Investigation of Optical Properties of Zinc Oxide Photodetector

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Abstract

UV photodetection devices have many important applications for uses in biological detection, gas sensing, weaponry detection, fire detection, chemical analysis, and many others. Today’s photodetectors often utilize semiconductors such as GaAs to achieve high responsivity and sensitivity. Zinc oxide, unlike many other semiconductors, is cheap, abundant, non-toxic, and easy to grow different morphologies at the micro and nano scale. With the proliferation of these devices also comes the impending need to further study optics and photonics in relation to phononics and plasmonics, and the general principles underlying the interaction of photons with solid state matter and, specifically, semiconductors. For this research a metal-semiconductor-metal UV photodetector has been fabricated by using a quartz substrate on top of which was deposited micropatterned gold in an interdigitated electrode design. On this, sparsely coated zinc oxide nano trees were hydrothermally grown. The UV photodetection device showed promise for detection applications, especially because zinc oxide is also very thermally stable, a quality which is highly sought after in today’s UV photodetectors. Furthermore, the newly synthesized photodetector was used to investigate optical properties and how they respond to different stimuli. It was discovered that the photons transmitted through the sparsely coated zinc oxide nano trees decreased as the voltage across the device increased. This research is aimed at better understanding photons interaction with matter and also to open the door for new devices with tunable optical properties such as transmission.
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Dedication

Dedication for this thesis goes to my parents, Kennith and Lisa Chism.
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1. Introduction

1.1 Motivation

It can be argued that modern research and technology development should go beyond new devices, new methods, or improvements on devices. Researchers should go beyond by continuing to flesh out fundamental physics, optics, and materials’ principles that have yet to be understood in totality. Much has been learned and many advancements have been made in these realms, especially dealing with electronics and semiconductor devices; however, it would be foolish of the scientific community to abandon further research into fundamental physics principles and even to abandon questioning established scientific principles. The interaction of light with matter is a foundational interaction that is the cornerstone for many semiconductor technologies, but this reaction still has facets that have yet to be fully explored such as in plasmonics. Even an understanding of the nature of light and what it actually is has not been fully realized. It is the goal of this research to reveal new results that could stimulate further experimentation to create new science and add to our existing understanding of light and its interactions with materials and devices.

1.2 Review of Photodetection

A photodetector is a device that often uses a semiconductor of a certain bandgap in which incoming photons, with enough energy, will excite electrons in the valence band to the conduction band creating an electron that can then freely move and leaves a hole which can also move within the valence band. This charge-hole pair will respond to a bias much the same as a conductor and a resulting current can be seen. These charge-hole pairs are subject to a lifetime at the end of which they will recombine generating heat.[1] Often, metal oxides are used along with other semiconductors, many of which have large bandgaps.
1.2.1 Background of UV Photodetectors

Large bandgap semiconductors are extensively used for UV light detection as the photons of light in the UV range have the higher energy needed to excite an electron from the valence band to the conduction band. The UV range consists of electromagnetic waves with wavelengths from 10 nm to 400 nm. Wavelengths from 400-700 nm are the visible range. Photodetectors that are only responsive to photons in the UV range and not those with a wavelength above 400 nm, are known as “visible blind.” The UV range is then divided into three subdivisions known as UVA (315-400 nm), UVB (280-315 nm), and UVC (100-280 nm). UVA, specifically, is of interest in this research as it constitutes the range studied for the majority of the experiments conducted for this work.

UV photodetection devices draw great interest as they are useful in applications such as gas sensing, solar UV monitoring, biological analysis, space-to-space communications, flame detection, space exploration and more.[1-3] In these areas and others more advanced and better photodetectors are sought after that have high stability, speed, sensitivity, selectivity, and high signal to noise ratio.

Photodetectors such as these often come in the form of metal-semiconductor-metal (MSM) designs that consists of two metal electrodes separated by one-dimensional, two-dimensional, three-dimensional, or a thin film of some semiconductor. Figure 1.1 illustrates this design.[3] This metal to semiconductor contact is known as an ohmic contact, where the metal, as a natural conductor, has extra electrons that it can pass to the semiconductor under certain conditions which can generate varying electrical and optical properties. Of late, one dimensional nanostructures as the semiconductor in MSM photodetectors have been researched more heavily as their higher photoconductive gain and responsivity makes for a useful photodetection
device.[3] This is due to the larger surface-to-volume ratio of the nanostructures giving photoexcited carriers a short transit time and long lifetime.[2, 3] For this case, metal oxides are often sought as the material of choice to construct one dimensional nanostructures. Examples of these metal oxides include: SnO$_2$, Ga$_2$O$_3$, In$_2$Ge$_2$O$_7$, ZnO, and WO$_3$.[3]

Figure 1.1. Example of MSM photodetector design[3]

1.2.2 Zinc Oxide for a MSM UV Photodetector

Zinc oxide (ZnO) has a large direct bandgap of about 3.34 eV which corresponds to absorptions in the UVA range.[2] It also has an exciton binding energy of 60 meV which is relatively large, and these qualities in part make ZnO a very suitable candidate for UV photodetection devices. ZnO is even more promising due to its high thermal and mechanical stability, high sensitivity, and ease of which a multitude of morphologies can be made at the nanoscale. A device that is responsive and resistant to high temperature electronic degradation is
possible with this metal oxide. This, along with its cheapness, abundance, and non-toxicity make it rival other promising high performance wide bangap semiconductors such as gallium nitride (GaN).[4]

As shown in Figure 1.2, one dimensional ZnO structure surface trap states are formed by oxygen molecules from the atmosphere which absorb on the surface of the crystal. Under illumination, when the electrons are excited to the conduction band, the holes will often be trapped by these surface trap states.[2] The resulting effect is an increase in photocurrent gain and, thus, response time in air, which also results in a lower peak current, and a slower response in inert environment with a higher peak current.[1]

Figure 1.2. Diagram of surface trap states on a nanorod. a) ZnO rod exposed to light. b) Oxygen molecules adsorb on the ZnO rod. c) Positive holes created by photoexcited electrons are trapped by the oxygen molecules.[2]

In the research of this thesis, one dimensional ZnO nanorods formed the basis for the morphology used on the final photodetection device. Branches were grown on these rods to
make a hierarchical three-dimensional structure. These three-dimensional structures were assumed to be affected by the same oxygen absorbed trap states as the one dimensional structures and the data supported this assumption.

1.3 Review of Fabrication Techniques and Characteristics of ZnO Photodetectors

One of the earliest cheap fabrication processes of ZnO film for use in optoelectronic devices was by Fernandez and Sebastian in 1991.[5] They reported a conversion of zinc sulfide film to zinc oxide film by annealing. The ZnS films were made by combining 2.5 ml of 1 M ZnSO$_4$, 3 ml of 3.75 M triethanolamine (TEA), 2 ml NH$_3$/NH$_4$Cl (pH 10) buffer solution, 1 ml of 1M thioacetamide (TA), and 41.5 ml de-ionized water in a 50 ml chemical bath. Glass slides were inserted in the bath and reacted from 1 to 24 hr at either 25 °C or 50 °C. These samples were then annealed at over 400 °C in air to convert ZnS to ZnO. Optical properties of the films showed that for more annealing, the greater the photocurrent that was achieved and indicated more ZnO compared to ZnS. This analysis was confirmed by XRD which showed higher ZnO peaks after longer annealing in air.[5]

Although this demonstrates the early rise in popularity of ZnO for optoelectronic devices like photodetectors, the use of nanostructures for use in optoelectronic photosensitive devices was not explored until 2002. Kind et al.[7] was one of the first to use nano structures, and in particular ZnO nanowires, for applications such as photodetection and optical switching. The year prior, the same group published a paper explaining a growth technique to produce highly ordered ZnO nanowires.[6] Figure 1.3 shows the resulting wires which were synthesized using gold thin film as the substrate and catalyst upon which ZnO nanowires were epitaxially grown. The gold thin film could be patterned before growth to produce nanowires which were highly oriented.[6]
The same group in their 2002 paper reported using this same growth technique for the creation of an optoelectronic circuit utilizing 50 to 300 nm diameter nanowires connecting gold electrodes.[7] Figure 1.4 shows the resulting dark current and photocurrent of the device which was one of the first utilizing nanostructures.

![Figure 1.3. Epitaxial ZnO nanowires on patterned gold thin film.][6]

![Figure 1.4. Dark current (darker) and photocurrent (lighter) of ZnO nanowire.][7]

The large photoresponse, evidenced by the difference in current with and without illumination, makes photonic devices such as optical switches possible. Such a device relies on the difference in current when the device is exposed to light and when it is not, the low current
from no light and the higher current from exposure to light, will render an “off” and “on” signal respectively. They also discovered that a photoresponse can be seen with very low intensities of UV light from sources such as incandescent light bulbs.[7]

Most of the work in optoelectronics in recent years has been focused on utilizing nanostructures because of their superior properties when creating smaller and more efficient devices. A review of the fabrication and working principle of several of these devices and their advancements in recent years should distinguish the research of this thesis and their fabrication and design. Although many UV photodetection devices exist which utilize many semiconductor materials, a focus will be made on those using ZnO. These devices, in general, take advantage of the capability of the material, and nanostructures of the material, to convert photons into an electrical signal. This is achieved by connecting electrodes by some network of ZnO nanostructures such as dense nanorods, nanobelts, nanotetrapods, horizontal nanowires, or others.

In 2012, Hassan and Hashim from University Sains in Malaysia made their novel UV photodetector using a network of self-assembled ZnO nanotetrapods to bridge electrodes on a silicon substrate.[8] Their motivation for neglecting one-dimensional nanostructures was to improve photosensitivity and shorten the lifetime of photogenerated carriers. Figure 1.5 shows the resulting network of nanotetrapods while Figure 1.6 shows the resulting photocurrent of the device compared to the dark current.

![SEM images of ZnO nanotetrapod network](image_url)
The nanotetrapod structures were obtained by placing a sample of ZnO powder in a boat along with the silicon substrate target material in a quartz tube which was placed inside a furnace. A thermal evaporation method was used in which nitrogen buffer gas and oxygen reaction gas were flowed into the quartz tube which was heated up to 900 °C. The target silicon substrate was downstream of the ZnO powder and, thus, the powder that reacted with the oxygen was deposited on the substrate.

Later in the same year, a group at National Taiwan University (NTU) sought to address the problem of adsorption/desorption of oxygen molecules on the surface of ZnO materials (as shown previously in Figure 1.2) and its effects on slowing the photocarrier relaxation time.[9] Before their work, efforts to speed up responsivity of photodetectors had focused on decreasing nanowire diameters thus reducing surface barrier height. This was pointed out by the NTU group to be high cost and low yield. Figure 1.7 shows their proposed solution of using a ZnO nanobelt (NB) network. Figure 1.8 shows the proposed mechanism by which these structures speed up the
recovery time of the device by alleviating effects of oxygen adsorption and desorption with and without illumination, respectively.

Figure 1.7. Photodetector using ZnO nanobelt network.[9]

For this particular device, the titanium/gold electrodes were not only used as electrodes but also as catalysts for the reaction which is described below. Also of note is that this is one of the few devices reviewed here which did not utilize the interdigitated design. This could possibly have influenced that group’s results and indicated that not all of the observed effect was from the nanobelt network but some may be from the design and spacing of the electrodes.

Figure 1.8. Schematic of (a) the carrier generation in a single ZnO NB and (b) the NB–NB junction barrier for the electron transport in the NB network device. CB and VB represent the conduction band and the valence band, respectively.[9]
For the fabrication of this device, a vapor-liquid-solid method was used by which a carrier gas, argon, was flowed over zinc oxide and carbon powders mixed 2:1 at 930 °C for 1 hour. The product was deposited onto the substrate made from Ti/Au electrodes which acted as catalysts for the reaction.

At the beginning of 2013, Campos et al. [10] reported on the manipulation of surface trap states to alter recombination and diffusion. They altered gate voltage to change the sensitivity and performance of the device. The nanowire would accumulate charges according to the gate voltage when under illumination. Figure 1.9 shows the device which was fabricated by dispersing ZnO nanowires obtained from sonicating Zn foil that had undergone thermal oxidation, onto the doped silicon substrate. Their work showed that the adsorption and desorption of oxygen surface traps states could be altered not only by nanocrystal morphology but also by electrical field and voltage.

![Figure 1.9. Schematic of ZnO nanowire transistor which manipulates gate voltage.][10]
In March of 2014, Gaoming and Jingwen reported the possibility of temperature also affecting oxygen desorption which alters the photosensitivity and response time.[11] Their device and the resulting photocurrents at different temperatures are shown in Figure 1.10 and Figure 1.11, respectively. A simple thin film of ZnO was used instead of complex nanostructure systems.

![Figure 1.10. ZnO thin film photodetector.][11]

![Figure 1.11. Photocurrent and dark current of ZnO thin film photodetector.][11]

The thin film device was assembled by depositing a ZnO thin film using radio frequency magnetron sputtering. The thin film was deposited on a quartz substrate and on top of the thin
film an aluminum electrode was evaporated on and patterned into an interdigitated pattern. As shown in Figure 1.11, the difference in dark current at room temperature and 100 °C and photocurrent at room temperature and 100 °C were both negligible up to 10 V.

In December of 2015, Al-Hardin et al.[12] reported a UV photodetector they made from densely grown ZnO nanorods and how the different aspect ratio of the rods (grown under different reaction conditions) affected the photoresponse of the device. The ZnO nanorods were grown by hydrothermal synthesis in which glass slides were first cleaned then coated with a ZnO seed layer then put into a zinc nitrate, hexamethylenetetramine solution after heat treating. DC reactive sputtering was used to apply the seed layer to the glass substrate which was placed in the reaction solution and reacted for 6 hours at 95 °C. The resulting ZnO network of nanorods can be seen in Figure 1.12.

![Figure 1.12. FE-SEM image of ZnO nanorods network on glass substrate.[12]](image)

Different molar amounts of the precursor were used to change the aspect ratio of the ZnO nanorods. The resulting photoresponse of the device was measured comparing the different
morphologies that resulted from the change in precursor concentration. Figure 1.13 shows the different photoresponses of the device with different morphologies.

Of note for this reaction was the use of a seed layer for the growth of the dense nanorods. Often a seed layer is not necessary for the nucleation and growth of ZnO nanostructures on many different substrates with different crystal facets on the surface. However, for dense nanorod growth, a seed layer is often used to initiate the nucleation of well-oriented nanorods onto the surface being used.

Figure 1.13. Photocurrent vs time for ZnO photodetectors with nanorods of different aspect ratios.[12]

In Figure 1.13, sample A through D had aspect ratios of 10.86, 7.79, 3.95, and 1.76, respectively. These various aspect ratios were obtained mostly by altering the zinc nitrate concentration. The ZnO photodetectors were exposed to illumination on and off over the length of time represented under the peaks. The higher peaks represent a higher responsivity which was
found to occur for the higher aspect ratio nanorods and was probably due to there being more surface exposed to illumination.[12]

In 2015, Zou et al.[13] showed that for their ZnO thin film UV photodetector, a different photoresponse was seen when the device was exposed to white light compared to only UV light. Figure 1.14 and Figure 1.15 show the fabrication process for the ZnO thin film and the final device, respectively. The group used a thin film to simplify the structure and better understand the mechanism at work when comparing the different photoresponses of the device. It was not clear why this particular fabrication technique was favored for making the ZnO thin film.

Figure 1.14. Fabrication schematic of ZnO film.[13]

Figure 1.15. Schematic of flat UV photodetector device.[13]
Figure 1.16 shows the resulting SEM of the thin film structure which was fabricated by screen printing ZnO paste mixed with an organic solvent onto a gold interdigitated electrode on an alumina substrate. The ZnO was dispersed in the organic solvent to make a paste by ball milling the mixture for 2 hours at 300 rpm. The resulting device was then dried for 30 minutes at 80 °C, heat treated at 250 °C for 30 minutes, then sintered at 550 °C in a furnace for 2 hours. All of the thermal treatments were done in air ambient. This fabrication technique might not be as cost effective as other methods of ZnO synthesis.

Figure 1.16. SEM image of ZnO thin film.[13]

Zou et al.[13] focused their research on the photoresponse when exposing the UV photodetector to UV and white light. Figure 1.17 and Figure 1.18 show that the photocurrent response was unexpectedly different for the two light sources.

Figure 1.17. Photocurrent response of ZnO thin film photodetector exposed to UV.[13]
The exact same UV photodetector, under the exact same conditions and exposed to the same bias voltage, exhibited a photocurrent that changed for each cycle when exposed to white light. From Figure 1.17, the measured photocurrent was as expected; when the light was shut off, the photocurrent decreased as valence band electrons recombined with holes and the number of free electrons decreased. According to the researchers, almost all electrons and holes recombined before the next switch on where an almost identical cycle was seen. However, for the white light it seemed that after the light was switched off, there must have remained some free electrons that had not recombined with holes and, thus, each previous cycle appeared to have affected the next cycle as the amplitude gradually increased. Also, it can be seen from Figure 1.18 that the amplitudes of each “on” switch were much lower for white light than for the UV photocurrent response. The group proposed a new parameter for use in understanding the photoelectric response of ZnO. Namely, they defined a way to calculate the remaining free electrons after the switch off and how those might affect the photoresponse of the device. [13]

Figure 1.18. Photocurrent response of ZnO photodetector exposed to white light. [13]
It is clear from reviewing this literature there are many fabrication techniques for creating different variations of UV photodetectors with varied properties and there are likely many ways still to be discovered for making better, more advanced, and cheaper devices. Also, some properties of the ZnO nanostructures’ optical activity have yet to be exploited and understood fully. Many papers address a particular optical property or structural behavior that can be altered via some variable manipulation. This makes it clear that those properties should be studied in more depth and the variables that tune those properties should be studied in order to fabricate a device that utilizes all of these different variable manipulations to increase the sensitivity and efficiencies of these UV photodetectors.

Particular attention is given to a paper from 2006 which defined a clear framework for how structure directing agents in hydrothermal synthesis of ZnO hierarchical nanostructures worked to produce different morphologies to be used for various applications.[14] The focus on growth methodology paved the way for the research presented here in Chapter 2. The fabrication method also has unique ties to the research of this thesis because it represented, at the time, the forefront of combining different concepts of growth kinetics and site specific nucleation manipulation by using structure directing agents such as organoamines and sodium citrate.

This was the earliest work found in literature which created ZnO nanostructure morphologies other than simple one dimensional rods/wires or tetrapods. Instead, morphologies were created that focused on hierarchical ZnO structures, most all of which had a primary rod structure and some type of grown secondary structure which resulted in complex nanostructures. They examined the effect of different diaminopropane (DAP) concentrations on the resulting primary rod and secondary branch structures grown on the rods (see Figure 1.19). Figure 1.19a represents the primary rod which was grown without DAP.
The primary rods were grown by placing the substrate in 20 to 30 ml of aqueous solution in which was dissolved zinc nitrate and hexamethylenetetramine (HMT) at concentrations of 20 mM. This solution along with the substrate were sealed in a bottle in a 60 °C oven for 17 hours to yield rods which are about 1.5 microns in height and about 0.8 microns in diameter. Figure 1.19b through Figure 1.19i represent a second reaction in which diaminopropane was added. This organoamine was thought to induce site specific nucleation on the facets of the primary rod by adsorbing to the surface. The paper also explained the possible role of the chain length of the hydrocarbon noting that a short chain length was tried but failed to give well-oriented branches. This could possibly have been a result of the two amine groups at either end of the hydrocarbon chain coming together to adsorb on the primary rod surface and initiate nucleation and growth of the secondary rod structures thus requiring a long enough chain to bend properly and guide well
aligned growth. As seen from Figure 1.19i, too much DAP concentration could hinder proper nucleation possibly due to either too much adsorption on the surface or to the higher pH degrading the ZnO rod growth. Reaction time for the secondary reaction was also studied by this group as shown in Figure 1.20 for the same concentration of DAP that yielded the secondary branches shown in Figure 1.19e.[14]

Structures from Figure 1.20a through f represent growths of 0.5 hours, 1.0 hours, 2.0 hours, 4.0 hours, 6.0 hours, and 24 hours, respectively. The researchers fleshed out the role of citrate in the reaction process as well as adding a tertiary growth utilizing citrate and DAP for either or both secondary and tertiary steps. Results from this research group provide an understanding of the mechanisms at work for the growth processes later outlined in Chapter 2 of this thesis. Of particular interest is utilizing the aforementioned complex hierarchical structures utilized as the ZnO network to bridge the electrodes creating a UV photodetector. Most of the literature to date has shown a focus on either simple non-hierarchical rod structures or thin films.

![Figure 1.20](image_url)

Figure 1.20. SEM images of hierarchical ZnO structures grown with 87.5 mM of DAP for different amounts of time.[14]
2. Methodology

2.1 Fabrication of Zinc Oxide Photodetector

The following techniques used for fabricating the ZnO UV photodetector proved to be cost effective and easy. As described, the substrate was cut, coated with the gold electrode, then the ZnO nanostructures were grown. It should be noted that this fabrication differed from most techniques reviewed in literature in that the ZnO morphology used was a complex hierarchical structure as opposed to simple rod structures or a thin film.

2.1.1 Creating Interdigitated Pattern

The zinc oxide (ZnO) photodetector device was made by first obtaining a quartz slide as the substrate. The slide was cut to several pieces each with dimensions 1 cm x 3.5 cm x 1 mm. The quartz substrate was then cleaned using a standard cleaning procedure by first placing the samples in an acetone bath in an ultrasonic cleaner for ten minutes followed by an ethanol bath, then in 2-propanol, and finally rinsed in double-deionized water (DDI). The substrate was allowed to air dry before placing copper masks in a line long ways down the clean face of the quartz slide piece as shown in Figure 2.1. The quartz substrate was then coated with gold using a Polaron SC7620 sputtering coater.[15] Once coated, the copper masks were removed to reveal an interdigitated gold pattern left on the quartz. This substrate was then annealed at 350 °C for 0.5 hour.

Figure 2.1. Interdigitated masks on quartz substrate.
2.1.2 Growth of Zinc Oxide

The substrate was then put into hydrothermal growth overnight in 20 mM zinc nitrate [Zn(NO$_3$)$_2$] and 20 mM HMT in order to grow the sparse single nanorods. Thereafter, the sample was subjected to two more growths under the same reaction conditions except with 60-80 μL of DAP added for three hours each in order to grow primary and secondary branch structures on the sparsely coated rods. The sample was rinsed in DDI water for two hours and annealed for 0.5 hour at 350 °C between each growth step.

2.1.3 Creation of Photodetector Device

Figure 2.2 shows the resulting 3D branched zinc oxide nanostructures, which were sparsely coated across the gold interdigitated quartz substrate. The sparse coating of ZnO was desirable in order to allow space for light to travel between the ZnO “nano-trees,” and through the quartz. The resulting interdigitated gold pattern is shown in Figure 2.3 and Figure 2.4 and an actual optical microscope image of the device with deposited ZnO is shown in Figure 2.5. A wire was then attached to each gold electrode using conductive paste. The resulting device was a photodetector that utilized ZnO to absorb mostly UV range photons and gave a resulting photocurrent under applied bias.

![SEM of zinc oxide rod with primary branches.](image)

Figure 2.2. SEM of zinc oxide rod with primary branches.
Figure 2.3. Representation of resulting interdigitated electrode.

Figure 2.4. Photo of interdigitated device with silver paste and wire excluding zinc oxide growth.

Figure 2.5. Optical microscope image of interdigitated fingers with branched zinc oxide structures.
Compared to previously reviewed literature, this device was unique for a few reasons. Firstly, the device utilized a simple mask technique along with sputter coating to synthesize the interdigitated gold pattern. This had the upside of being cheap and quick while the downside was that this technique is not really scalable to larger fabrication demands. Also, the ZnO network that bridges the electrodes was a hierarchical ZnO nanotree-like structure network which was far different from the thin films and densely coated simple rod ZnO nanostructures previously reported.

2.2 Experimental Setup

The experimental setup that was used allowed for each test that was conducted to be very uniform and consistent with previous tests. Many trials were conducted with a voltage sweep across the photodetector while being exposed to incident photons from a light source. This meant the distance and orientation of the sample relative to the light source had to be very consistent from trial-to-trial to give accurate results.

2.2.1 Fabrication of Sample Holder

Due to the small size of the of the photodetector device, a holder was created that would snuggly fit the sample in it and also allow the sample to be hooked to an electrochemical workstation and be open to incoming light from the light source. Shown in Figure 2.6, the central box holds the photodetector sample and solar cell in the path of the light source. The back wall of the holder can be interchanged to be static or dynamic, moving closer or further from the sample, if desired. To this mobile wall could be attached the solar cell whose voltage was measured constantly. The sample holder was black and had a black lid to reduce reflection of the incident photons when exposed to the sample.
2.2.2 Selection and Assembly of Solar Cell

For this research, a solar cell was utilized for the purpose of giving an estimation of the number of photons which were transmitted through the photodetector device. A simple solar cell from a standard calculator was used as it matched the dimensions of the device. Several calculators were disassembled and the solar cell removed from the circuitry with a soldering iron. Of those samples, the ones finally chosen for experimentation were those that showed a very consistent, steady voltage.

2.2.3 Arrangement and Method of Experimentation

The experimental setup consisted of a sample holder which contained the aforementioned grown ZnO photodetector, a simple solar cell, a holder for magnets of varying strengths and distances, a light source whose output electromagnetic radiation was equivalent to one sun of intensity, an electrochemical workstation with desktop computer which could apply variable DC voltage sweeps, an AC power generator, and two multimeters to measure the ZnO photodetector
and solar cell voltage. The sample holder was placed 23.25 inches from the light source. The light source was an ABET Technologies Solar Simulator[16] with an adjustable intensity. The assembled ZnO photodetector showed a consistent photocurrent as its distance from the light source remained unchanged.

As previously stated, the voltage of the solar cell was continuously measured by a multimeter. A second multimeter could be connected to the zinc oxide photodetector if a current measurement was needed. Also connected to the ZnO photodetector was one of two different power sources: either the electrochemical workstation which applied a biased DC voltage sweep and recorded the resulting current on a desktop computer, or an AC power generator for which the resulting current could be measured by the multimeter attached to the sample. Finally, between the light source and sample an optical filter could be added in order to observe the effects of different wavelengths — or ranges of wavelengths — of light.
3. Results and Discussion

3.1 Efficacy of Photodetector

First, the behavior of the ZnO photodetector was examined under the most basic conditions. The full spectrum of light was applied to the sample, and a DC voltage sweep was applied from 0 to 10 V at a rate of 0.075 V/s. The resulting ZnO sample current is shown in Figure 3.1 along with the current of the sample under dark conditions. These graphs are typical for these kinds of ZnO solar devices. Sensitivity is equal to the ratio of photocurrent to dark current. Sensitivity for this device averaged about 10, with maximum values reaching around 40 at less than 1 V of bias voltage. These values seem to be on the lower end when compared to higher sensitivity (60-100) ZnO nanorod UV photodetectors with higher aspect ratio dense nanorods reported in literature.[12]

However, Figure 3.2 shows abnormal data where the current passing through the sample changed (increased) with consecutive voltage sweeps despite no change in the DC sweep parameters. This increase seemed to be affected by at least a couple variables. First, the time between voltage sweeps. As more trial sweeps were run, if no time was allowed after the previous sweep, the current of the next sweep would increase by a relatively small amount. If, however, time was allotted between sweeps (approximately 5-10 minutes), the next sweep would result in a sample current that had increased by a greater amount. This “recovery time” seemed to greatly influence the sample current of the subsequent voltage sweep.

It should be noted that the device remained under illumination for the entirety of the consecutive sweeps. This could have possibly changed the behavior of the free electrons when not under bias.
Figure 3.1. Photocurrent compared to dark current when bias voltage sweep from 0 to 10 V is run across the ZnO device.

Figure 3.2. "Saturation" of zinc oxide photodetector.
Eventually, as shown in Figure 3.2, the sample current stopped increasing and stabilized at a certain value. This slow down and eventual leveling off of current increase was designated “saturation.” If the voltage sweep was applied again, with no recovery time from the last sweep, the current was observed to actually be less than the “saturated” current. Figure 3.3 shows this as well as the next trial in which a recovery time was allotted and the current returned to the “saturated” level. Trials 8, 9, and 10 were done consecutively but with recovery time allotted between each trial. Trial 10 was at saturation and was the highest current achieved. Trial 11 was ran directly after trial 10 with no recovery time and, as shown in Figure 3.3, this caused the current to be about 10% less than trial 10. Trial 12 was then run with recovery time after trial 11 and the current returned to normal saturation level. For each test conducted in this research, recovery time was 10 minutes whereas no recovery time meant there was 0 minutes between voltage sweeps. Unless otherwise stated, data presented in this thesis was from trials taken after the ZnO sample had reached saturation and with a recovery time of 10 minutes between trials.

![Graph](image)

Figure 3.3. “Saturation” of ZnO sample affected by “recovery time.”
When the device was no longer under the influence of the bias, it was expected that the electrons would possibly begin to recombine. From this data it seems that not allowing them to recombine, or at least rearrange in some way, actually caused the next voltage sweep to have less effect on the free electrons than the previous sweep. Whereas, a sweep done with time allotted after the previous sweep affected the electrons more than, or exactly as much as, the previous sweep.

No conclusions could be reached as there were many variables at work for consecutive voltage sweeps with and without time allotted. Such variables included the temperature from one sweep to the next as well as electron transit and recombination times. Also, the adsorption and desorption of oxygen on the ZnO crystals likely came into play.

Figure 3.4 shows the resulting current when the visible range of light was blocked and only UV light from 320 to 400 nm was allowed to interact with the ZnO sample. This filtering out of visible light seemed to have no effect on the resulting current of the semiconductor. This was expected as ZnO absorbs UV light with peak absorption at 365 nm; wavelengths in the visible range should have no effect.

![Graph showing photocurrent with and without UV optical filter.](image)

Figure 3.4. Photocurrent with and without UV optical filter.
The resulting fabricated ZnO photodetector worked as expected. It gave a proper signal when exposed to light in the UV range (320-400 nm). The sensitivity was calculated to be about 10 to 20. The saturation and recovery time trends were strange in that without changing any variable there was an observed change in photocurrent. To better understand these results, a few conditions were changed and the resulting photocurrent was observed. Firstly, the rate of bias sweep could be changed on the electrochemical workstation. Figure 3.5 shows the resulting photocurrent when three different sweep rates were tried. Each of these were done after the ZnO sample had reached saturation and with recovery time of 5 minutes between each trial.

![Figure 3.5. Photocurrent comparison of different voltage sweep rates.](image)

This indicates that at a slower sweep (0.025 V/s), the current passing through the ZnO sample ended up being about 15% less than the current through the sample at a faster sweep of 0.3 V/s. Consideration of this data will become important later when transmission of photons through the device is discussed. The differences in current for the different sweep rates may have
been due to temperature. Figure 3.6 shows that as the sweep rate became slower, the temperature of the device increased. This was expected as the device was exposed to the electric current for a longer period of time. Also, the sweep rate that gave the higher temperature also gave a lower photocurrent which literature showed is expected for ZnO MSM photodetectors.[11] In the case of Figure 3.6, the temperature at a sweep rate of 0.035 V/s started at 40.6 °C and reached a maximum temperature of 48.8 °C at 10 Volts to give a temperature change of 8.2 °C. In other words, the temperature of the ZnO photodetector increased at 0.025 V/s by 10% more than the increase at a sweep rate of 0.075 V/s. The current through the ZnO sample at 0.025 V/s was about 8% lower than the current at 0.075 V/s.

![Figure 3.6](image.png)

Figure 3.6. Temperature change of ZnO sample normalized to starting temperature compared to bias across ZnO sample.

The data shown thus far in this section led to questioning what could be causing the abnormal shifts in current that were seen for the ZnO photodetector device. The voltage could possibly induce interactions with oxygen in the air causing crystal structure changes that would change properties of the device such as resistivity. This interaction with oxygen could also be
responsible for the saturation and recovery time trends that were seen where time between voltage sweeps altered the current of the next sweep. In such cases, the time allotted when oxygen was diffusing back out of the sample and was interacting with the sample under the high potential conditions. This effect could also be working in conjunction with any thermal effects causing the changes that were seen. Simply altering the surface traps states could change recombination and give the observed effect. Therefore, the next tests altered the atmospheric conditions surrounding the device. A container was placed around the sample holder setup and argon was pumped into the container to purge out the air. Once in a completely argon environment, the same bias voltage sweep was run across the sample and the resulting current was measured. Figure 3.7 shows that for a totally argon atmosphere, the resulting current through the ZnO sample actually increased by about 12% compared to trials done with the sample in regular air atmosphere.

![Figure 3.7. Photocurrent of zinc oxide sample in air compared to in argon.](image)
A decrease in surface trap states should give lower responsivity and a higher peak current, and this is what was seen. When oxygen was purged out, however, there was still a saturation process that took place, and the sample was still affected by recovery time. Figure 3.8 shows the same trend as seen in Figure 3.3. After trial 11 there was no recovery time allotted before the next voltage sweep which resulted in a decrease in solar cell voltage for trial 12. So the diffusion or surface interaction with oxygen cannot fully explain the effects seen. These results indicate that for the sparsely coated ZnO photodetector device, there was something happening on the device that was altering the device electrical and photonic properties. The next section details steps taken to study any changes in absorption or transmission of the device.

![Figure 3.8. Saturation of ZnO sample affected by recovery time in argon.](image)

### 3.2 Introducing Solar Cell in Experimental Setup

The unique experimental setup used allowed for easy insertion of a solar cell behind the ZnO photodetector and measurement of the voltage of this solar cell while bias sweeps were ran across the ZnO sample. The position of the ZnO photodetector did not change, and it was hooked
up to the electrochemical station and exposed to the same intensity and wavelength of incident photons as in previous trials. Then, with the measured solar cell voltage, it could be determined if the number of photons transmitted through the ZnO sample changed while the bias was applied across the ZnO sample. An increase in solar cell voltage would indicate an increase in photons traveling through the sample; a decrease in solar cell voltage would indicate fewer photons traveling through the sample. With this in mind, a bias sweep was run across the ZnO sample from 0 to 10 volts just as in previous trials, and simultaneously recorded the voltage of the solar cell. Figure 3.9 makes it clear that as the voltage across the zinc oxide sample increased, the voltage of the solar cell located behind the ZnO sample decreased. This seems to indicate that with a greater voltage across the ZnO photodetector, fewer photons were transmitted through the photodetector.

![Figure 3.9](image)

**Figure 3.9. Voltage of solar cell behind ZnO sample vs. voltage across ZnO sample.**

It is postulated that the biased voltage induced charges (i.e. electrons and holes) to flow across the sample. These charges interacted with the photons, blocking them and, thus, reducing the number of photons transmitted through the substrate and reaching the solar cell behind the sample. With a higher voltage and current, there should have been more charges moving across
the sample, and thus, less light reaching the solar cell. This would have produced a lower solar cell voltage, which was observed. As well, when the biased voltage reached 10 volts and immediately stopped, the current should have stopped, i.e. the charges stop moving across the sample, causing the photons to freely transmit through the sample. This should have resulted in the voltage of the solar cell immediately returning to its starting value.

The data indicates, however, that there was a large delay in the time it took for the solar cell voltage to return to normal. When the biased voltage across the ZnO sample reached 10 volts and stopped, the voltage of the solar cell did not immediately return to its starting voltage, but instead, the voltage slowly climbed as indicated in Figure 3.10. Here the time was recorded instead of the voltage. In this example, and in the figures throughout this thesis, time 0 is equal to the start of the biased voltage sweep across the ZnO sample. It is hypothesized that the charges were still moving across the ZnO sample, or rearranging themselves after the biased voltage sweep. This charge “rearranging” continued for several seconds, as the voltage of the solar cell slowly recovered to its original starting voltage.

![Solar cell voltage vs. time relative to voltage sweep across ZnO sample. Dashed line indicates time of end of voltage sweep.](image)

Figure 3.10. Solar cell voltage vs. time relative to voltage sweep across ZnO sample. Dashed line indicates time of end of voltage sweep.
In fact, the time it took for the sample to return to its original starting voltage was used as the standard for “recovery time” shown in Figure 3.3. When time was allotted for the voltage of the solar cell to return to its starting value before running the next voltage sweep, a more pronounced increase in photocurrent was observed as long as the sample had not already reached saturation. Without this recovery and if the voltage sweeps were ran consecutively, the photocurrent would increase only slightly, or if the sample was already at “saturation” there was a decrease in photocurrent, as shown in Figure 3.3. This means the recovery time was crucial in allowing more current to flow through the sample, and possibly increasing efficiency in the device. This could be a result of a slow recombination time, whereby the electrons, not under the influence of the bias anymore but still in the conduction band because of the incoming photons, were bound up in the metal electrode for some time before returning to the ZnO semiconductor. This would indicate some capacitance, and possibly a result of the gain created by excess electrons of the metal conductor flowing into the conduction band of the semiconductor during the bias sweep. More electrons from the gain could build up on the lower potential electrode. At any given time, the holes and electrons in the semiconductor must be equal so all the electrons built up on one side could not all travel back across to the other electrode at once. The unbalanced charge on the electrodes after the bias sweep ended would then slowly be restored.

In combination with the previously stated phenomenon, the data also indicated a “lag time”, in which the cell voltage continued to decrease after the biased voltage across the ZnO sample ended. As indicated by the vertical dashed line in Figure 3.10, for a few seconds after the biased voltage across the ZnO sample ended, the voltage of the solar cell continued to decrease, stopped decreasing and eventually increased back to the starting value. Even though there was no detectable current through the ZnO sample, there seemed to still be movement or rearrangement
of charges across the sample. These charges continued to interact with incoming photons and blocked the light transmitting to the solar cell.

It would be expected then, that a greater current through the ZnO sample should produce a greater decrease in solar cell voltage as more photons would be blocked by the increase in charges traveling across the sample. However, this was not seen as illustrated in Figure 3.11 where the change in solar cell voltage was no different for trial 1 and the final trial where the sample reached saturation. Figure 3.2 shows there was about an 8% increase in current through the ZnO sample from the first trial to saturation, however, this seemed to produce no change in the amount of photons that were transmitted through the sample as there was no difference in the amount of decrease of solar cell voltage.

![Figure 3.11. Solar cell voltage during bias sweep across sample before and after sample has reached saturation.](image-url)
3.2.1 Effect of altering wavelength and intensity of incident photons

As shown in Figure 3.4, the photocurrent through the ZnO sample did not change when the visible range of light was filtered out and only 320 to 400 nm UV was allowed to reach the sample. However, when comparing the voltage of the solar cell behind the ZnO sample, there was a difference in the amount of light that reached the solar cell. When visible light was filtered out, the voltage of the solar cell decreased even more as shown in Figure 3.12. This can be explained by the fact that ZnO absorbs UV only, so the affect that was seen has taken place as the ZnO absorbed UV light and became conductive. With an applied voltage, the moving charges across the ZnO interacted with the light, and thus fewer photons reached the solar cell, which decreased its voltage. With no visible light coming through because of the filter, it was expected that more of a decrease in solar cell voltage would have been seen. Removing the filter and introducing the visible light again should have shown that the voltage of the solar cell decreased less. The data supported this hypothesis.

![Figure 3.12. Solar cell voltage during bias sweep across sample with UV (320-400 nm) compared to the full spectrum.](image-url)
Unexpectedly, however, when the intensity of light was increased, there was more of a decrease in the voltage of the solar cell. With the optical filter in place and only UV light passing through to the sample, the voltage of the solar cell was recorded as a voltage sweep was applied across the ZnO sample. As expected, as the voltage across the ZnO sample increased, the voltage of the solar cell behind the sample decreased. When the intensity of light was increased, the voltage of the solar cell decreased even more, when compared to a lower intensity, as shown in Figure 3.13. It appears that the intensity of light was directly related to the photon blocking effect that was seen. As light intensity was increased, more photons were blocked by the ZnO sample thus decreasing even more the voltage of the solar cell. It seems that incident photons induced the photon blocking effect that was seen. As the intensity of light was increased, thus increasing the number of incident photons, the number of photons that were blocked also increased.

![Figure 3.13. Solar cell voltage during bias sweep across sample with a lower intensity light compared to a higher intensity.](image-url)
3.2.2 Effect of Altering Electric Field

Modifying the incident photons that were coming to the photodetector seemed to have an impact on its transmittance. As shown in Figure 3.5, altering the sweep rate of the applied bias of the sample seemed to change the resulting current. The behavior of the solar cell was then looked at as the rate of bias sweep was applied across the ZnO sample. Figure 3.14 shows that with a higher rate of voltage sweep, and thus a higher current, there was less of a decrease in solar cell voltage. The resulting current of the 0.025 V/s sweep was about 15% less than the current of the 0.300 V/s sweep (see Figure 3.5), but the slower sweep produced about an 11% larger decrease in solar cell voltage. So, there were fewer charges moving across the sample yet more photons were blocked from passing through the sample.

![Graph showing decrease in solar cell voltage during bias sweep across ZnO comparing different rates of bias sweep.](image)

Figure 3.14. Decrease in solar cell voltage during bias sweep across ZnO comparing different rates of bias sweep.

What was of further interest when it came to varying voltage sweeps was the difference for “lag time” seen for the different sweeps. Figure 3.15 shows that for the faster sweeps there
was a greater lag time for the time it took for the voltage of the solar cell to stop decreasing after the bias sweep across the ZnO sample ended.

Figure 3.15. Decrease in solar cell voltage with different rates of voltage sweeps across ZnO sample. Dashed vertical line (blue) represents end of voltage sweep, dashed and dotted line (pink) represents minimum solar cell voltage decrease.

As shown by the dashed line (end of voltage sweep) and dashed and dotted line (minimum of solar cell voltage decrease) the lag time for the fastest sweep (0.300 V/s) was over 20 seconds whereas the lag time for the slower sweep (0.065 V/s) was less than 15 seconds. In fact, for the slowest sweep at 0.025 V/s there was no lag time at all; as soon as the voltage sweep ended across the ZnO sample, the voltage of the solar cell immediately started to increase back to its starting voltage. It seemed that the faster voltage sweeps induced changes in the device that did not have time to “catch up” to the quickly changing voltage. For some time after the sweep had ended and there was no more potential across the device there still seemed to be photons being blocked which could have been from some charge-hole pairs that had yet to recombine.
This data shows that the rate of sweep influenced the free electrons to recombine or rearrange more quickly or more slowly depending on what rate of voltage sweep had been just applied to them. It is not clear why exactly the sweep rate affected the recovery time in such a way, but could have been due to temperature differences which were explored and are reported in the next section.

3.2.3 Measuring and Altering Atmospheric Conditions

The data obtained from different sweep rates applied across the ZnO sample showed both changes in temperature and a decrease of solar cell voltage. In fact, Figure 3.6 and Figure 3.14 look inversely similar. Considering this, the inverse of the temperature of the three different voltage sweeps was calculated. Figure 3.16 is the resulting graph which showed a very strong similarity between slopes of the sweep rate graph and that of the temperature change graph when comparing the number of photons which were apparently blocked.

![Figure 3.16. Comparison of inverse temperature change at different sweep rates across zinc oxide sample.](image)
The direct comparison of inverse temperature change and solar cell voltage change shows that there was almost a one-to-one correlation between the two. However, the inverse temperature change deviated from the change in solar cell voltage in magnitude. This meant that the change in solar cell voltage, i.e. the blocking of photons, was not 100% dependent upon the temperature of the ZnO device. There must have been some other effects that were causing photons to be blocked that were not entirely related to thermal induced changes. These other effects might have come from the oxygen in the air as postulated previously. As such, the atmosphere surrounding the device was purged and a resulting current vs voltage graph was obtained for the ZnO device comparing the current in air to the current in an argon atmosphere. Figure 3.17 shows the resulting data for the decrease in solar cell voltage when the device was in air compared to argon. In argon, there was about a 12% higher current as shown in Figure 3.7, whereas there was about a 2% less of a decrease in solar cell voltage. In the case of the ZnO sample in an argon atmosphere, fewer photons seemed to be blocked.

![Graph showing solar cell voltage during bias sweep across sample in argon compared to in air.](image-url)

Figure 3.17: Solar cell voltage during bias sweep across sample in argon compared to in air.
If the charge trap states induced by oxygen absorbing to the surface is compared to the change in transmittance, perhaps some of the observed effect can be made clear. With no oxygen to bind up holes there would have been a higher photocurrent which was seen. There was, however, fewer blocked photons which showed that oxygen and the resulting trap states could have played some role in blocking more photons under influence of the bias.
4. Conclusions and Future Work

4.1 Conclusions

The conclusions drawn from this research are twofold. Firstly, a device has been fabricated that shows efficacy at being a UV photodetection device that has a sensitivity of about 10 to 20. Due to the increases in need for such devices in cases of solar, biological, and other detection applications, the development of improved novel alternatives that can perform better than previous alterations is greatly sought after. Not only does this device perform, but is made from a cheap, non-toxic, easily workable metal oxide semiconductor. The substrate for the device is made from a simple, quick, cheap sputtering deposition process and most notably, the fabrication of the hierarchical ZnO tree structure network is grown using a cheap, low temperature hydrothermal process.

Secondly, this research indicates a need for further study into the optical phenomenon of MSM photodetection devices and the ultimate implications of such phenomena. For the case of branched ZnO nanostructures there seems to exist a transmission spectrum which is tunable. This could be a result of some plasmonic effects from the ohmic contacts perhaps creating a polariton which interacts and blocks incoming photons. As this is an investigation, no hard conclusions are drawn as to what exactly is responsible for the transmission data that is seen in these experiments. However, it is clear that more work should be done to come to an understand of what is taking place at the interface where light meets matter that is causing a change in transmission under bias. With a better understanding of these physics and optics phenomenon, the field of photodetection can be expanded. New technology is a likely and promising result of the end of this study. Tunable optical properties of a transparent semiconductor device means likely avenues into solar harvesting, windows, and even new photodetection capabilities. If fully
realized these technologies could change the way photodetection, and even optics and physics are studied.

4.2 Future Work

This work demonstrates the need for further investigation into the proposed photodetector and also opens possible doors for technology that uses these findings. Proposed work in this area would be to determine what is causing the observed change in transmittance.

Specifically, it is recommended that similar tests be performed that alter variables such as temperature, oxygen concentration, and applied electric field. A capacitance tester that can detect current in picoamps and smaller could be used to determine if, and how much, capacitance is playing a role in the slow recovery and possibly lag time of the device. Also, applying an AC current to the device and modifying the frequency could be tested to see the effects of different frequencies on the transmittance of the device. To get a better understanding of any thermally induced effects, the temperature of the device during experimentation could be modified and the resulting transmittance change observed. Further testing with atmosphere purging could also be conducted which would include introducing extra oxygen gas into the environment to see if the transmittance decreases even more as would be expected from the current results. Also, with further research, the impact of applying a magnetic field to the device could be tested.

Devices that could be created as a result of this work include tunable transmittance windows that would only need a small potential applied across a thin film of transparent semiconductor such as ZnO. This window could double as a UV photodetector and could be modified, depending on the application, to do chemical or biological sensing.
References


[34] N. M. Gasanly, "Effect of temperature and isomorphic atom substitution on optical absorption edge of TlInS2xSe2(1-x) mixed crystals (0.25 <= x <= 1)," *Crystal Research and Technology*, vol. 45, pp. 525-528, May, 2010.


[52] S. K. Mishra, S. Bayan, P. Chakraborty and R. K. Srivastava, "Defect-dominated optical emission and enhanced ultraviolet photoconductivity properties of ZnO nanorods synthesized by


Appendix A: Description of Research for Popular Publication

UV Photodetection Device Used to Broaden Fundamental Scientific Principles

UV photodetectors have many useful applications in a broad range of categories such as biological sensing, weapons, communications, and fire detection. Often these photodetectors are made from a semiconductor (responsive to UV light) deposited between two metal electrodes. These metal-semiconductor-metal photodetectors will show current when exposed to light and when a voltage is applied. For the case of a UV light detector, a higher current indicates that more UV light is shining on the sample, thus a UV light detector is created.

A research group at the University of Arkansas has went a step beyond photodetection, however, by using their newly created UV photodetection device to explore some unique physics that has not yet been explored. They created their photodetection device by growing branched rods of zinc oxide at the nano scale. These nano trees are thought to more efficiently absorb light at wide angles, but more than that, they are spaced apart so that some photons actually pass between them. This wide spacing allowed for the group to study what happens to these photons as they pass in between the nano trees. It should be expected that the photons would pass between these trees and transmit through the device. The only way that the photons would be diverted from their path would be to physically change the spacing of the nano trees by moving them closer together. They found, however, that the number of photons that pass in between the nano trees of zinc oxide actually decrease when there is a voltage applied to the photodetector. To their knowledge, the research group knows of no other study that has given similar results.

It is speculated by the group that as the photons pass between the zinc oxide nano trees there is some kind of communication, or influence, from the photon to the tree and from the tree to the photon. This influence becomes more prominent with a larger voltage applied across the
sample and, thus, the photon is diverted from its original path and is absorbed in some way by the nano trees. This absorption is thought, by the group, to take place in a few different ways. They speculate that the moving charges across the sample from the applied voltage may jump from tree to tree and, in the process, interact with a photon that is also passing between the trees. Or, it could also mean that the influence of the nano trees actually extended outwards as the voltage increased, increasing the radius by which the tree can interact with light. In any case, the findings suggest a phenomenon that has yet to be characterized by the scientific community. This phenomenon of photons diverting from their path and interacting with zinc oxide nano trees that are a distance away is a very new concept.

These findings suggest that the interaction of light waves with matter may hold more mysteries that have yet to be discovered and could impact future technology. New technologies from these findings could include transparent materials such as windows with a tunable transmission allowing the user to alter the amount of light passing through. Furthermore, these findings could have a large impact within the physics and optics community by providing data that could open the door for new scientific principles related to light interacting with matter.
Appendix B: Executive Summary of Newly Created Intellectual Property

The fabricated photodetector device described herein is a novel MSM photodetector that uses hierarchical 3D ZnO structures sparsely coated on micropatterned interdigitated gold electrodes on quartz substrate. This device represents the only intellectual property created in this research.
Appendix C: Potential Patent and Commercialization Aspects of Listed Intellectual Property Items

C.1 Patentability of Intellectual Property (Could Each Item Be Patented)

Because of the novelty of the fabrication and the components of the devices, the UV photodetector could possibly be patented.

C.2 Commercialization Prospects (Should Each Item Be Patented)

The photodetector described in this research was used as an example of tunable transmission as a result of changing variables. However, the device could be patented as a novel UV MSM photodetector.

C.3 Possible Prior Disclosure of IP

The photodetector device has been presented at conferences in which its fabrication and specifications were disclosed.
Appendix D: Broader Impact of Research

D.1 Applicability of Research Methods to Other Problems

The results found in this research has significance that could greatly impact other areas of science. Photonics, optics, physics, and materials science are but a few fields that might benefit from this newly found data because of the special methodology used to investigate the optical properties of the device researched in this thesis. Also, semiconductors in general can now perhaps be researched further to better understand fundamental principles especially for solar devices using the researched methods that have been presented in this thesis.

D.2 Impact of Research Results on U.S. and Global Society

Photovoltaics and photodetectors are already a widely used technology utilizing semiconductor devices similar to the one used in this research. This research gives evidence that new photodetection devices with tunable properties are possible. With new developments in these technologies the global economy and way of life for society is greatly impacted. New photodetection devices open the door for sensors in many areas which broadly impacts technology and increases quality of living. This research also has shown that the interaction of light with matter may be able to be better understood by the application of the research methodology presented here. Newly found physical principles and light matter interaction phenomenon also carry a great impact to the scientific community and the global society by providing new avenues of research and creating new sciences.

D.3 Impact of Research Results on the Environment

While it is true that photodetectors are normally an energy consumer, they also pave the way for better photovoltaic devices which are clean energy. Photodetectors also play a large role in sensing for chemical, biological, and photonic needs all of which help all technologies in
general. Overall, new photodetection devices that might result from this research, and the resulting new science learned from them, positively impact the state of technology and thus improve the global way of life.
Appendix E: Microsoft Project for MS MicroEP Degree Plan

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<th>Duration</th>
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<th>Finish</th>
</tr>
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<td>1. Create project file</td>
<td>613 days</td>
<td>Mon 8/14</td>
<td>Mon 8/15</td>
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<tr>
<td>2. Download Template</td>
<td>1 day</td>
<td>Mon 8/14</td>
<td>Mon 8/15</td>
</tr>
<tr>
<td>3. Read Instructions (in notes)</td>
<td>1 day</td>
<td>Mon 8/14</td>
<td>Mon 8/15</td>
</tr>
<tr>
<td>4. Fill Project Title in Project Information</td>
<td>1 day</td>
<td>Mon 8/14</td>
<td>Mon 8/15</td>
</tr>
<tr>
<td>5. Set up Auto Schedule</td>
<td>1 day</td>
<td>Mon 8/14</td>
<td>Mon 8/15</td>
</tr>
<tr>
<td>6. Double-click on a task and click ‘Select a task’ tab</td>
<td>1 day</td>
<td>Mon 8/14</td>
<td>Mon 8/15</td>
</tr>
<tr>
<td>7. Set start date</td>
<td>1 day</td>
<td>Mon 8/14</td>
<td>Mon 8/15</td>
</tr>
<tr>
<td>8. Add/edit subtasks</td>
<td>1 day</td>
<td>Mon 8/14</td>
<td>Mon 8/15</td>
</tr>
<tr>
<td>9. Link tasks</td>
<td>1 day</td>
<td>Mon 8/14</td>
<td>Mon 8/15</td>
</tr>
<tr>
<td>10. Select Professor</td>
<td>27 days</td>
<td>Mon 8/14</td>
<td>Mon 8/15</td>
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<td>11. Read Publications</td>
<td>280 days</td>
<td>Mon 9/24</td>
<td>Fri 10/22</td>
</tr>
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<td>12. Paper 1</td>
<td>3 days</td>
<td>Mon 11/14</td>
<td>Mon 11/15</td>
</tr>
<tr>
<td>13. Paper 2</td>
<td>4 days</td>
<td>Wed 1/14</td>
<td>Wed 1/15</td>
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<tr>
<td>14. Paper 3</td>
<td>3 days</td>
<td>Wed 2/15</td>
<td>Wed 2/16</td>
</tr>
<tr>
<td>15. The last paper you read before your defense</td>
<td>5 days</td>
<td>Wed 9/24</td>
<td>Wed 9/25</td>
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<tr>
<td>16. Research</td>
<td>255 days</td>
<td>Mon 9/29</td>
<td>Fri 10/23</td>
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<td>17. Define Experiment</td>
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<td>Mon 11/15</td>
<td>Mon 11/16</td>
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<td>18. Create Apparatus</td>
<td>4 days</td>
<td>Fri 10/31</td>
<td>Fri 11/1</td>
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<td>19. Verify Function of Known Samples</td>
<td>1 day</td>
<td>Mon 11/1</td>
<td>Mon 11/2</td>
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<td>20. Perform Experiments</td>
<td>1 day</td>
<td>Mon 11/15</td>
<td>Mon 11/16</td>
</tr>
<tr>
<td>21. Collect Data</td>
<td>1 day</td>
<td>Mon 11/15</td>
<td>Mon 11/16</td>
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<tr>
<td>22. Analyze Data</td>
<td>1 day</td>
<td>Mon 11/16</td>
<td>Mon 11/17</td>
</tr>
<tr>
<td>23. Write Report</td>
<td>1 day</td>
<td>Mon 11/17</td>
<td>Mon 11/18</td>
</tr>
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<td>24. Presentations</td>
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<td>Mon 11/19</td>
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<td>25. Final Exam</td>
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<td>Mon 11/19</td>
<td>Mon 11/20</td>
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<td>Task Name</td>
<td>Duration</td>
<td>Start</td>
<td>Finish</td>
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<td>Analyze Results</td>
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<td>Fri 10/3/14</td>
<td>Mon 7/6/15</td>
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<td>Experiment 1</td>
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<td>Fri 10/3/14</td>
<td>Fri 10/3/14</td>
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<td>Experiment 2</td>
<td>1 day?</td>
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<td>Wed 10/8/14</td>
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<td>Experiment 3</td>
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<td>Mon 5/18/15</td>
<td>Mon 5/18/15</td>
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<td>Experiment 4</td>
<td>1 day?</td>
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<td>Fri 6/5/15</td>
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<tr>
<td>Experiment 5</td>
<td>1 day?</td>
<td>Mon 7/6/15</td>
<td>Mon 7/6/15</td>
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<td>Write Thesis</td>
<td>105 days</td>
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<td>Fri 10/9/15</td>
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<td>Chapter 1: Background of area</td>
<td>10 days</td>
<td>Mon 5/18/15</td>
<td>Fri 5/29/15</td>
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<td>Chapter 2: Description of Experiment</td>
<td>7 days</td>
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<td>Tue 5/26/15</td>
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<td>Chapter 3: Results</td>
<td>3 days</td>
<td>Mon 8/24/15</td>
<td>Wed 8/26/15</td>
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<td>Chapter 4: Analysis</td>
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<td>Fri 10/9/15</td>
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<td>Chapter 5: Conclusion</td>
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<td>Mon 10/5/15</td>
<td>Fri 10/9/15</td>
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<td>Appendix</td>
<td>5 days</td>
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<td>Fri 10/9/15</td>
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<td>END GAME</td>
<td>51 days</td>
<td>Mon 10/12/15</td>
<td>Sat 12/19/15</td>
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<td>Review by Major Professor</td>
<td>0.6 wks</td>
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<td>Correct issues found</td>
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<td>Final approval by Major Professor</td>
<td>2 days</td>
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<td>QC by iEP Director - permission to send to committee</td>
<td>4 days</td>
<td>Tue 11/10/15</td>
<td>Fri 11/13/15</td>
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<tr>
<td>Send thesis to committee members</td>
<td>1 day</td>
<td>Mon 11/16/15</td>
<td>Mon 11/16/15</td>
</tr>
<tr>
<td>Send Title, Abstract &amp; Scheduling Information to iEP</td>
<td>1 day</td>
<td>Mon 11/16/15</td>
<td>Mon 11/16/15</td>
</tr>
<tr>
<td>Last Day for Public Presentation Events</td>
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<td>Tue 11/24/15</td>
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<td>Last day for Defense Before Committee</td>
<td>0 days</td>
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<td>Graduate School Dead Line</td>
<td>0 days</td>
<td>Fri 12/11/15</td>
<td>Fri 12/11/15</td>
</tr>
<tr>
<td>Dead Day</td>
<td>1 day</td>
<td>Fri 12/11/15</td>
<td>Fri 12/11/15</td>
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<tr>
<td>Graduate</td>
<td>0 days</td>
<td>Sat 5/7/16</td>
<td>Sat 5/7/16</td>
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</table>
Appendix F: Identification of All Software Used in Research and Thesis Generation

Computer #1:

Model Number: DCSM1F Dell Optiplex 780  
Serial Number: 1ST3WN1  
Location: DISC building room 218  
Owner: Department of Chemistry & Biochemistry, University of Arkansas

Software #1:  
Name: Microsoft Office 2013  
Owner: University of Arkansas Fulbright College of Arts and Sciences

Computer #2:

Model Number: PP11L Dell Latitude D610  
Serial Number: 4ZBX181  
Location: DISC building room 217  
Owner: Department of Chemistry & Biochemistry, University of Arkansas

Software #1:  
Name: Microsoft Office 2007  
Owner: University of Arkansas Fulbright College of Arts and Sciences
Appendix G: All Publications Published, Submitted and Planned

Conference Proceedings:
- Tyler Chism, Garrett Torix, Ryan Tian “Exploring New Physics in Photon-Photoelectron Interactions on Micropatterned, Zinc Oxide Hyper-Branched Nanorods”, American Chemical Society regional meeting, November 4th, 2015, Memphis, TN.