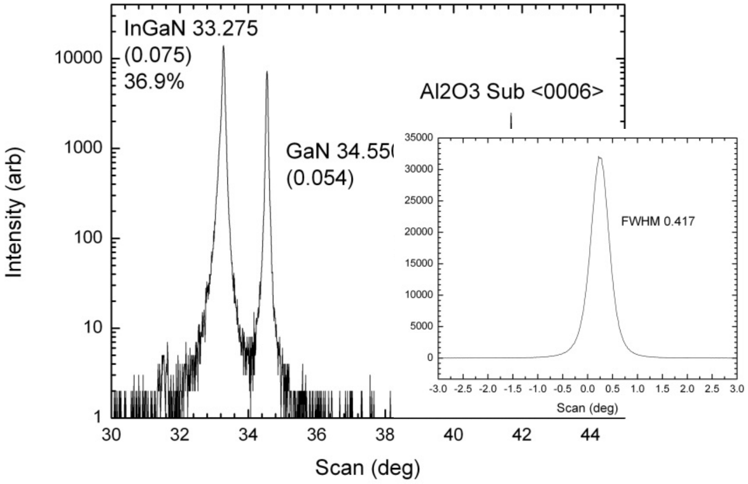
“red” In-rich InGaN film with 2.0 eV band gap grown by ENABLE

Approach – Milestones

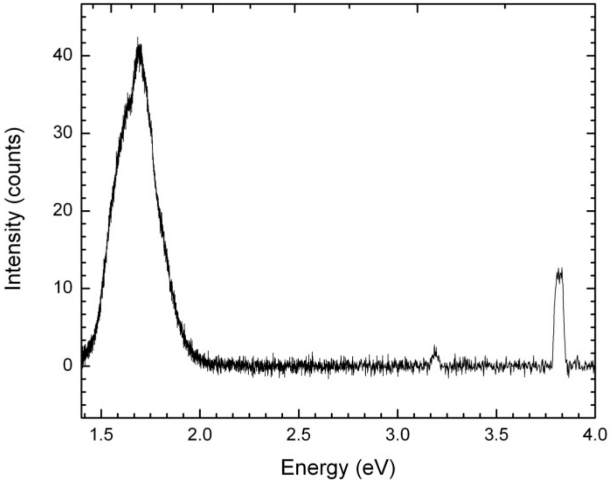
Milestone	Completion Date	Status
Demonstrate growth of single phase n-type InGaN with In compositions 15% - 30% on double-side polished sapphire and p-type Si with carrier concentrations ~$10^{18}/cm^3$ or less and carrier mobilities ~100 $cm^2/V*s$ or greater. Films will be sent to NREL for PEC performance characterizations.	**January, 2013**	50%
Demonstrate growth of single phase p-type InGaN with In compositions 15% - 30% on sapphire and p-type Si with carrier concentrations between $5x10^{17}/cm^3$ – $1x10^{19}/cm^3$ and mobilities greater than 10 $cm^2/V*s$. Films will be sent to NREL for PEC performance characterizations.	**May, 2013**	25%
With NREL, complete evaluation of InGaN material for direct water splitting or as part of a mechanically stacked tandem system and based on achievable efficiency and stability make go/no-go decision on additional studies.	**September, 2013**	10%

Accomplishments and Progress - Characterization results for InGaN on sapphire ~37% In and ~39% In contents

XRD measurements



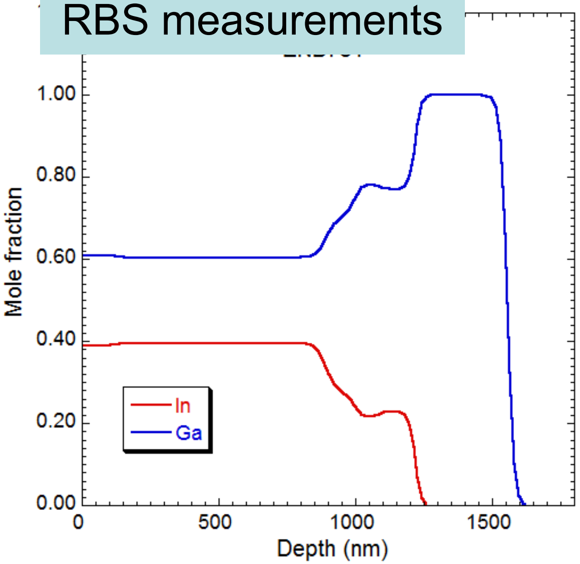
Photoluminescence

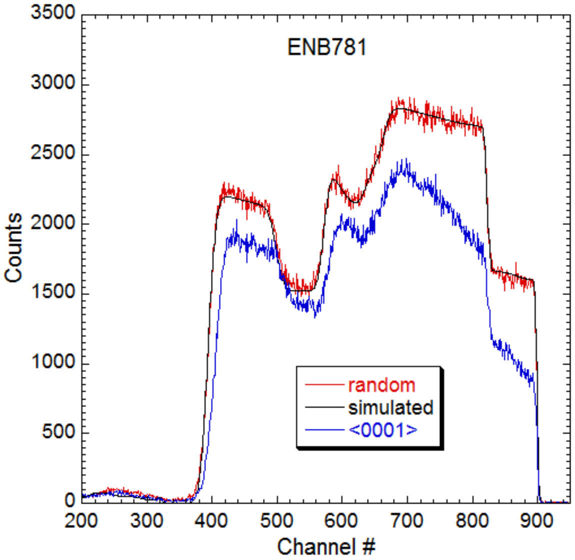


37% In InGaN has bandgap luminescence ~ 1.8 eV, suitable for PEC electrode

XRD shows good crystal structure

RBS measurements





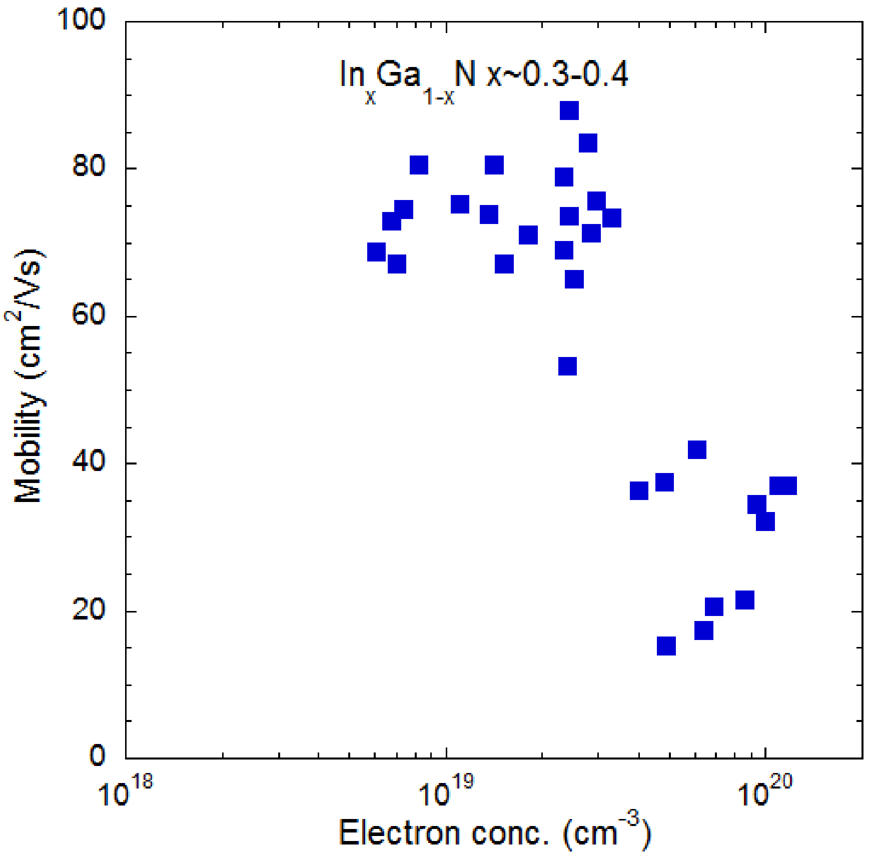
39% In content graded from ~20% to 39%.

Hall: $n = 1.32 \times 10^{19}/cm^3$

$\mu = 55.6\ cm^2/Vs$

Grading of film from low In content to high produces higher quality films

Accomplishments and Progress- Mobility of InGaN alloy films with In content in the 30 to 40% range



Noteworthy achievement for InGaN films:

- In-rich (30 to 40% In) InGaN films
- residual electron concentration in the mid-10^{18} range
- mobility ~80 cm^2/Vs
- thicknesses suitable for use as PEC electrodes

Still actively working to improve:

- film quality
- further reduce the electron concentrations to lower levels to improve performance and stability

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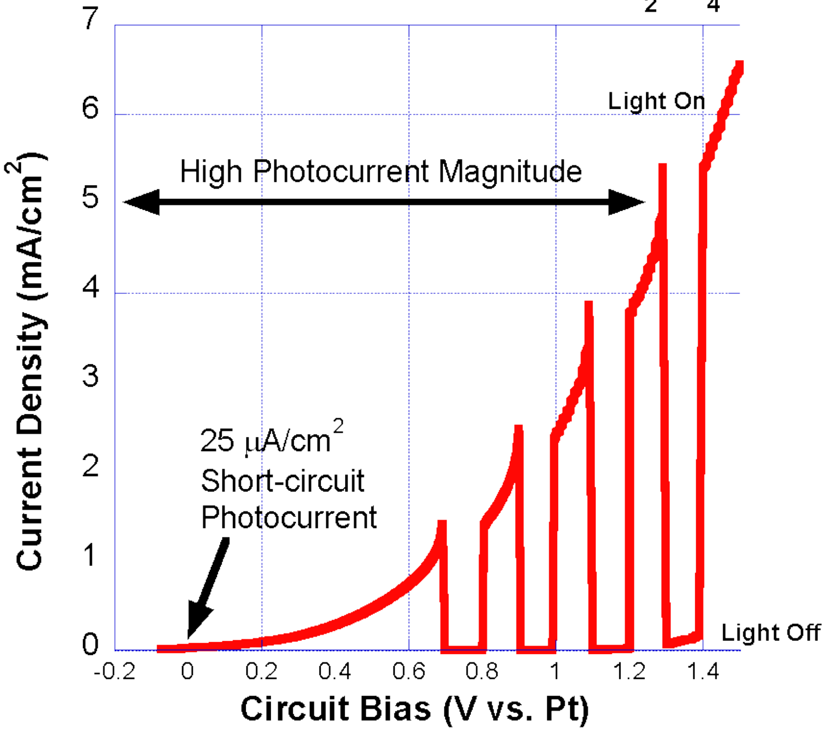
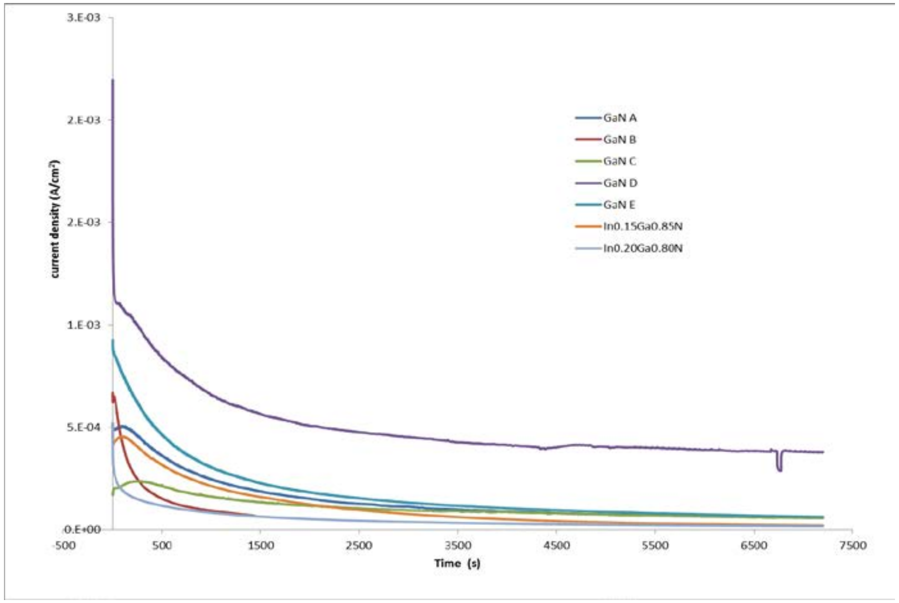
Accomplishments and Progress – PEC Performance of InGaN Under Illumination



Two-electrode Chopped-Light J-V for n-InGaN on Sapphire in 0.5 M H_2SO_4

5mA/cm^2 is about 50% of theoretical AM1.5G max for this ~2.2 eV band gap material

Performance may be increased by using conductive substrates and p-type films



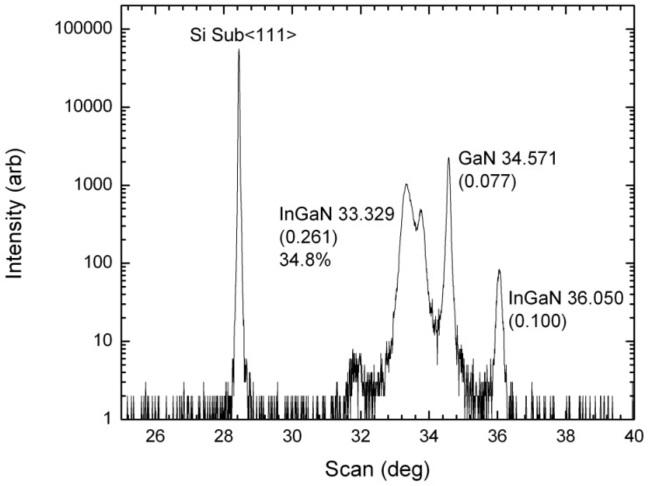
InGaN films show photocurrent at 0 V applied bias, suggesting the interfacial energetics are favorable for spontaneous photoelectrolysis

Both InGaN and GaN films show degradation with time.

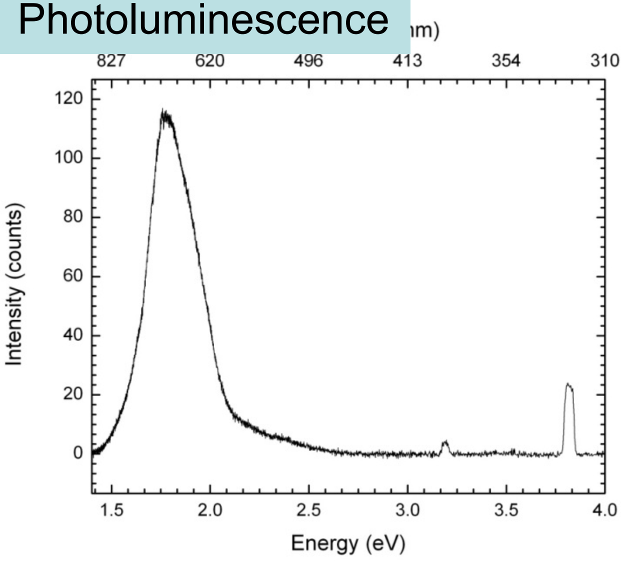
Films are N-polar, and n-type, which may be reason for stability problem.

Accomplishments and Progress - Characterization Results for InGaN on Si(111) ~35% In Content w/ AlN Buffer

XRD measurements

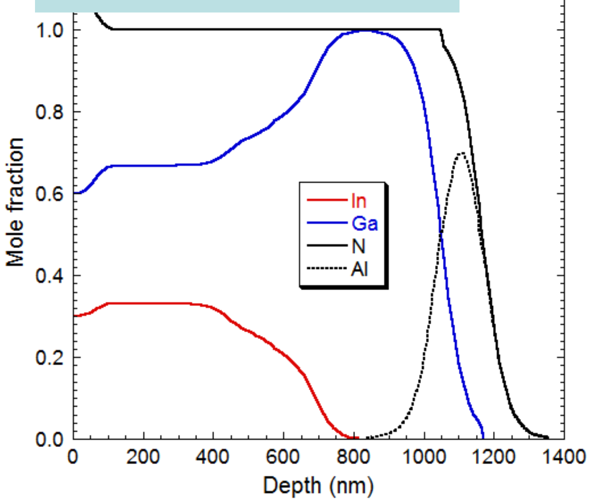


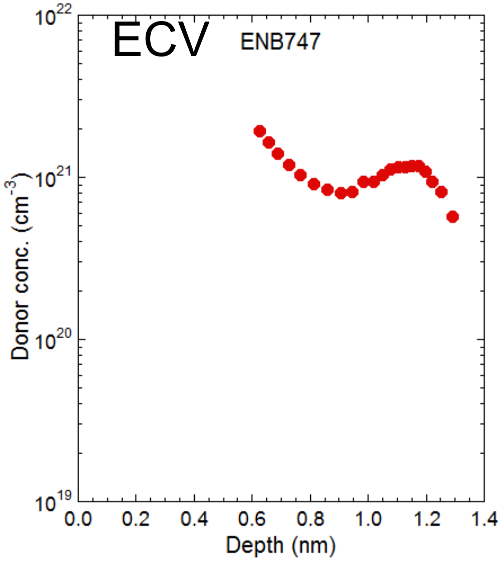
Photoluminescence



Growth of conductive substrate (Si<111>) may lead to improved electrode performance

RBS measurements



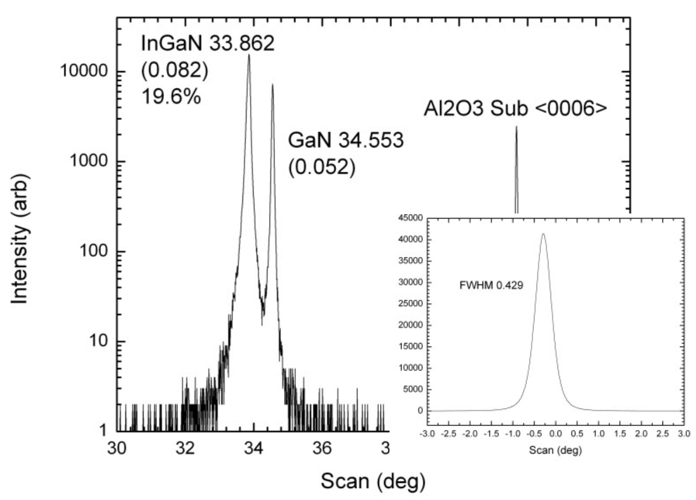


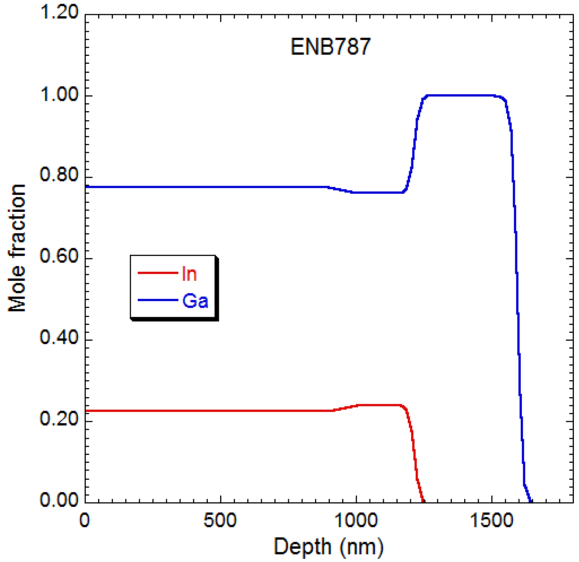
35% In content grown with composition grading

ECV: n-type ~1x10^{21}/cm^3

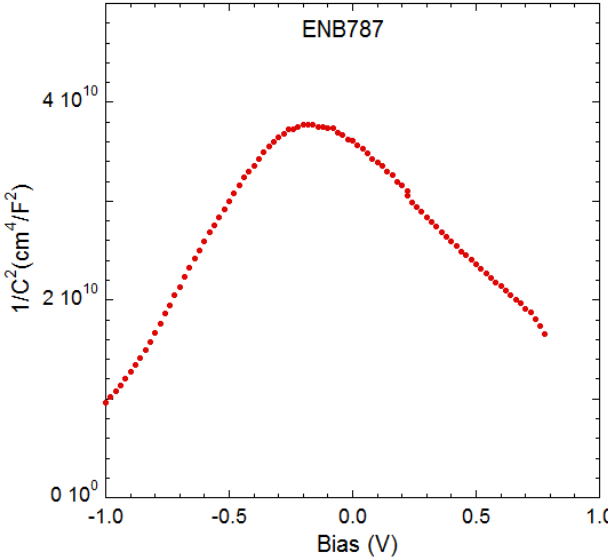
AFM surface roughness: ~30 nm RMS

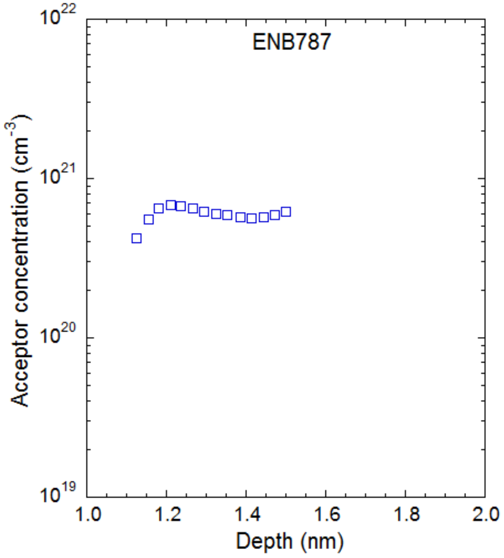
Accomplishments and Progress - InGaN (~20%In) p-type film growth


ENB-787 2 Theta



P-type films, with majority hole carriers, should be more stable under illumination

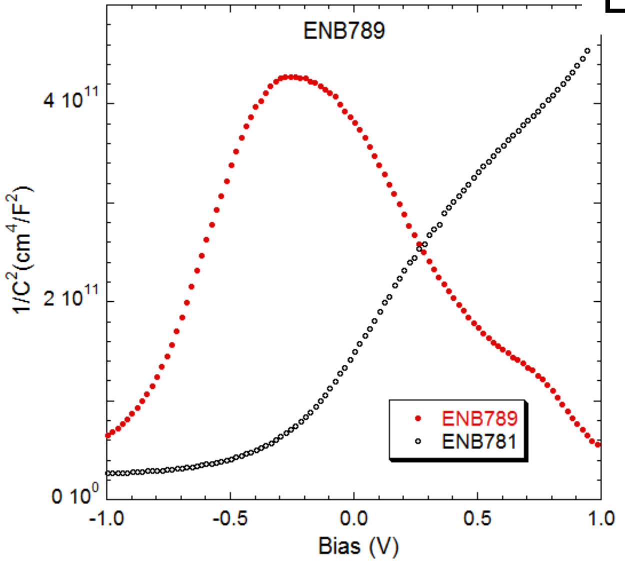




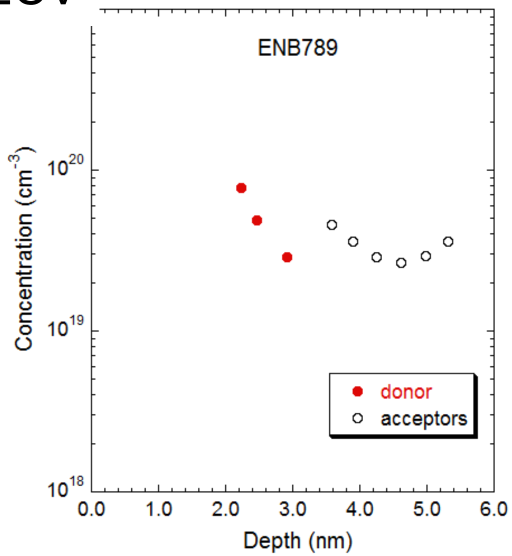
p-InGaN ~20% In:
Mg doped film, PL quenched, as expected

Hall: (p-type)
$p=2.2\times10^{19}/cm^3$(assuming 0.3 μm)
$\mu=2.75\ cm^2/Vs$
~3.5% active acceptors

Accomplishments and Progress - InGaN (~40%In) p-type film growth

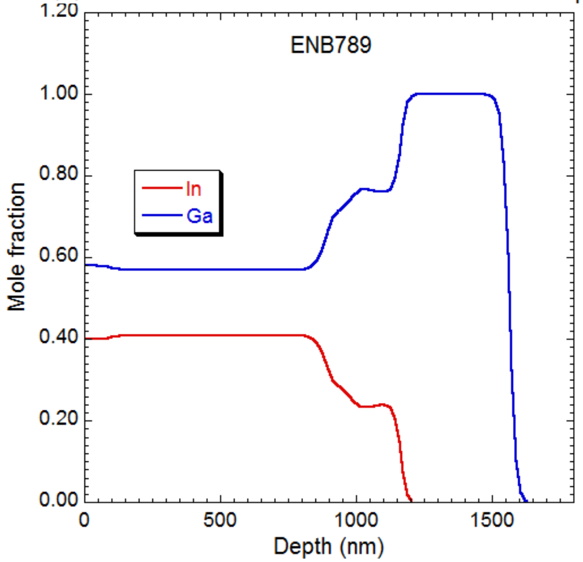


ECV



P-type InGaN films with In content above ~33% have surface electron accumulation, which may offset some of stability improvement gained from p-type doping.

In content may need to be limited to less ideal values

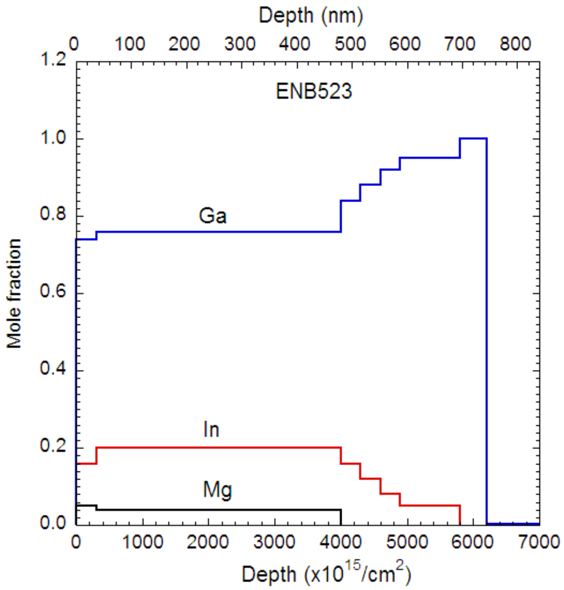


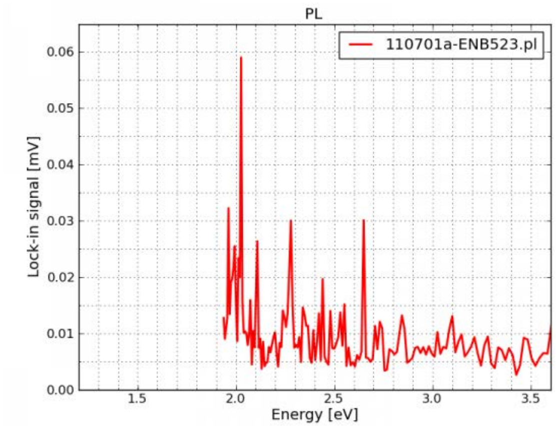
p-type InGaN graded
from 20%In to 40%In
p-InGaN ~40% ~1200 nm

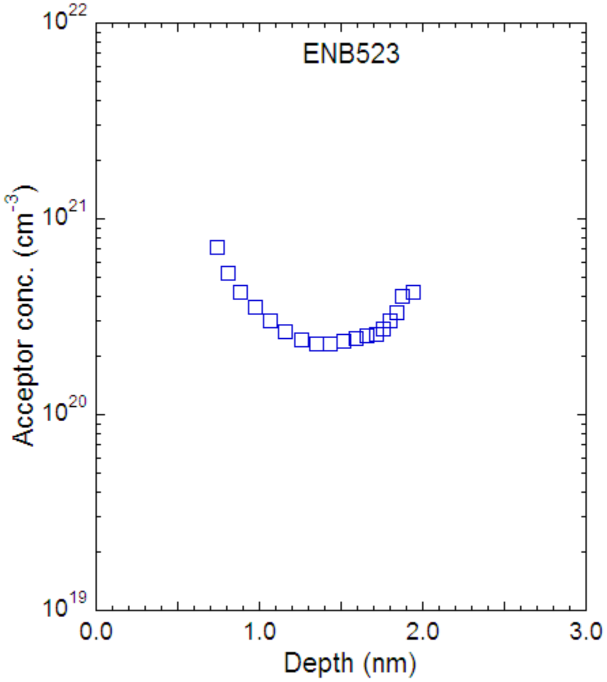
Hall: (n-type)
n=2.25x10^{17}/cm^3
(assuming 1 μm)
μ=4.6 cm^2/Vs

Accomplishments and Progress - 20% InGaN on <111> Si, Mg-doped

- InGaN on <111> Si with AlN and graded InGaN buffer, with graded layer starting at 5% InGaN
- Graded buffer was graded over ~200 nm from 5% InGaN to 20% InGaN
- InGaN film is 500 nm thick
- Film was Mg-doped, shows active acceptors by ECV, PL quenched







Collaborations

Within DOE Hydrogen and Fuel Cells Program

- National Renewable Energy Laboratory (NREL)
  - InGaN films' PEC electrode performance evaluated by John Turner and Todd Deutsch. Team is prime POC for this work, NREL analysis is key for ongoing work on InGaN for PEC H_2 Production

Outside of DOE Hydrogen and Fuel Cells Program

- Lawrence Berkeley National Laboratory
  - Materials characterization on InGaN films including RBS, electrical characterization, and PL performed by team of W. Walukiewicz, K.M. Yu, and L. Reichertz
- Arizona State University
  - C. Honsberg and F. Ponce groups assist with InGaN film growth strategies and provides advanced XRD and PL characterization of films.

Proposed Future Work

Address issue of low photocurrent

- Low photocurrent is most likely related to material quality and use of n-type films. To improve, we will seek to improve material quality and improve p-type doping.

Address issue of electrode stability

- N-polar InGaN material, that is currently produced, is know to corrode in conditions similar to what is used during PEC H_2 production.

Investigate tandem cell configurations for improved efficiency

$In_{.29}Ga_{.71}N$ $In_{.33}Ga_{.67}N$ $In_{.40}Ga_{.60}N$ $In_{.41}Ga_{.59}N$ $In_{.48}Ga_{.52}N$

Mandatory Summary Slide

Relevance:	The objective of this work is to explore the use of Group III Nitrides, specifically InGaN, for Photoelectrochemical Hydrogen Production
Approach:	Utilize unique MBE capability at LANL to produce InGaN with quality, thickness, and In-content not available by conventional film synthesis techniques
Technical Accomplishments:	InGaN films show photocurrent at 0 V applied bias, suggesting the interfacial energetics are favorable for spontaneous photoelectrolysis. However, N-polar InGaN appears to corrode under operating conditions. To address this issue, we have begun to produce p-type material and are investigating strategies for producing more stable, Metal-polar InGaN
Collaborations:	Collaborations with NREL for evaluation of InGaN PEC performance; Collaborations with LBNL and ASU for film characterizations and film growth strategies
Proposed Future Work:	Address issue of low photocurrent; Address issue of electrode stability; Investigate tandem cell configurations for improved efficiency