

**GALLIUM NITRIDE AND INDIUM GALLIUM NITRIDE BASED
PHOTOANODES IN PHOTOELECTROCHEMICAL CELLS**

by

John D. Clinger

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Science with a major in Electrical and Computer Engineering

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ABSTRACT

Photoelectrochemical (PEC) cells are integrated electrolyzers that split water into hydrogen and oxygen, using energy from the sun to create an energy storage medium that does not release undesirable emissions. New materials for both the photoanode and cathode of the device are needed to reduce cost as well as increase efficiency. An effective photoanode must be non toxic, have the ability to split water, absorb most of the solar spectrum, and demonstrate stability in aqueous solutions. Gallium nitride is stable and non toxic and has the ability to split water, but can only absorb a small fraction of the solar spectrum due to having a bandgap of 3.2eV. This thesis focuses on introducing indium into the gallium nitride, lowering the bandgap of the photoanode, while maintaining the desirable characteristics inherent with GaN. GaN, InGaN and GaN/InGaN samples were grown using Metal-Organic Chemical Vapor Deposition (MOCVD) and were electrochemically tested to determine stability as well as performance, through the use of cyclic voltammetry, linear scan voltammetry, and incident photon conversion efficiency measurements. GaN sample behavior resembles that of titanium dioxide, another commonly used material for photoanodes with a similar wide bandgap, primarily producing photocurrent in the ultraviolet (UV) range of the spectrum. InGaN samples with compositions of

$\text{In}_{.10}\text{Ga}_{.90}\text{N}$ and $\text{In}_{.15}\text{Ga}_{.85}\text{N}$ show an increase in photocurrent in the visible spectrum, with n-type doped samples generating more photocurrent than p-type samples of similar composition due to higher resistivity in the p-type samples. GaN/InGaN devices show poor performance, due to recombination at the junction formed between the GaN and InGaN layers at the surface. Further study is required to investigate using higher compositions of indium that have a band gap closer to the theoretical minimum energy needed to split water, 2.0eV.

Chapter 1

INTRODUCTION

The United States is a very large energy consumer, using 100 Quadrillion Btu annually, 21% of the global annual consumption. [1] Fossil fuels currently provide over 85% of all the energy consumed in the U.S., nearly two-thirds of our electricity and virtually all of our transportation fuels. [2] Relying heavily on fossil fuels while convenient and cheap, causes three major problems that are storming to the forefront of important issues in our society:

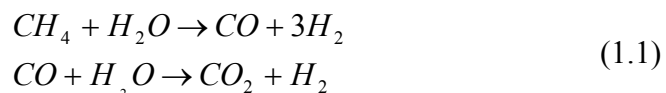
1. Fossil fuels are non-renewable. As the amount of easily accessible oil and natural gas decreases over time prices will rise as supply will not be able to keep up with demand, which is likely to increase significantly with the rapidly developing world.
2. The United States imports a significant portion of its fossil fuel needs from foreign nations. This poses a possible national security threat as well as an extra burden on the economy. [3]
3. Global atmospheric concentrations of CO₂ have increased markedly as a result of human activities since 1750 and now far exceed pre-industrial values determined from ice cores spanning thousands of years. This increase in CO₂ is primarily due to fossil fuel use and could lead to sea level rise, ecological destruction and other climate disasters. [4]

One solution that could turn our country away from fossil fuel dependence is combining renewable energy generation such as solar, wind, and geothermal with a clean energy carrier such as hydrogen. The adoption of fuel cell technology in the

transportation sector would significantly reduce emissions from automobiles, while using fuel cells as a way to store excess energy created during off peak time by solar and wind can help make renewable energy a more stable component of the national power grid.

Fuel cells are more efficient than the internal combustion engine and only produce water as a byproduct. Unfortunately several challenges remain with fuel cell technology, including high cost of materials and durability. Another hurdle is that hydrogen is a very light gas; therefore storage requires large tanks or extremely high pressurization. One final barrier is that there is no current distribution system that can provide the service required for a national adoption of fuel cell vehicles. Despite these challenges large scale fuel cell systems such as solid oxide fuel cells are being successfully used for power backup systems in large hospitals and in industry. Flexibility in the ways that hydrogen can be produced can also promote fuel cell adoption.

Currently 95% of hydrogen produced in the U.S. is made via steam-methane reforming. [5] While the efficiency of this reaction is 80%, it relies on natural gas which is a non renewable source. The reaction emits a large amount of CO₂ which does not help solve the climate change problem. Equation 1.1 shows the chemical reaction of steam-methane reformation.



Using electricity created by renewable energy to perform electrolysis is a carbon free pathway to create hydrogen. Electrolysis is the decomposition of water into oxygen and hydrogen gas due to an electric current being passed through the water.

Commercial electrolyzers are between 50-70% efficient. Total efficiency of a 20% efficient PV module powering a 70% efficient electrolyzer is 14%. At this efficiency hydrogen generation from renewable sources is not a viable commercial option for direct large scale production, however using this technology as an energy storage mechanism for the grid could provide a way to capture excess energy produced during off peak times by sources such as wind power. This low cost hydrogen can be stored for later use.

A closer look into using power from the sun to split water reveals the option of directly generating hydrogen in one chemical reaction using sunlight rather than electricity to power an electrolyzer. In this scenario, a photo catalyst absorbs photons and chemically splits water into hydrogen and oxygen. This device is called a photoelectrochemical cell.

1.1 Photoelectrochemical Cells

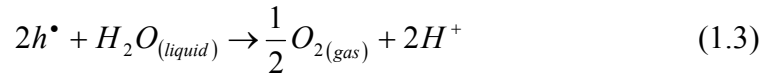
Photoelectrochemical (PEC) cells are cells that replace a solid-state p-n junction with a solid-liquid junction. A working electrode (photoanode) and a counter-electrode (cathode) are immersed in an aqueous electrolyte. The photoanode absorbs light and provides the energy for electrochemical reaction at its surface. There are two

types of PEC cells, photosynthetic and regenerative cells. Photosynthetic PEC cells absorb light and activate two redox reactions at the photoanode and the cathode. The main focus of this cell is to electrochemically produce desired byproducts. Regenerative PEC cells continually renew the cycle of oxidation and reduction within the electrolyte, with the purpose of producing current to power a load. [6]

Photosynthetic cells can be used to form hydrogen and oxygen from water. In this cell, incident light causes intrinsic ionization of the photoanode over the band gap, forming electrons in the conduction band and holes in the valance band. This is shown in Equation 1.2.



In this equation, h is Planck's constant, ν the frequency of light, e' the electron and $h^{\bullet}$ the hole. This initial reaction occurs when the energy of the incident photons ($h\nu$) is equal or larger than the band gap of the photoanode. The holes produced in this reaction cause surrounding water molecules to split into hydrogen ions and gaseous oxygen. This process takes place at the photoanode/electrolyte interface.



The hydrogen ions formed in Equation 1.3 travel though the electrolyte to the cathode, while the electrons travel from the photoanode and external circuit to the cathode. The migration of electrons to the cathode causes a reduction of the hydrogen ions into gaseous hydrogen shown in Equation 1.4.



The overall reaction in the photosynthetic PEC cell takes place when the energy of the photon ($h\nu$) is equal to or greater than 1.23eV, which is the required electromotive force needed for water splitting. This overall reaction is given by Equation 1.5 and can be seen in Figure 1.1.

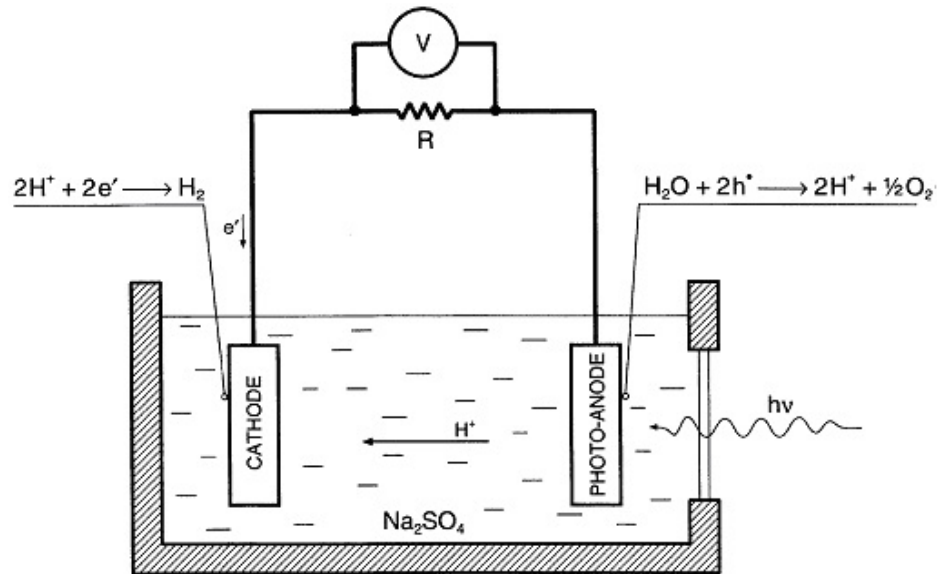
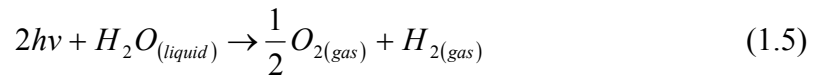


Figure 1.1: Diagram of a photoelectrochemical cell (PEC): Bak, T. et al. *Int J Hydrogen Energy* 27, p. 997; and Macmillan Publishers Ltd: Fujishima, A. and Honda, K. *Nature* 238, p. 37, copyright 1972.

The following Figure 1.2 shows the band structure of a PEC cell with an n-type photoanode. In this schematic, the photoanode valence band E_v , and conduction

band E_c are separated by the band gap E_g , with Fermi levels E_F and work functions ϕ given for both the photoanode and the cathode. In the center reduction potentials of the H^+ and O_2 half reactions are shown, with a necessary electromotive force of 1.23V required to split water.

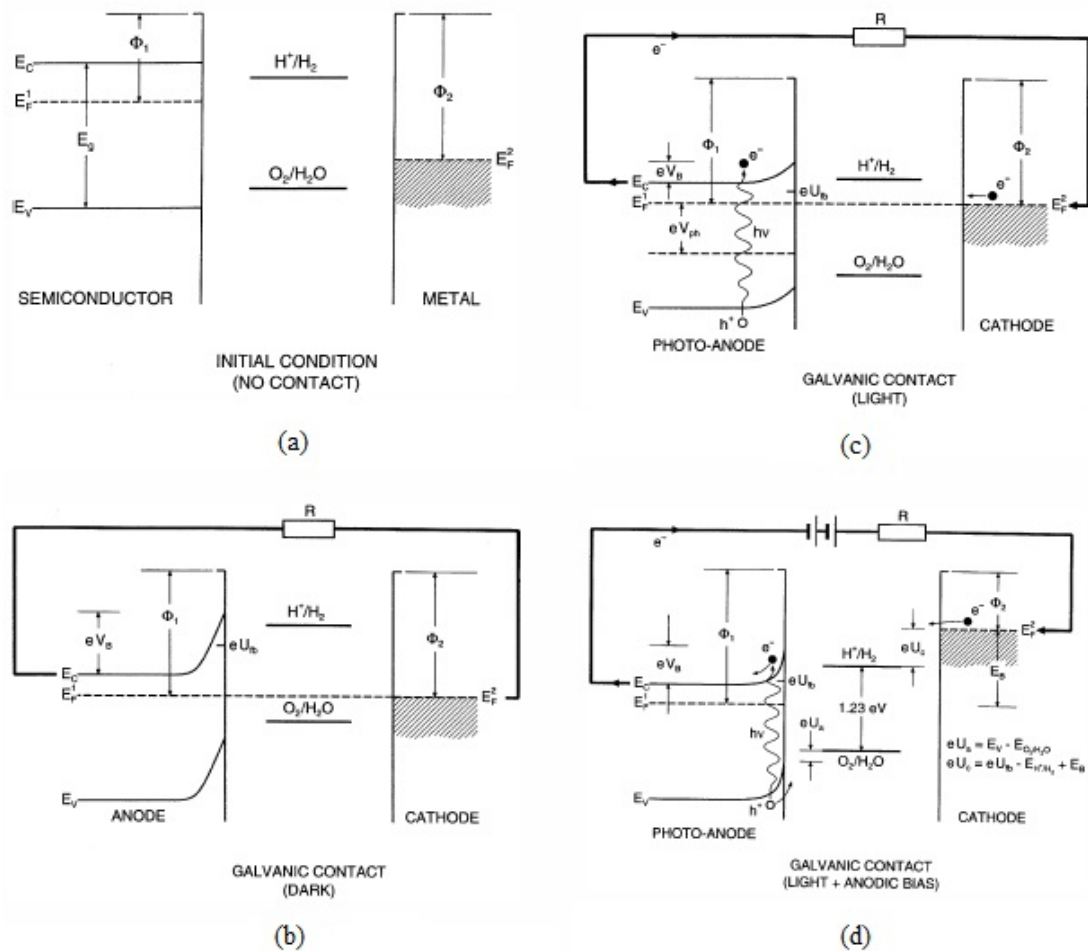


Figure 1.2: Energy band diagram for a photoelectrochemical cell: Bak, T. et al. *Int J Hydrogen Energy* 27, p. 998; and Macmillan Publishers Ltd: Fujishima, A. and Honda, K. *Nature* 238, p. 38, copyright 1972. Panels a-d show the process of water splitting through light exposure and applied bias

Panel (a) shows the energy diagram before galvanic contact is made between the two electrodes. Panel (b) shows contact between the two electrodes in the absence of light, resulting in electronic charge transfer from work function of the photoanode to the work function of the metal until the Fermi energies equalize. This action changes the electrical potential of the photoanode V_B causing band bending. This band bending causes the development of a charged depletion layer at the photoanode surface which prevents additional electron flow once equilibrium is reached. Water splitting can not occur because the H^+/H_2 energy level is above E_F of the cathode. Panel (c) shows light exposure, which lowers the H^+/H_2 potential, but still not below E_F of the cathode. Photo carriers are generated by all photons with $h\nu$ greater than E_g but water splitting still can not occur. Panel (d) shows light exposure combined with an applied bias on the photoanode. In this case the E_F of the cathode rises above the H^+/H_2 energy level, generating electron hole pairs that are split by the difference of potential in the depletion region. Electrons travel through the circuit and reduce H^+ ions at the cathode creating hydrogen. [7]

1.2 Photoanode Material Requirements

The photoanode is the device that allows hydrogen generation to occur in a PEC cell. The optimal photoanode material must fulfill the following requirements:

1. The material must be stable in aqueous solution. [8]
2. The band gap of the device must be large enough to split water ($E_g \geq 1.23\text{eV}$).

3. The conduction and valence band edges must straddle the H^+/H_2 and $\text{O}_2/\text{H}_2\text{O}$ redox potentials.

Though the minimum band gap required to split water is 1.23eV, in practice a higher band gap is required due to losses from the following:

- Polarization within the PEC cell
- Recombination of the photo-excited electron-hole pairs in the photoanode
- Resistance in the electrodes
- Resistance in the electrical connections
- Voltage losses at the contacts

The estimated total of these losses is approximately 0.8eV. [7] This loss creates a practical photoanode band gap minimum of 2.0eV to split water. Figure 1.3 shows the available solar energy spectrum as well as the area of internal losses in range J_2 and the target area of photoanode improvement in range J_3 . The range of bulk TiO_2 in J_4 matches the area of bulk GaN, both having a band gap of 3.2eV.

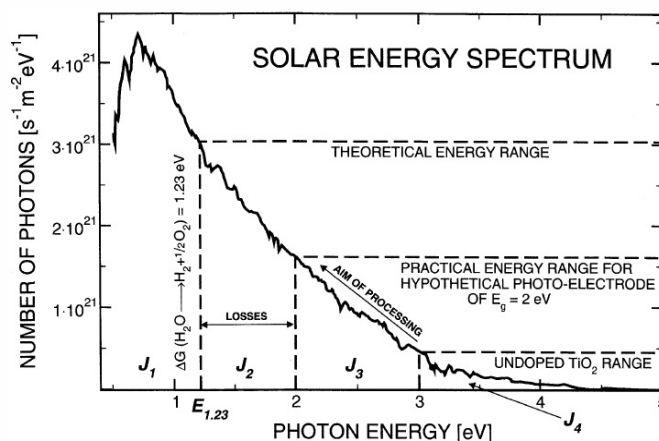


Figure 1.3: AM 1.5 Solar Energy Spectrum showing power available for water splitting: Bak, T. et al. *Int J Hydrogen Energy* 27, p. 999; and Macmillan Publishers Ltd: Fujishima, A. and Honda, K. *Nature* 238, p. 39, copyright 1972.

The band gap of GaN prohibits absorption of 95% of the solar spectrum which is not ideal for maximizing excitation of photocarriers. This high band gap is directly responsible for GaN stability in aqueous solution, as band gap size is related to bond strength in the material. [9] For this reason materials with lower band gaps are generally not suitable for photoanodes due to material degradation. Figure 1.4 shows the band edges of InGaN quantum dots vs. popular TiO₂ photoanode.

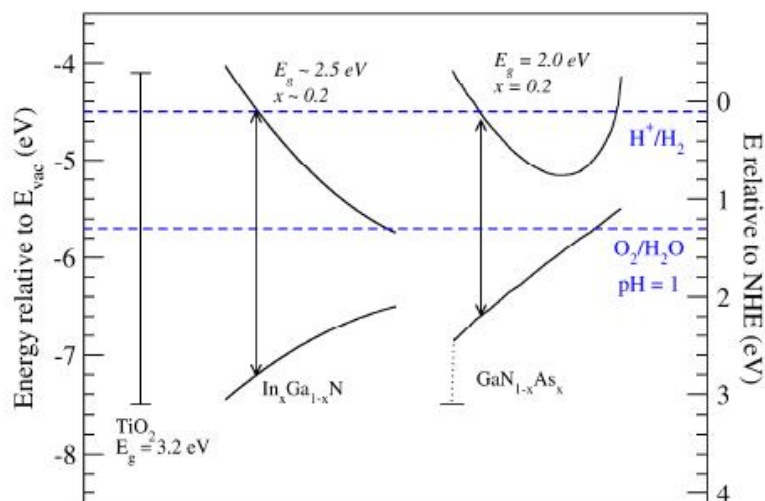


Figure 1.4: Comparative band diagrams for TiO₂/InGaN/GaNAs photoanodes:
Joel W. Ager III, W. Walukiewicz, K. M. Yu, W. Shan, J. Denlinger, J. Wu,
Material Research Society, 884E

There is a large area of possible improvement in GaN photoanodes if the band gap of the material can be lowered, while maintaining stability in aqueous solution. This is achievable with the introduction of indium into the GaN samples.

1.3 Properties of Gallium Nitride and Indium Gallium Nitride

Properties	
Molecular formula	GaN
Molar mass	83.73 g/mol
Appearance	yellow powder
Density	6.15 g/cm ³
Melting point	>2500°C
Solubility in water	Reacts
Band gap	3.2 eV (300 K)
Electron mobility	440 cm ² /(V*s) (300 K)
Thermal conductivity	1.3 W/(cm*K) (300 K)
Refractive index	2.429
Structure	
Crystal structure	Wurtzite
Space group	$C_{6v}^4-P6_3mc$
Coordination geometry	Tetrahedral

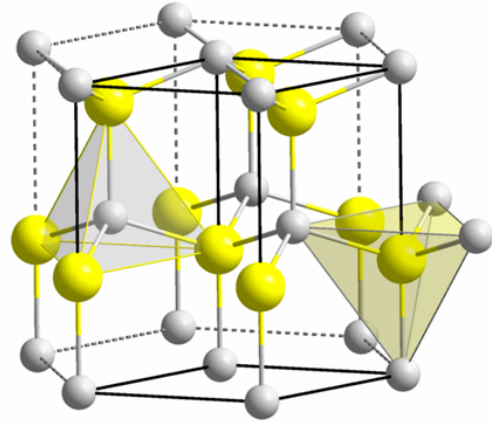


Table 1.1: Properties of GaN

Figure 1.5: GaN Crystal Structure

Gallium Nitride (GaN) is a III/V semiconductor that has a wurtzite crystal structure. It is a very hard, mechanically stable material with a band gap of 3.2eV. GaN can be doped with manganese to create p-type samples or silicon to create n-type samples. The electrochemical properties of GaN are very similar to TiO₂, with a wide band gap (3.2eV) and very high stability in aqueous solution. When indium is introduced into the GaN growth process indium gallium nitride (In_xGa_{1-x}N) is formed. InGaN alloys typically have an In/Ga ratio between .02/.98 and 0.3/0.7. The range of device band gaps that can be created with InGaN span from 3.2eV in pure GaN, to 0.7eV which is pure InN. [10] InGaN has a tendency to form In-rich and Ga-rich clusters due to phase separation, but this undesirable effect can be minimized with

careful growth controls. [11] Other materials such as TiO_2 and ZnO are commonly used in photoanode research but have not yet shown the band gap levels that InGaN can allow. [12]

1.4 Project Overview

In this study, we proposed to study GaN and InGaN thin films grown on Al_2O_3 wafers, by the process of metal-organic chemical vapor deposition, and their use as photoanodes in photoelectrochemical cell systems. Samples with 0%, 10% and 15% indium composition were grown to observe the level of increased photo response generated by lower band gap material. Both n-type and p-type samples were grown with the appropriate ohmic contacts on the surface. Samples were cut to 1x1cm size for uniformity and to aid in making consistent efficiency calculations. The GaN and InGaN samples were tested for stability in .1M NaOH . The thin films were characterized electrochemically through the use of cyclic voltammetry, linear scan voltammetry and incident photon conversion efficiency to determine photoanode activity and photo current levels produced by the photoanode. The goal is to create devices with lower band gaps to capture a larger portion of the solar spectrum, while maintaining the necessary electromotive force to split water.

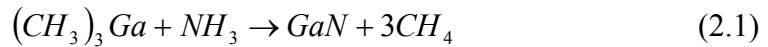
Chapter 2

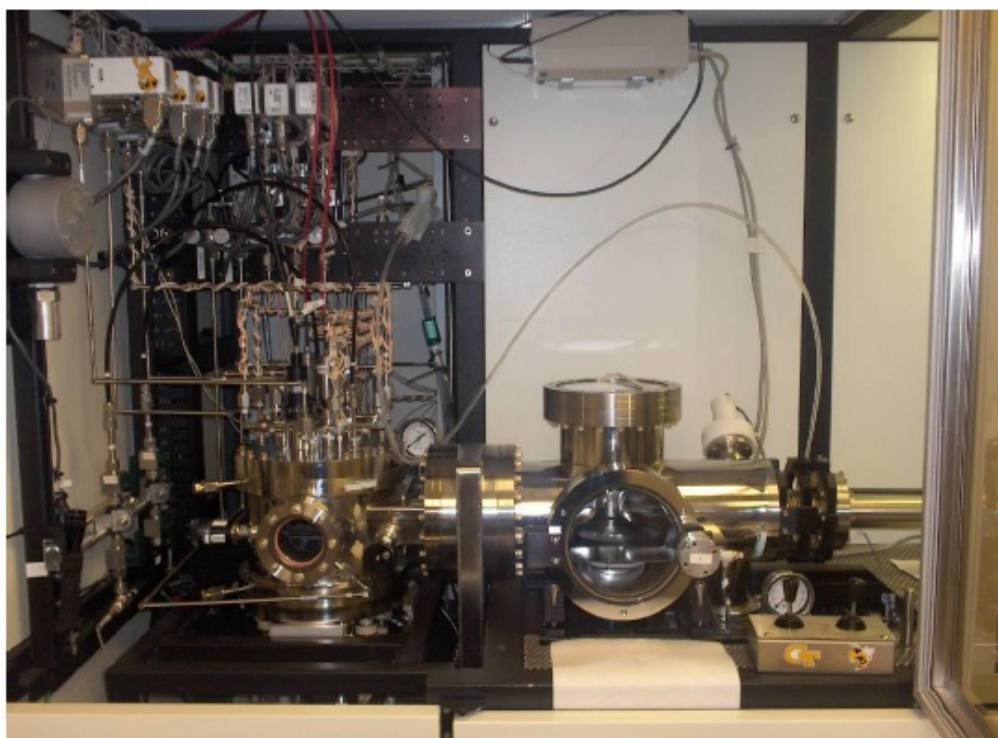
EXPERIMENTAL

2.1 Epitaxial Growth and Fabrication of GaN and InGaN Photoanodes

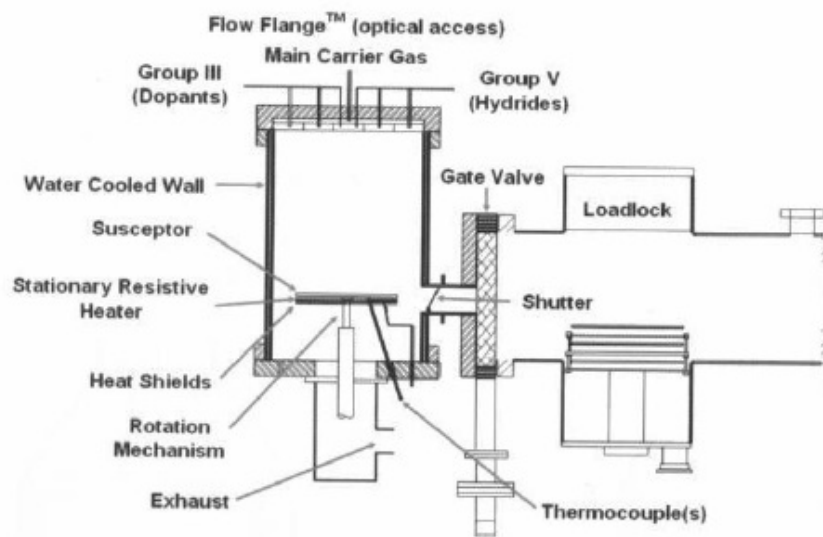
2.1.1 Metal-Organic Chemical Vapor Deposition Growth

Metal-organic Chemical Vapor Deposition (MOCVD) is the most commonly used technique for growing III-V semiconductor based solar cells [13]. The growths for GaN and InGaN photoanodes are performed in an Emcore MOCVD D-125 rotating disk reactor with a short jar configuration shown in Figure 5.1. A carrier gas, usually H_2 , is used to transfer the precursors into the reactor as they have a high vapor pressure at room temperature. Trimethylgallium (TMGa) $\{(CH_3)_3Ga\}$ is the common precursor used for the gallium source and Ammonia (NH_3) is used as the nitrogen source. The precursor gases are introduced and mixed in the reaction chamber. Temperature and pressure drives the reaction of the gases to form GaN. The basic reaction is described in Equation 2.1.





(a)



(b)

Figure 2.1: (a) Photograph, (b) schematic of Emcore MOCVD reactor

This reaction is utilized to create the GaN template on an Al_2O_3 substrate. This GaN layer is grown at 1050°C at a growth rate of $2\text{ }\mu\text{m/hr}$ to yield a high quality bulk. All of the InGaN layers were grown on these $2\text{ }\mu\text{m}$ thick GaN templates.

The primary variables of InGaN epitaxial growth are the precursor gas flow rates, which dictates the III-V ratio and growth rate; temperature which governs the indium composition in the InGaN, and the epitaxial layer thickness. Trimethylindium {TMIn} is used as the precursor gas source of indium. These layers are grown at 720°C with a TMGa flow rate of 30 sccm and a TMIn flow rate of 200sccm. The increased flow rate of TMIn limits the phase separation in the InGaN, increasing the quality of the sample while maintaining the desired indium composition. Phase separation of InGaN is also caused due to strain relaxation at higher epitaxial thicknesses. Therefore controlling thickness is another method to reduce phase separation in the sample.

In both GaN and InGaN layers, Bis cyclopentadienyl magnesium (Cp_2Mg) $\{(\text{C}_5\text{H}_5)_2\text{Mg}\}$, is used to carry Mg, which is a p-type dopant, while silane $\{\text{SiH}_4\}$, is used to carry Si, which is the n-type dopant during the growth. P-type samples require Mg-activation for InGaN samples. This activation requires a standard anneal of 800°C for 4 minutes in a N_2 Rapid Thermal Annealer. Due to the low growth temperature of InGaN, such an intense anneal causes lattice rearrangement resulting in defects. Lower anneal temperatures can be utilized to reduce defect occurrence if the anneal

time is increased accordingly. The appropriate anneal temperature is at least 100 °C less than the growth temperature which was 720 °C. Three optimized anneal conditions for InGaN are presented in Table 2.1, with condition three being the most effective for reducing defects.

	Temperature	Time	N ₂ flow rate
1	800 °C	4 minutes	2 Liters/min
2	700 °C	20 minutes	2 Liters/min
3	625 °C	30 minutes	2 Liters/min

Table 2.1: Optimized anneal conditions for InGaN contacts

2.1.2 Cleaning Techniques

Hydrofluoric Acid is a common surface treatment for GaN and InGaN surfaces. This technique uses a concentration of 15% HF and exposing the sample to a 20 second dip. This process is very effective in removing oxygen from the surface but not as effective in removing carbon. Another approach is the use of H₂SO₄:H₂O₂ (3:1), also known as piranha solution. With this solution a 10 minute exposure removes carbon residue from the sample, but leaves a substantial oxide layer. This layer can be removed with a brief anneal. [14] After sample contacts have been grown, a standard acetone – methanol – water rinse followed by N₂ blow-drying is used to clean any grease, dust or organic impurities off the sample. This process is not as effective as the previously mentioned techniques but is sufficient for electrochemistry work.

2.1.3 Application of Sample Contacts

Ohmic contacts are required on the surface of the photoanode to collect current in the cell and transport it through the circuit. Square 2x2mm contact pads were grown near the corner of the photoanode surface. Figure 2.2 shows the location of the contacts.

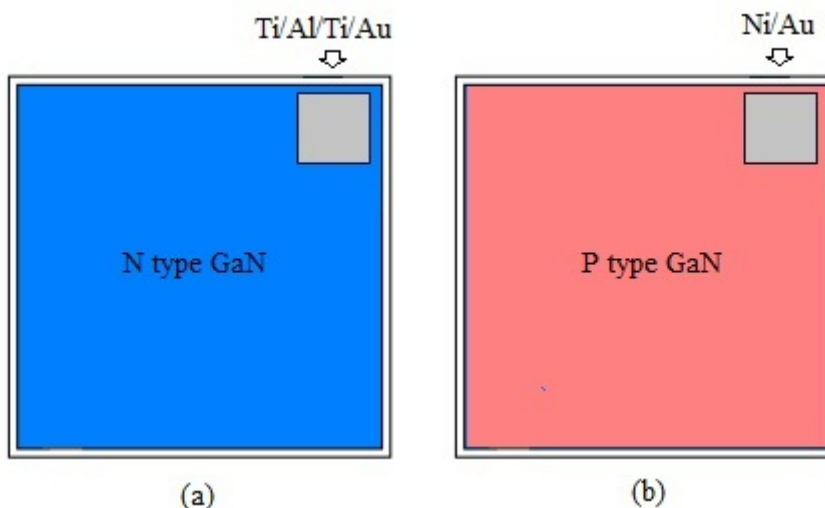


Figure 2.2: Contact schematics for (a) n-type and (b) p-type GaN samples

The n-type ohmic contacts are a four layered and composed of Titanium, Aluminum and Gold. P-type contacts are composed of a layer of Gold covered by a layer of Nickel. The layers of both contacts are grown using electron beam evaporation, a form of physical vapor deposition where source substrate metal is heated to its boiling point using an electron beam under vacuum conditions.

2.2 Electrochemistry Setup

2.2.1 Photoelectrochemical Cell Setup

The setup for the electrochemical measurements is shown in Figure 2.3 below. The cell is a custom made Teflon casing with a fused silica window. The typical three-electrode setup includes a saturated calomel reference electrode (SCE), a working electrode, in this case the GaN or InGaN photoanode, and counter electrode which was a thin platinum wire in this setup. Cell bias is controlled using a Pine Instruments model AFRDE three-electrode potentiostat. Cell bias is controlled using a Pine Instruments model AFRDE three-electrode potentiostat.

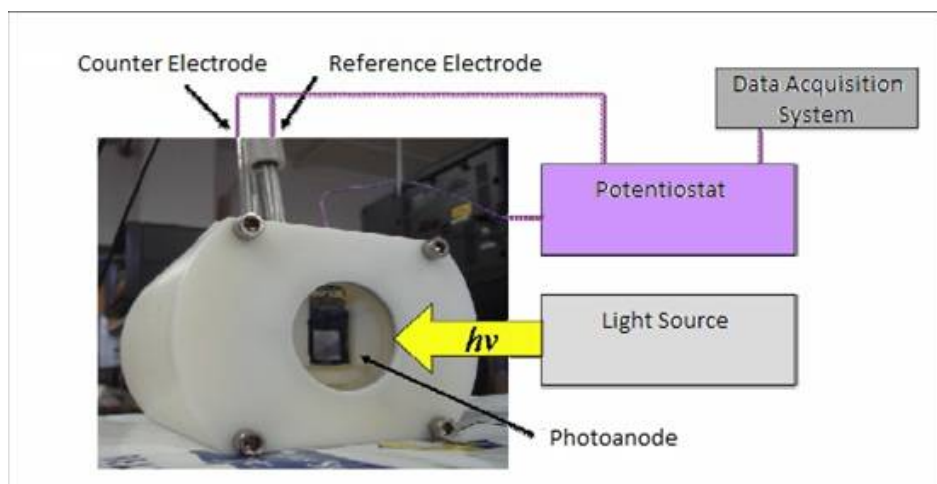


Figure 2.3: Photoelectrochemical Cell Setup

The light source used in these experiments was a monochromatic excitation source (Model RF-5301) that was used to observe photoresponse at specific wavelengths and energy levels. Incident power from the light source was measured using a Newport 70260 radiant power light meter.

The electrolyte used in the cell was 0.1M NaOH. It has been observed that using a higher molarity degrades photoanode performance over a four hour period. [12] The 0.1M NaOH used in this cell was made in a 10-L batch with a pH of 13. Prior to each experimental run, the electrolyte was de-gassed by a combination of vacuum pumping and sonication. Inert argon gas was bubbled through the electrolyte during electrochemical experiments through the sealed cell. This technique reduces dissolved oxygen in the cell and also perturbs the solution to prevent double layer buildup on the electrode surfaces. [15]

2.2.2 Photoanode Electrochemical Preparations

The 1x1cm GaN and InGaN photoanodes were first attached to 3x3cm soda-lime glass using silicone sealant. Once the sealant dried, a thin layer of silicone sealant was applied around the edge of the photoanode/glass interface to eliminate reactions on the side of the electrode. The next step was contacting the copper wire to the contact pad using high purity silver paste. Once the paste dried, a layer of sealant was applied over the contact area as well as up the copper wire to protect the circuit from aqueous surroundings. Finally a thick layer of sealant was applied around the edges of the glass backing to enable the photoanode to attach firmly next to the quartz window inside the cell setup. Figure 2.4 displays the photoanode electrochemical preparations.

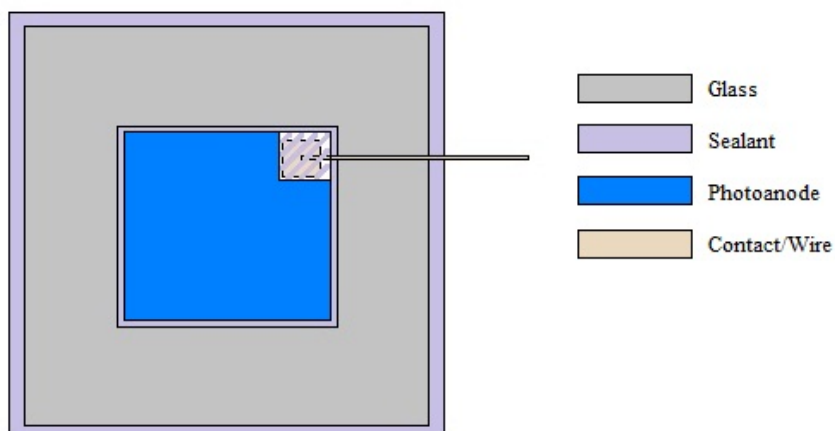


Figure 2.4: Photoanode Prepared for Electrochemistry Experimentation

2.3 Characterization and Electrochemical Methods

2.3.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy scans a sample with a high-energy beam of electrons in a raster scan pattern. The emitted electrons interact with atoms in the sample which produces signals that can be used to observe topography, composition and conductivity of the sample. Scanning electron microscopy was used to observe cross sectional views of GaN and InGaN photoanodes to measure changes in thickness after exposure to NaOH. Samples were cut using a diamond tipped scribe and then snapping the sample for a sharp edge. Carbon tape was used to attach the samples to a mount to help increase conductivity in the sample. Images were taken using a JEOL scanning electron microscope, model JSM 7400F. An accelerating voltage of 3kV was required to obtain clear images of p-type samples due to their highly resistive nature.

2.3.2 Cyclic Voltammetry (CV)

Cyclic Voltammetry involves increasing the photoanode potential linearly versus time from a minimum point to a maximum point. Once the maximum set potential is reached the photoanode potential is inverted and is lowered to a set minimum. This process is repeated three times because the first sweep often does not match the following sweeps due to mass transfer effects. [16] Argon gas bubbling in the cell limits this effect.

CV studies were performed by starting at 0V vs. SCE and sweeping upward to +1V, then down to -1V, and then back to 0V. This sweep was repeated three times in succession at a scan rate of 10 mV/s. CV curves were collected for each sample under three conditions; photoanode under no illumination, UV illumination, and visible light illumination.

2.3.3 Linear Scan Voltammetry

Linear Scan Voltammetry (LSV), commonly referred to as “on-off” voltammetry, is a special form of CV where only one voltage sweep from -1V to +1V vs. SCE is recorded at 10mV/s intervals. During the scan, the experimenter manually opens and closes the spectrometer shutter every 0.05V. This produces an “on-off” effect. The purpose of this scan is to enable the separation of the dark current and photocurrent of the photoanode at desired illumination levels. LSV sweeps were conducted under UV

and visible light exposure. The total current density of the device j is composed of dark current and photocurrent, shown in Equation 2.2.

$$j_{tot} = j_{dark} + j_{photo} \quad (2.2)$$

We can use the total current density to determine hydrogen generation reaction rate r in Equation 2.3.

$$r(molH_2/cm^2) = \frac{j_{tot}(A/cm^2)}{nF} \quad (2.3)$$

2.3.4 Incident Photon Conversion Efficiency (IPCE)

This technique allows the evaluation of quantum efficiency at each wavelength. It compares the ratio of photo-generated electrons to the number of incident photons at a given wavelength. This relationship is shown in Equation 2.4.

$$IPCE = \frac{j_{photo} N_A hc}{\lambda PF} \quad (2.4)$$

In this equation j_{photo} is the photocurrent density in A/cm^2 , N_A is Avogadro's number, h is Planck's constant, c is the speed of light, λ is the wavelength in meters, P is the incident power in W/cm^2 and F is the Faraday constant.

Photocurrent data was collected at five applied potentials, V_{bias} : 0V, +0.25V, +0.5V, +0.75V and +1V vs. SCE. Data sets at each voltage consisted of current I at wavelengths 260-700nm, in 20nm intervals. Each interval consisted of a short data

recording with the shutter starting shut and then being opened for approximately 20 seconds and then closing the shutter. Total current i_{tot} was taken at $t = 0$ the instant after the shutter was opened. This can be seen in Figure 2.5. Photocurrent i_{photo} or density j_{photo} was determined using Equation 2.2 and then was used to complete the IPCE calculations in Equation 2.4.

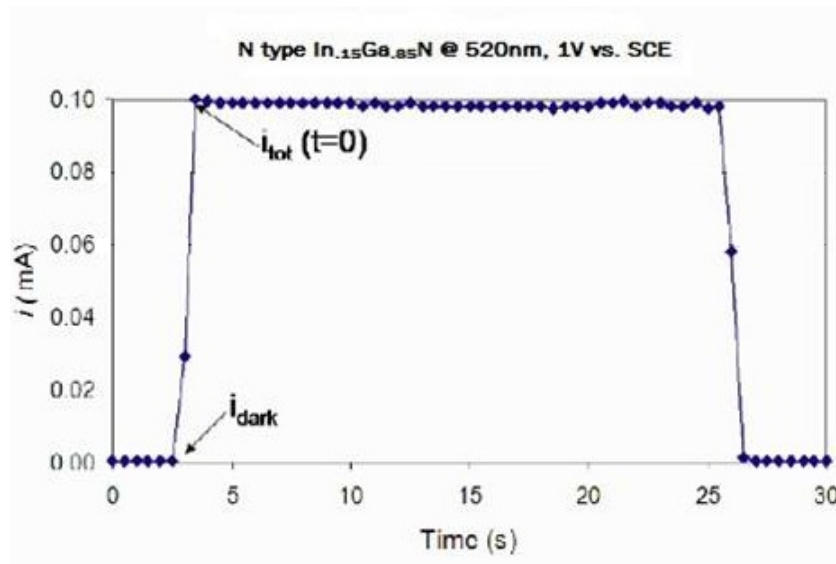


Figure 2.5: Single Interval of IPCE Measurement

Chapter 3

RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy

SEM was used to observe sample thickness before and after prolonged exposure to .1M NaOH. Images of the GaN samples were taken in 3 different areas along the cross-section of the sample before and after NaOH exposure to observe noticeable changes in thickness. Figure 3.1 below shows a cross-sectional view of an n-type pure GaN sample after 4 hours of exposure to NaOH under UV light. Thicknesses in both n-type and p-type GaN did not noticeably change after exposure to the NaOH solution, verifying that stability has been maintained. Surface images were also taken to detect the presence of major defects on the surface of the samples after NaOH exposure. The samples remained smooth, with no major defects recorded on any of the tested GaN samples.

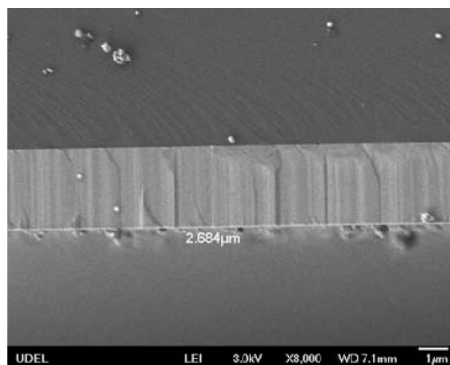


Figure 3.1: Cross-sectional view of n-type GaN sample after NaOH exposure

3.2 Cyclic Voltammetry

Cyclic voltammetry plots are shown in figures 3.2 through 3.8, labeled by their sample type and composition. Curves representing dark conditions are marked in black, UV illumination in red and visible light in blue. Dark current produced no electrochemical results in any of the samples tested. Photoanode activity in these figures is represented by the portion of the curves above the y-axis, while cathodic activity is represented by the area under the y-axis. Since we are studying the photoanode in the system, negative values are less important than those above the y-axis.

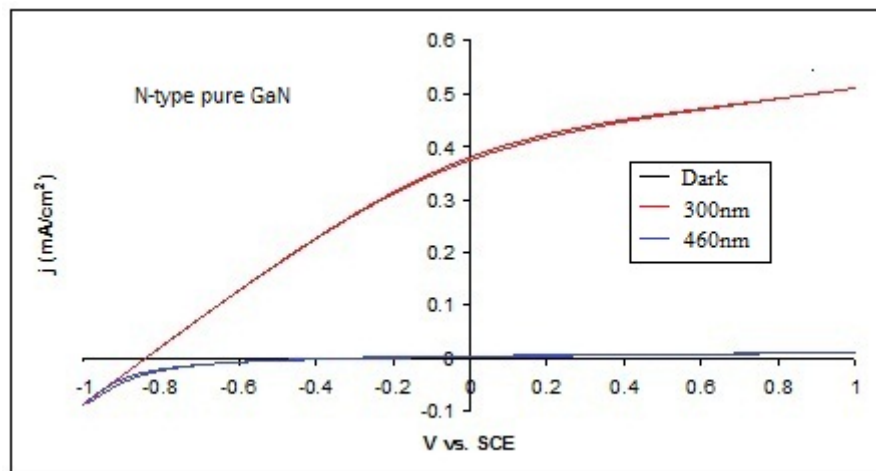


Figure 3.2: CV of N-type pure GaN Sample

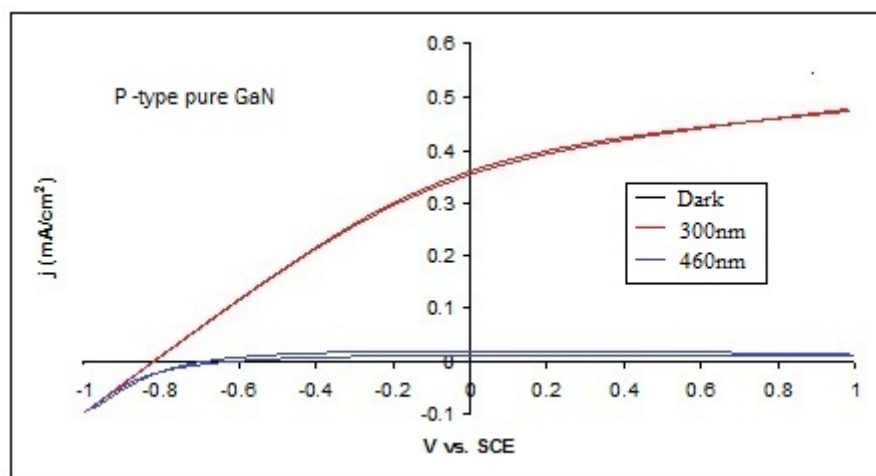


Figure 3.3: CV of P-type pure GaN sample

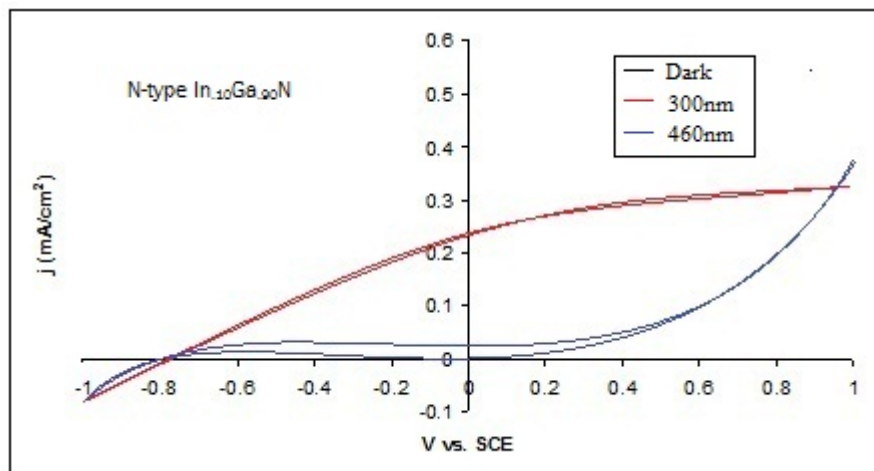


Figure 3.4: CV of N-type $\text{In}_{0.10}\text{Ga}_{0.90}\text{N}$ sample

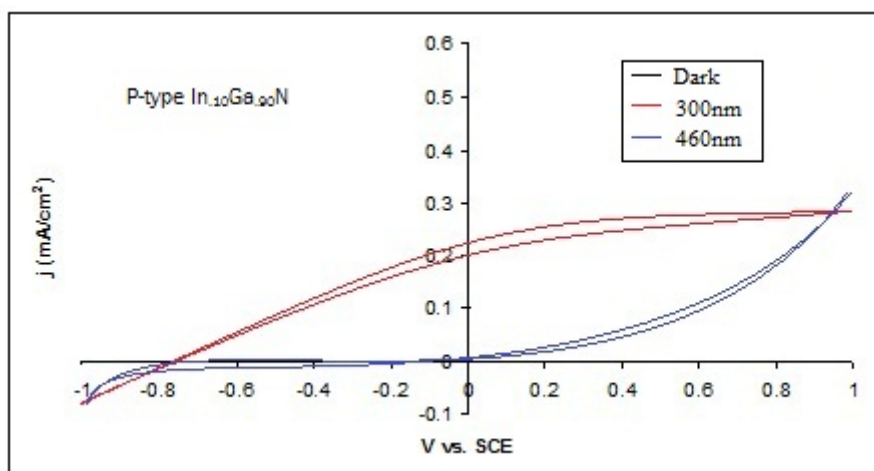


Figure 3.5: CV of P-type $\text{In}_{0.10}\text{Ga}_{0.90}\text{N}$ sample

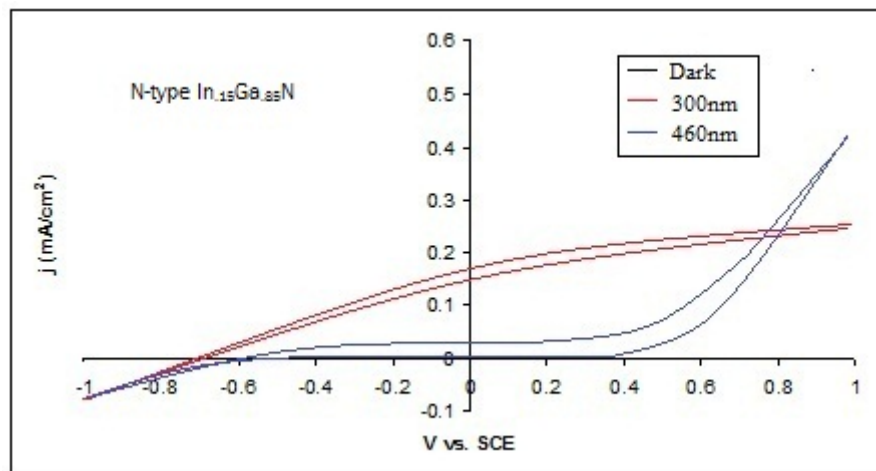


Figure 3.6: CV of N-type $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$ sample

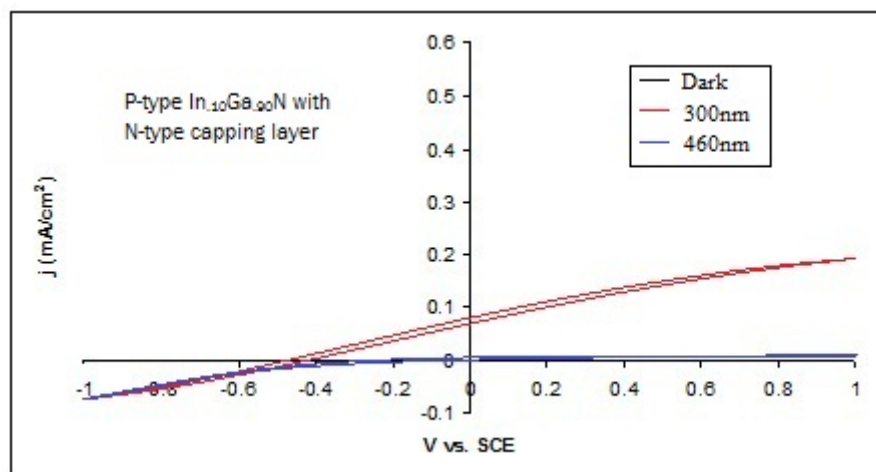


Figure 3.7: CV of P-type $\text{In}_{0.10}\text{Ga}_{0.90}\text{N}$ with N-type capping layer

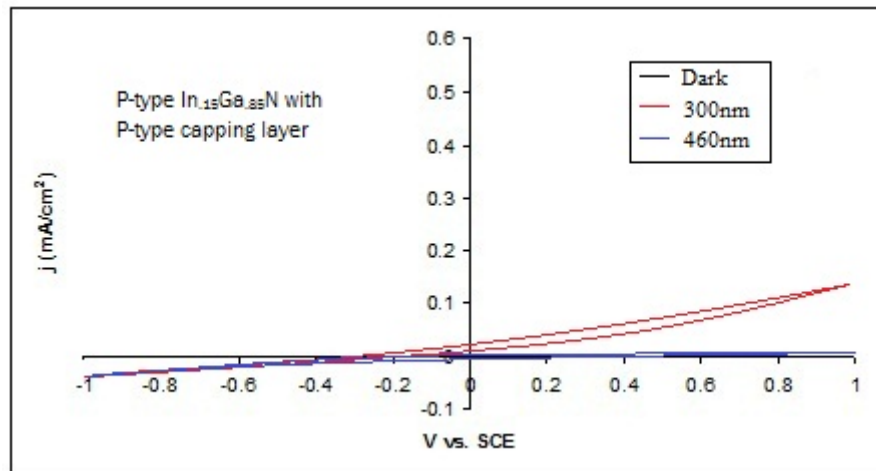


Figure 3.8: CV of P-type $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$ with P-type capping layer

First let us examine the behavior of the pure GaN samples. Both n-type and p-type samples of similar thickness ($2.6\mu\text{m}$) were observed. Visible light activity is negligible below the band gap of the material which is 3.2eV . Figures 3.2 and 3.3 show a minimal response on the 460nm curve. The UV illumination curves for both samples are not limited by mass transfer affects due to bubbling of inert argon gas in the system, allowing for smooth curves up to the +1V limit. The n-type sample peaks at $.50\text{mA/cm}^2$ where it reaches the mass transfer limit of the reaction. [15] The p-type sample peaks at $.45\text{mA/cm}^2$, with a slightly lower mass transfer limit. This result would suggest that the p-type sample has slightly reduced photoactivity compared to the n-type sample.

Next we can compare n-type and p-type InGaN samples that do not have a GaN capping layer, which are found in Figures 3.4, 3.5 and 3.6. In all three

samples, anodic current begins to increase from zero between -0.8V and -0.7V vs. SCE, with a quasi-linear upwards slope. The n-type $\text{In}_{.10}\text{Ga}_{.90}\text{N}$ sample had the highest photocurrent at zero applied bias of approximately $.23\text{mA}/\text{cm}^2$ under UV illumination. The p-type $\text{In}_{.10}\text{Ga}_{.90}\text{N}$ cell has a photocurrent of $.2\text{mA}/\text{cm}^2$ while the n-type $\text{In}_{.15}\text{Ga}_{.85}\text{N}$ cell has a photocurrent of $.16\text{mA}/\text{cm}^2$ under UV illumination. Under visible light, all three samples show positive photocurrent between 0V and $.2\text{V}$ vs. SCE. This photocurrent increases in all three samples, significantly surpassing the UV photocurrent in the n-type $\text{In}_{.15}\text{Ga}_{.85}\text{N}$ sample approaching $+1\text{V}$ vs. SCE with a value approaching $.42\text{mA}/\text{cm}^2$. These results show that the higher indium compositions have a significantly increased response to visible light, but a decrease in response to UV light. When comparing the n-type $\text{In}_{.10}\text{Ga}_{.90}\text{N}$ sample to the p-type $\text{In}_{.10}\text{Ga}_{.90}\text{N}$ sample the p-type sample once again shows slightly lower photocurrent levels for both UV and visible light response. The InGa N samples with a Ga N capping layer in Figures 3.7 and 3.8 have reduced UV response and no visible light response.

3.3 Linear Scan Voltammetry

LSV allows the ability to directly compare dark current to photocurrent in a sample through a sweep of set voltages. These results are intended to support the findings in Section 3.2. In the following figures, the blue curve represents UV light and the red curve represents visible light.

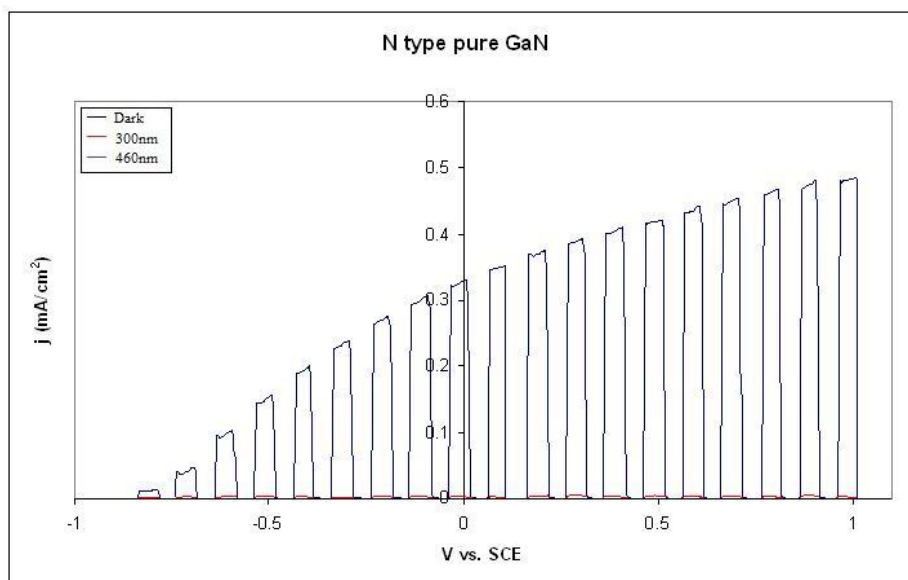


Figure 3.9: LSV of N-type pure GaN Sample

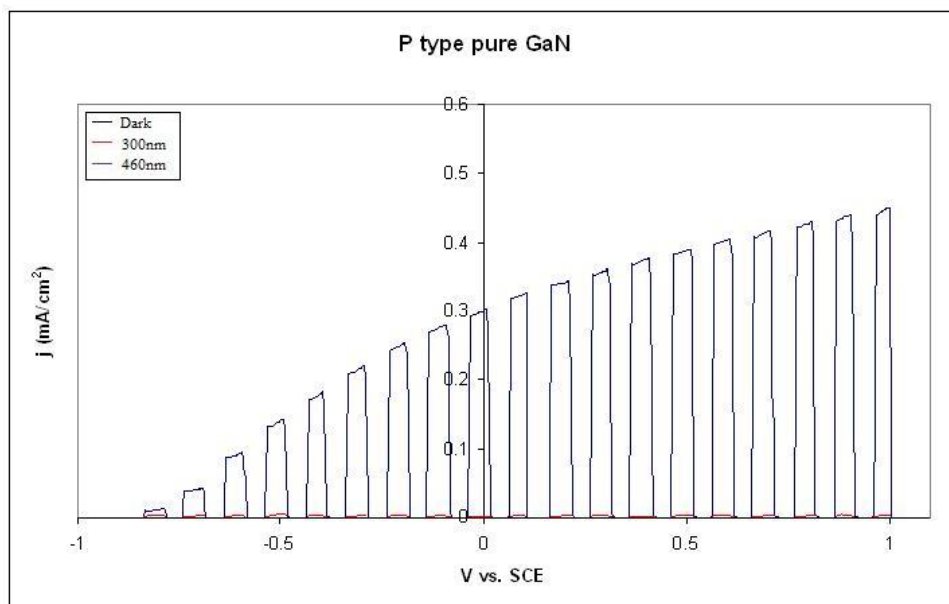


Figure 3.10: LSV of P-type pure GaN sample

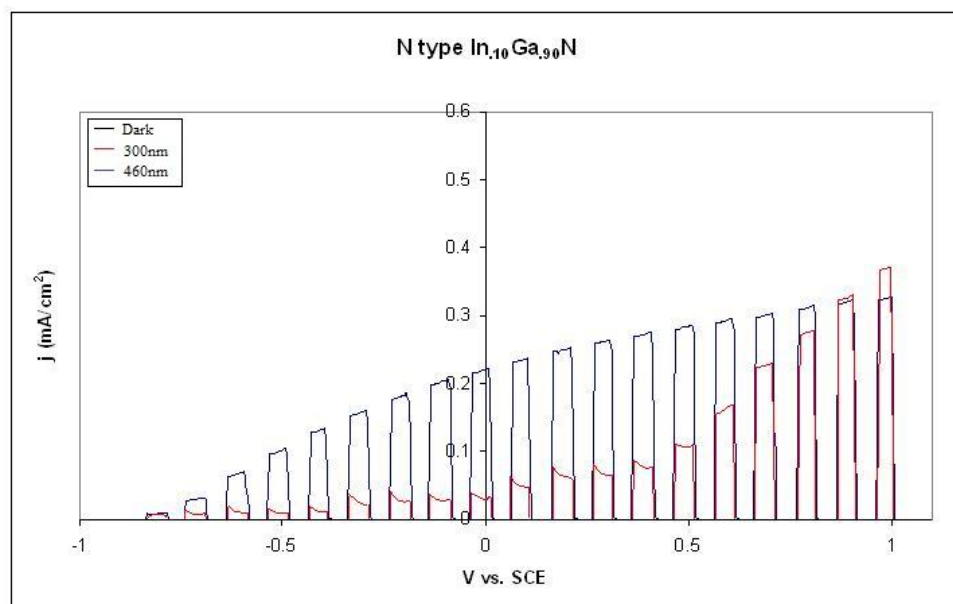


Figure 3.11: LSV of N-type $\text{In}_{0.1}\text{Ga}_{0.9}\text{N}$ sample

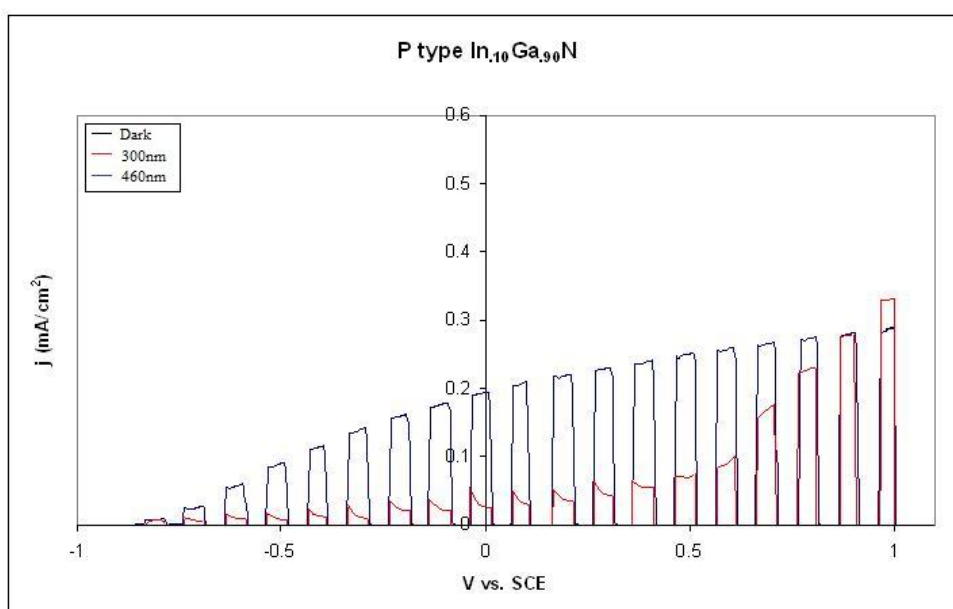


Figure 3.12: LSV of P-type $\text{In}_{0.1}\text{Ga}_{0.9}\text{N}$ sample

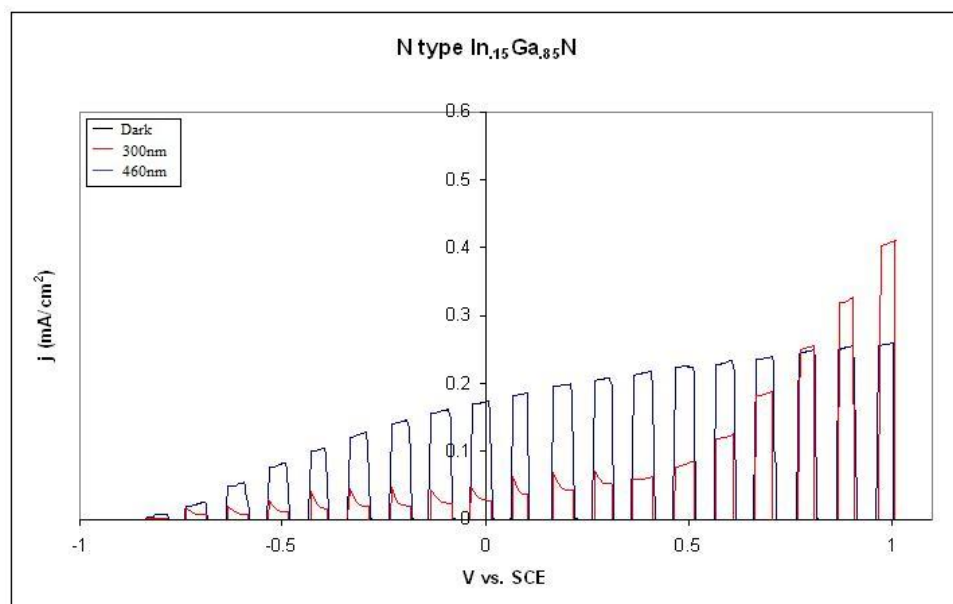


Figure 3.13: LSV of N-type $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$ sample

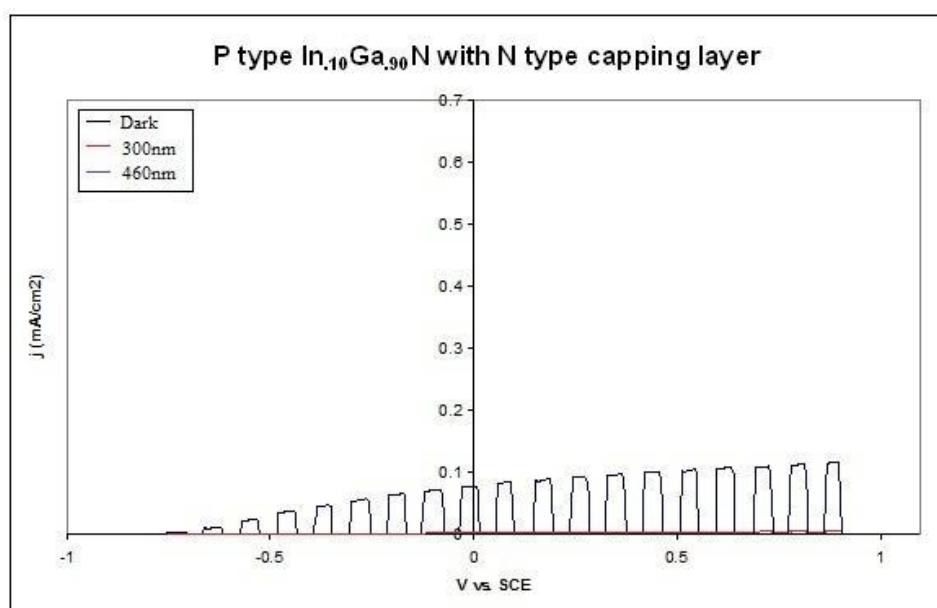


Figure 3.14: LSV of P-type $\text{In}_{0.10}\text{Ga}_{0.90}\text{N}$ with N-type capping layer

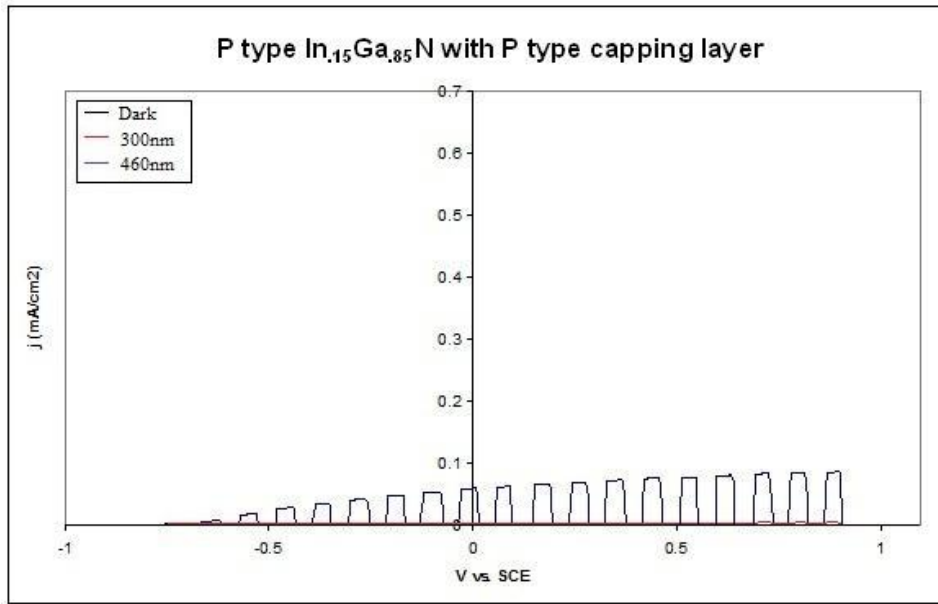


Figure 3.15: LSV of P-type $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$ with P-type capping layer

The results from the above figures support the findings in Section 3.2. In the pure GaN samples UV response is high, while visible light response is negligible. In the InGaN samples with no capping layer, UV response is reduced but visible light photocurrent increases greatly starting at approximately +.5V vs. SCE. The n-type $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$ sample produces the largest amount of photocurrent in the visible spectrum, as is expected having the lowest band gap, approximately 2.68eV. The InGaN samples with capping layers fail to produce useful results, with significantly reduced photocurrent in the UV range and no photoactivity in the visible range. Measurable photocurrent in the LSV curves shows a tendency to spike sharply as the shutter opened and then relax to a constant value at lower applied biases. This behavior may be caused by light trapping states in the sample.

In these states electron-hole pairs are generated but are unable to reach the conduction or valence bands due to their position deep within the band gap. [12]

3.4 Incident Photon Conversion Efficiency

IPCE is a technique to evaluate the quantum efficiency of the photoanode as a function of wavelength as well as applied bias. The following figures are labeled by sample type, with applied bias levels ranged between 0V and +1V vs. SCE. Efficiency in samples increases with higher applied voltage. This is supported in the previous CV and LSV curves where higher voltage produces more photocurrent.

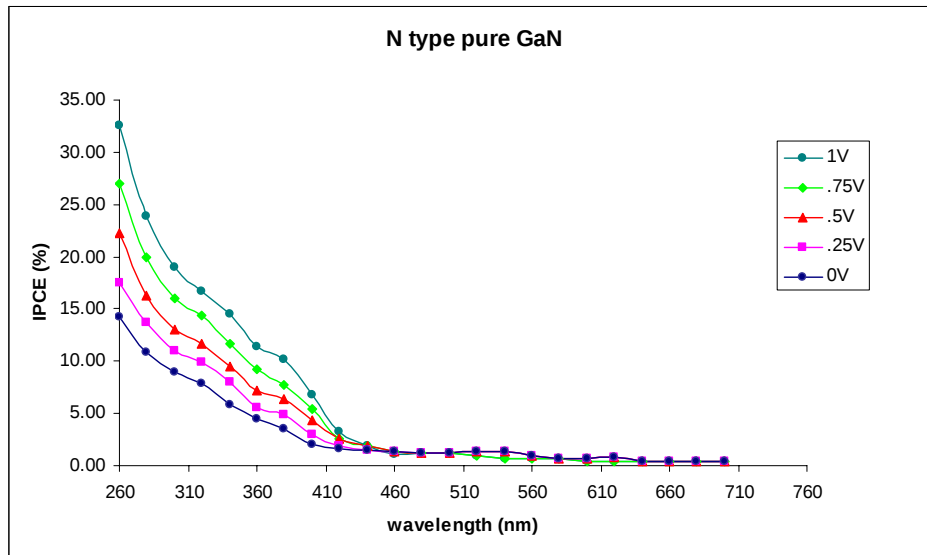


Figure 3.16: IPCE of N-type pure GaN

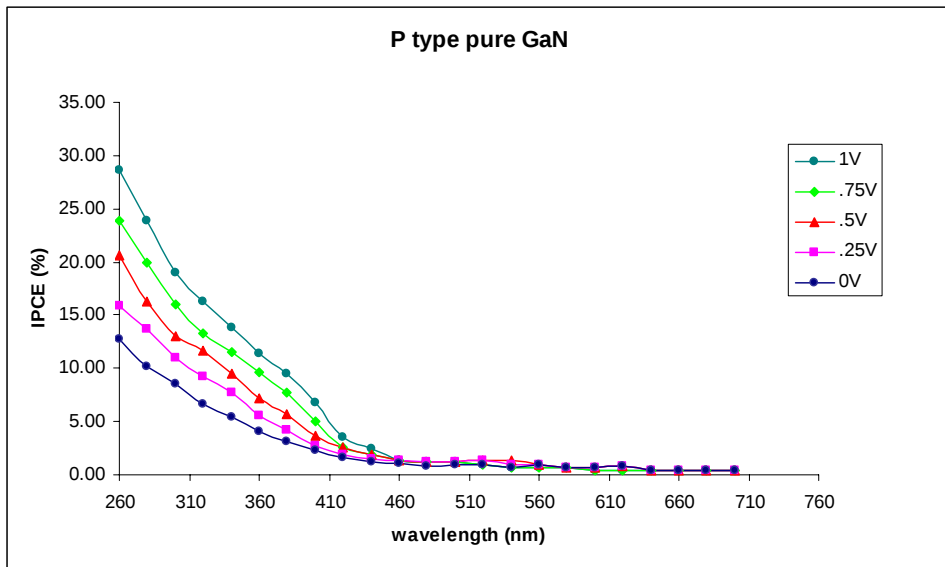


Figure 3.17: IPCE of P-type pure GaN

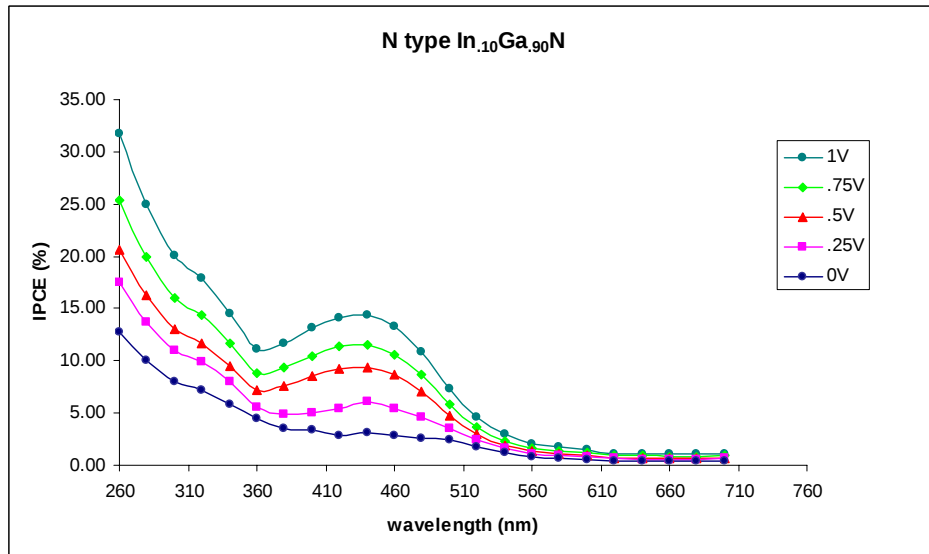


Figure 3.18: IPCE of N-type In_{.10}Ga_{.90}N

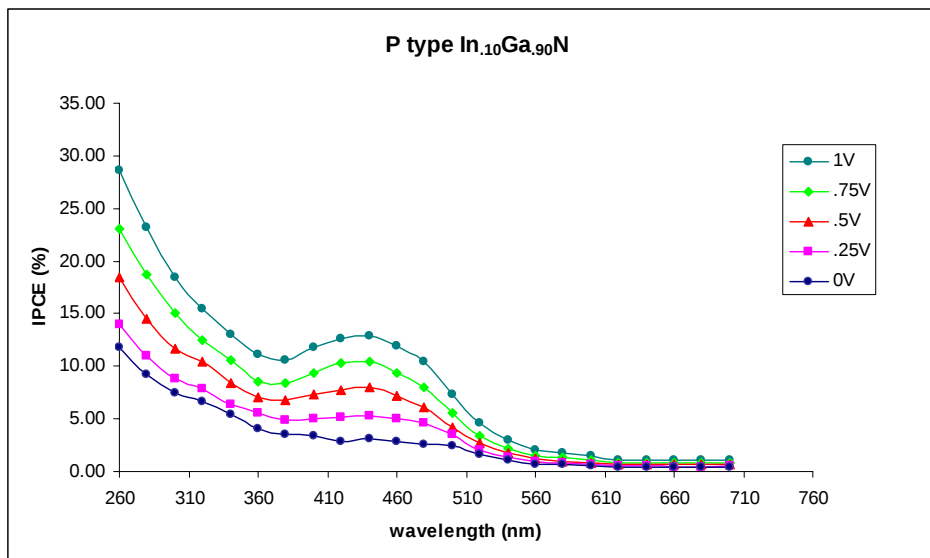


Figure 3.19: IPCE of P-type $\text{In}_{.10}\text{Ga}_{.90}\text{N}$

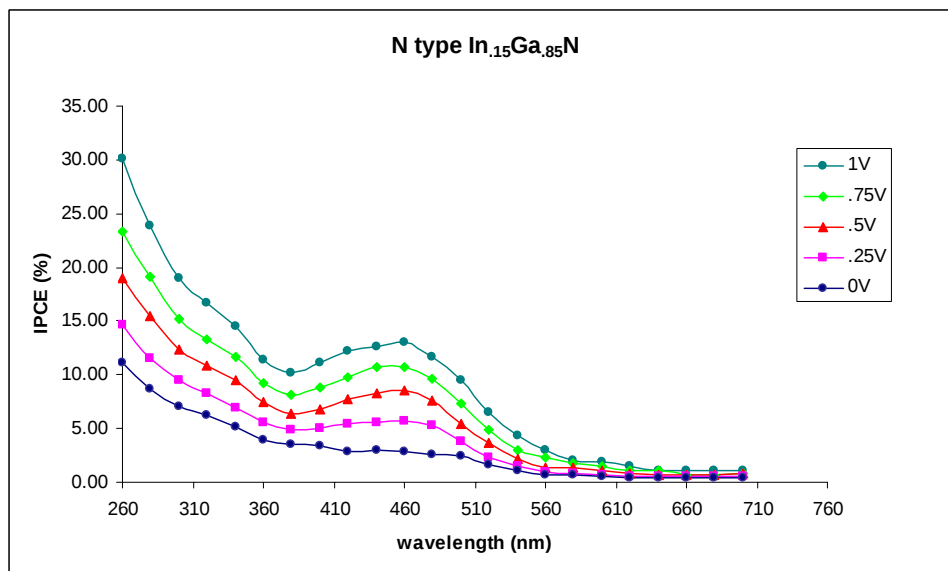


Figure 3.20: IPCE of N-type $\text{In}_{.15}\text{Ga}_{.85}\text{N}$

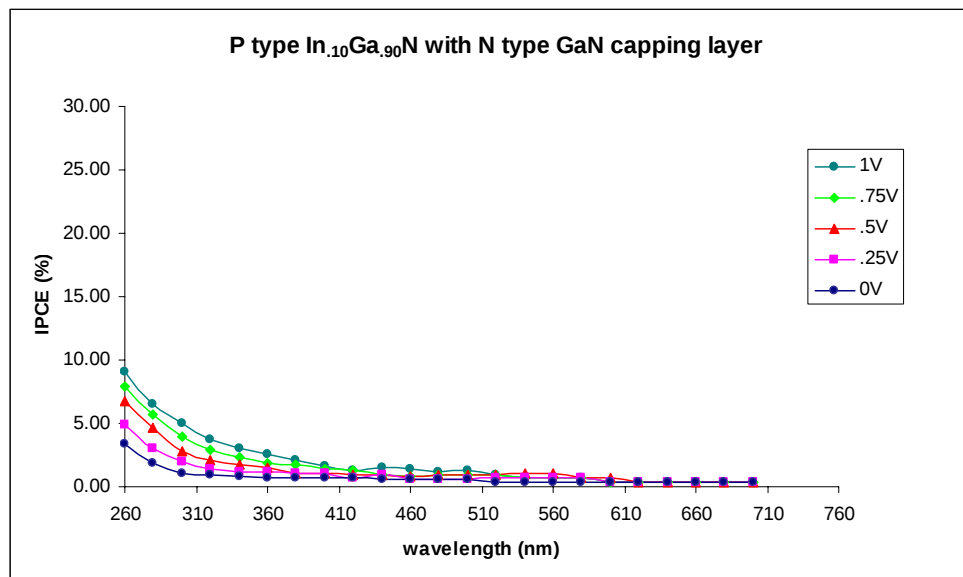


Figure 3.21: IPCE of P-type $\text{In}_{0.10}\text{Ga}_{0.90}\text{N}$ with N-type capping layer

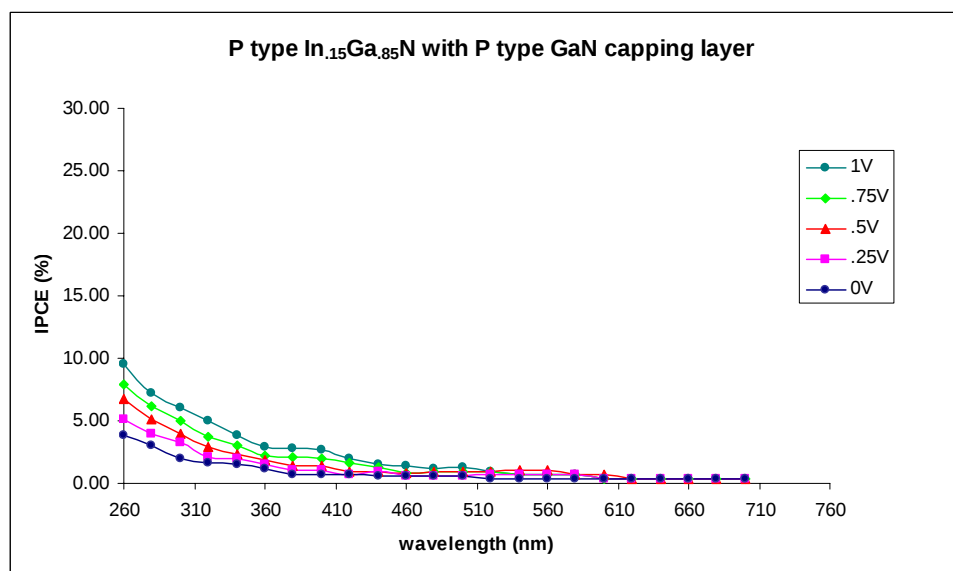


Figure 3.22: IPCE of P-type $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$ with P-type capping layer

The pure GaN samples in Figures 3.16 and 3.17 both exhibit high quantum efficiency in the UV light range up to their band gap 3.2eV (387nm), where quantum efficiency tails off to near zero. This is expected behavior for wide band gap materials such as GaN. The peak efficiency for the n type GaN was 5% higher than in the p-type samples, suggesting as in Sections 3.2 and 3.3, that p-type samples generate slightly less photoactivity than n-type counterparts.

The InGaN samples without capping layers in Figures 3.18 and 3.19 show increased quantum efficiency in the visible spectrum. A direct comparison of the n-type and p-type $\text{In}_{.10}\text{Ga}_{.90}\text{N}$ samples shows similar quantum efficiency peaks in the visible area of the spectrum near the band gap of the material 2.85 (430nm). The UV response in both samples diminishes slightly with the addition of indium into the sample. The n-type sample has peak quantum efficiency in the visible range of 15%, while the p-type sample has a peak at 13%, both under 1V applied bias. Once again there is a noticeable loss in photoactivity in the p-type sample with similar composition.

The n-type $\text{In}_{.15}\text{Ga}_{.85}\text{N}$ sample in Figure 3.20 shows a shifted quantum efficiency peak located near 460nm. This shift correlates with the band gap of the material which is 2.68eV (462nm). The efficiency peak for this sample at 1V applied bias is 13.5%. Although this efficiency is 1.5% less than the n-type $\text{In}_{.10}\text{Ga}_{.90}\text{N}$ sample, a larger portion of the visible spectrum is absorbed. With a higher power distribution available in visible range of the spectrum, the increased

visible light absorption outweighs the minor loss in quantum efficiency.

The capped InGaN samples in Figures 3.21 and 3.22 both show diminished quantum efficiency in the UV range and zero efficiency in the visible range. The peak efficiency of the p-type $\text{In}_{.10}\text{Ga}_{.90}\text{N}$ with n-type capping layer was 9% in UV illumination with a 1 V applied bias. The p-type $\text{In}_{.15}\text{Ga}_{.85}\text{N}$ with p-type capping layer showed a slightly higher peak efficiency of 9.5% under the same conditions.

Chapter 4

CONCLUSIONS AND FUTURE WORK

4.1 Conclusions

A series of GaN and InGaN photoanodes were grown using MOCVD. N-type samples were doped with silicon and p-type samples with manganese. Electrochemical experiments were conducted to reveal photocurrent generation and quantum efficiency of the cells in .1M NaOH solution.

Pure GaN samples show high levels of photocurrent and high quantum efficiency under UV light with applied bias, but little or no response in the visible range. InGaN samples with no capping layer show improved photocurrent generation and efficiency in visible light, with the peak quantum efficiency shifting upward in wavelength with higher indium compositions. These shifts correlate with decreasing band gaps of the samples as more indium is introduced. Under high applied bias, the photocurrent produced by visible light exceeded photocurrent produced under UV illumination. The n-type $\text{In}_{.15}\text{Ga}_{.85}\text{N}$ photoanode shows the highest photoactivity in the visible spectrum but has slightly smaller peak quantum efficiency than the $\text{In}_{.10}\text{Ga}_{.90}\text{N}$ samples. This loss could be attributed to an increase in defects in the material that naturally occurs as the composition of

indium increases, causing increased recombination of electron-hole pairs.[17] The GaN capped InGaN samples show reduced photocurrent and quantum efficiency in UV light and no photoactivity in the visible range. This is caused by recombination in the junction formed between the InGaN layer and the GaN capping layer. The thickness of the capping layer (~10nm) is too wide for electron tunneling; therefore these photoanodes show behavior of a very thin GaN photoanode.

In all of the electrochemistry experimentation, p-type samples produced slightly less photocurrent and lower quantum efficiencies than n-type samples of similar composition. This loss can be attributed to the fact that p-type GaN and InGaN samples have a higher resistivity than n-type material. [17] The reduced ability of the contacts to collect carriers results in slightly lower measured photoactivity.

4.2 Future Work

Further study is needed to determine the indium composition that can be grown to allow maximum visible light photoactivity while maintaining stability and sufficient material quality. Current results show a decreased band gap as low as 2.68eV while maintaining material quality. The eventual goal is to reach band gap levels closer to 2.0eV to maximize the amount of light absorption while still maintaining band edges for the redox reaction of water. Another consideration in

this technology is developing lower cost growth techniques for III/V materials to help make this technology more economically feasible. TiO_2 is a stronger candidate at this time for PEC cell photoanode commercialization due to its low cost and high availability.

REFERENCES

- [1] "U.S. Energy Statistics," *U.S. Energy Information Administration*, 2009.
- [2] "Fossil Fuel Overview," *U.S. Department of Energy*, 2009.
- [3] T.L. Friedman, *Hot, Flat, and Crowded*, Farrar, Straus & Giroux, 2008.
- [4] R.B. Alley, T. Berntsen, and N.L. Bindoff, "A report of Working Group I of the Intergovernmental Panel on Climate Change," 2007.
- [5] "Fuel Cell Technologies Program: Hydrogen Production," *U.S. Department of Energy*.
- [6] Y. Lin, S. Zhou, X. Liu, S. Sheehan, D. Wang, and O. Apex, "TiO₂/TiSi₂ Heterostructures for High-Efficiency Photoelectrochemical H₂O Splitting," 2009, pp. 2772-2773.
- [7] R. Article, T. Bak, J. Nowotny, M. Rekas, and C.C. Sorrell, "Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects," *International Journal of Hydrogen Energy*, vol. 27, 2010, pp. 991 - 1022.
- [8] J.W. Joel W. Ager III, W. Walukiewicz, K. M. Yu, W. Shan, J. Denlinger, "Group III-Nitride Materials for High Efficiency Photoelectrochemical Cells," *Materials Research Society*, vol. 884E, 2005.
- [9] M. Gratzel, "Photoelectrochemical cells," *Nature*, vol. 414, 2001, pp. 338-344.
- [10] J.I. Pankove and T.D. Moustakas, *Semiconductors and Semimetals - Gallium Nitride (GaN) II*, Academic Press, 1998.
- [11] R. Singh, D. Doppalapud, and M. T.D., "Phase separation in InGaN thick films and formation of InGaN/GaN double heterostructures in the entire alloy composition," *Applied Physics Letters*, vol. 70, 1997, p. 1089.

- [12] M.E. Schulz, "NITROGEN- AND CARBON-DOPED TITANIUM DIOXIDE THIN FILMS FOR SOLAR HYDROGEN GENERATION," 2009.
- [13] O.K. Jani, "DEVELOPMENT OF WIDE-BAND GAP InGaN SOLAR CELLS FOR HIGH-EFFICIENCY PHOTOVOLTAICS," *Doctor of Philosophy in the School of Electrical and Computer Engineering, Georgia Institute of Technology*, pp. 67-87.
- [14] M. Diale, F.D. Aurret, N.G. Berg, R.Q. Odendaal, and W.D. Roos, "Analysis of GaN cleaning procedures," *Applied Surface Science*, vol. 246, 2005, pp. 279-289.
- [15] A.J. Bard and L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications Second*, John Wiley & Sons, 2001.
- [16] S.P. Kounaves, "Voltammetric Techniques," *Handbook of Instrumental Techniques for Analytical Chemistry*, Prentice Hall, 1997, pp. 709-726.
- [17] I. Akasaki and H. Amano, "Crystal Growth and Conductivity Control of Group III Nitride Semiconductors and Their Application to Short Wavelength Light Emitters," *Japanese Journal of Applied Physics*, vol. 36, 1997, pp. 5393-5408.