To my family and my fiancée
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<tr>
<td>CCD</td>
<td>charged coupled device</td>
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<td>DMSO</td>
<td>dimethyl sulfoxide</td>
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<td>EQE</td>
<td>external quantum efficiency</td>
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<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
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<td>ITO</td>
<td>indium tin oxide</td>
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<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
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<td>MIS</td>
<td>metal insulator semiconductor</td>
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<td>MSM</td>
<td>metal semiconductor metal</td>
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<td>NP</td>
<td>nanoparticle</td>
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<td>photomultiplier tubes</td>
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<td>tetramethylammonium hydroxide</td>
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<td>wide band gap</td>
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SOLUTION-PROCESSED P-N JUNCTION ULTRAVIOLET PHOTODETECTORS
BASED ON P-NIO AND N-ZNO

By
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August 2012

Chair: Franky So
Major: Materials Science and Engineering

Ultraviolet (UV) photodetectors have a wide range of applications in the industrial and military areas, including biological and environmental research, astronomical studies, missile plum detection, flame sensing, optical communication, and so forth. Although several UV-detectors have recently been developed using Schottky junction diodes and pn-junction of wide-gap semiconductors such as ZnS, GaN, ZnSe, and diamond, these UV photodetectors still have limitations that make them inappropriate for many applications due to their high cost and low quantum efficiency of less than 40%. In this study, we report on a low cost of solution-processed and high quantum efficiency UV photodetectors fabricated using solutions of p-type NiO(Eg ~3.7eV) and ZnO(Eg~3.3eV).

NiO layer as a p-type were deposited on ITO (Indium Tin Oxide) glass by use of a spin-coat method. Then NiO layers were heated to a temperature at 270°C, 350°C, 450°C, 540°C for 40 minutes respectively. ZnO nanoparticle(NP) layers as a n-type were deposited same as NiO layer and heated to a temperature at 100°C for 10min. An Aluminum as electrode layer of around 80nm was deposited by thermal evaporation
onto the NiO / ZnO layer. This device was investigated by current-voltage (I-V) characteristics. The devices exhibit the dark current density are 36 nA/cm$^2$, 9.2 nA/cm$^2$, 6.8 nA/cm$^2$, 0.7 nA/cm$^2$ under -1V applied bias and quantum efficiency(QE) are 25,291%, 5,743%, 3,796%, 189% at a wavelength of 350nm with detectivity of $2.08 \times 10^{13}$, $9.44 \times 10^{12}$, $7.24 \times 10^{12}$, $1.11 \times 10^{12}$ were achieved at 350nm respectively.
CHAPTER 1
MOTIVATION

Many of the important applications of ultraviolet (UV) detection are in high
temperature flame detection, space research, gas sensing, missile warning systems, air
quality monitoring, accurate measurement of radiation for the treatment of UV
exposed skin, etc. [1-4]. The most common detectors recently in use are the
photomultipliers tubes (PMT’s) and the silicon photodetectors, but they are not blind and
demand costly filters to attenuate unwanted and infrared radiation. With the use of wide
band-gap semiconductors such as NiO, GaN, diamond and ZnO, the need for these
filters would be eliminated. Among them, NiO is a well-known transparent p-type
semiconductor with a band gap of about 3.7eV. It has a rock salt cubic structure and a
weak absorption band due to the d–d transition of 3d⁸ electron configuration in the
visible region [5-7]. Also ZnO, an environmentally friendly semiconductor with a room-
temperature band gap of 3.35 eV, is of great interest for UV detection because of its
various synthetic methods, diverse processing technologies, and the capability of
operating at high temperatures and in harsh environments. Liu et al. fabricated Schottky
UV photodetectors which exhibit fast response speed by growing high quality ZnO
epitaxial films on sapphire substrates [8]. Nevertheless, achieving high crystal quality of
ZnO thin films with suitable metal contacts is still challenging because of the lack of
high-quality and low-cost substrates for lattice-matched growth. Most ZnO thin films
deposited by metal-organic chemical vapor deposition, pulsed laser deposition, or radio
frequency sputtering have a large density of dislocations and grain boundaries.
Transport and UV photoconduction in these polycrystalline ZnO films depends
sensitively on stoichiometry, trap densities, and most importantly, gas adsorption and desorption on the crystal surfaces.

However, solution-processed electronic and optoelectronic devices have some advantages over conventional crystalline semi-conductor devices in terms of ease of fabrication, large device area, physical flexibility, and most importantly, low cost.

Therefore, in this paper, we developed the fabrication of pn-junction UV photodetectors by solution processed p-type NiO and n-typ ZnO NPs on the glass substrates with pre-patterned indium tin oxide (ITO), followed by annealing in air and evaporation of Aluminum contacts through a shadow mask.
CHAPTER 2
BACKGROUND

2.1 Ultraviolet Radiation

In 1801, the first reveal of ultraviolet (UV) radiation was made, when J W Ritter discovered that certain chemical reactions were catalyzed by exposure to non-visible radiation with a shorter wavelength than violet. After that, T Young showed that chemically active radiation tracked the interference laws in 1804. This observation, together with the work of many other researchers, made it possible to establish that visible and UV emissions both were expressions of the same sort of electromagnetic radiation, solely differing in their wavelength.

These days, it is broadly established that the UV region occupies the spectral interval of $\lambda = 400–10$ nm [9]. It is a greatly ionizing radiation, which triggers many chemical processes. The most important natural UV source is the Sun. Roughly 9% of the energy obtained from the Sun at the higher layers of the atmosphere is in the UV range [10], although the stratospheric ozone layer prevents wave lengths shorter than 280 nm from reaching the Earth’s surface. Besides, remaining UV radiation may be attenuated by pollution in the low troposphere.

2.1.1 Classification

Ultraviolet radiation (UVR) shows the spectral region within a wavelength interval [11] of $\lambda = 380–10$ nm ($hv = 3.2–124$ eV) and the UV spectrum is traditionally separated into a near region ($\lambda = 380–200$ nm, $hv = 3.2–6.2$ eV) and a far region ($\lambda = 200–10$ nm, $hv = 6.2–124$ eV). The near region contains as follows:

- Long-wavelength UVR (UV-A) at 380-315nm ($hv = 3.2-3.9$ eV). This is the less energetic range. It stimulates photosynthesis, and is involved in the synthesis of some vitamins and basic biochemical compounds. Overexposure may lead to erythema and premature ageing.
• Middle-wavelength UVR (UV-B) at 315-280nm (hv = 3.9-4.4 eV). Even though partially absorbed by the ozone layer, this composes 9% of the total UV radiation reaching the Earth’s surface. UV-B exposure is risky for human beings (causing burns, cataracts, erythema, and skin cancer), harmfully affects harvests and enhances the ageing of organic materials.

• Short-wavelength UVR (UV-C) at 280-200nm (hv = 4.4-6.2eV). This is the most energetic range, and it is also the more deleterious. However, it is almost completely absorbed by the stratospheric ozone layer.

The following division of the spectrum is frequently used in American publications:

near-UV, 400–300 nm; middle UV, 300–200 nm; far-UV, 200–100nm; extreme UV, 100–10nm [12].

2.1.2 Application of UVR

Biologically active UVR action is used in medicine (solar irradiation of people) and in agriculture.

Vitamin-synthesizing UVR action is used in biotechnology (synthesis of vitamins D2 and D3).

Bactericidal UVR action is used in water, air and food disinfection, especially for long storage and during epidemics, and for disinfection of blood intended for transfusion.

The detection of UV radiation is used in a broad range of military and civil applications, such as biological and chemical analysis (pollutants, ozone, and most organic compounds present absorption lines in the UV spectral range), flame detection (including fire alarms, missile warning or combustion monitoring), optical communications (particularly inter-satellite communications at λ< 280 nm), emitter calibration (instrumentation, UV lithography), and astronomical studies.
2.2 UV Photodetectors

2.2.1 Semiconductor Photodetectors

In semiconductor photodetectors, photons are absorbed in the semiconductor, creating electron–hole pairs. These photogenerated carriers are separated by the electric field, due either to the built-in potential or the applied voltage, producing a current proportional to the photon flux. The schematic operation of this device is depicted in Figure 2-1.

There are different types of semiconductor photodetectors [13]: photoconductors, Schottky barrier photodiodes, metal–semiconductor–metal (MSM) photodiodes, metal–insulator–semiconductor (MIS) structures, p–n and p–i–n photodiodes, and field-effect and bipolar phototransistors. The schematic structure of these devices is depicted in Figure 2-2.

2.2.2 Semiconductors for UV Photodetection

UV detection has conventionally been achieved by photomultiplier tubes (PMTs), thermal detectors, narrow-bandgap semiconductor photodiodes or charge-coupled devices (CCDs). PMTs show low noise and high gain, and can be reasonably visible-blind. However, they are fragile and bulky devices, demanding high power supplies. Thermal detectors are normally used for calibration in the UV region. Even though useful as radiometric standards, these detectors are slow, and their response is wavelength-independent.

On the other hand, semiconductor photodiodes and CCDs present the benefits of solid-state devices, demanding only moderate bias. Semiconductor photodetectors are small, lightweight, and insensitive to magnetic fields. Their good linearity, low cost, and
sensibility, and capability for high-speed operation make them a brilliant advance for UV detection.

Since their well-established technology, 'UV-enhanced' silicon photodiodes are the most common devices for UV photodetection, even though commercial GaAsP and GaAs based photodiodes are also accessible. Silicon-based UV photodiodes can be divided into two major families: p–n junction photodiodes and charge-inversion photodiodes [14, 15].

However, Si-based UV photodiodes exhibit some limitations natural to silicon technology. The main weak point for these narrow-bandgap semiconductor detectors is device ageing, since exposure to radiation of much higher energy than the semiconductor bandgap. Besides, passivation layers, typically SiO₂, reduce the QE in the deep-UV range, and are also degraded by UV illumination. Another limitation of these devices is their sensitivity to low-energy radiation, so that filters are demanded to block out visible and infrared photons, resulting in a major loss of effective area of the instrument. Finally, for high-sensitivity applications, the detector active area must be cooled to reduce the dark current; the cooled detector behaves as a cold trap for contaminants, which leads to a lower detectivity.

UV photodetectors based on wide-bandgap (WBG) semiconductors (diamond, SiC, III-nitrides, and some II-V compounds) are itself a significant benefit for photodetectors, since it allows room temperature operation, and provides intrinsic visible-blindness [15-18]. These materials are also apparent that the thermal conductivity of WBG materials is in general significantly higher than that of silicon, which makes them suitable for high temperature and high-power applications.
In spite of all their promising characteristics, there are still some drawbacks in WBG semiconductors. The main drawback is crystal quality. The lack of high-quality substrates for homoepitaxy or other lattice-matched substrates leads to material with a high density of dislocations and grain boundaries. These structural defects induce deleterious effects on device performance, such as an enrichment of visible detection and leakage currents, and the appearance of persistent effects [19, 20].

2.2.3 Photodetector Characterization

Photodetectors are photodiode with rectifying current density-voltage (J-V) characteristics. Typical J-V characteristics in the dark and under incident illumination are shown in Figure 2-3. The responsivity is the most important parameters in photodetectors and is calculated by the following formula.

\[
R = \frac{J_{\text{net photo}}}{P_{\text{inc}}} = \frac{(J_{\text{photo}} - J_{\text{dark}})}{P_{\text{inc}}}
\]

where \(J_{\text{net photo}}(\lambda)\) and \(P_{\text{inc}}(\lambda)\) are the net photocurrent, which subtracts the measured dark current density \(J_{\text{dark}}(\lambda)\) from the measured photo current density \(J_{\text{photo}}(\lambda)\), of the photodetector. The quantum efficiency and detectivity can be calculated from the responsivity using the following expression:

\[
QE = \frac{(hc/q\lambda) \times R \times 100\%}{(1-2)}
\]

\[
D^* = \frac{J_{\text{photo}}}{P_{\text{inc}}} \, (2qJ_{\text{dark}})^{1/2}
\]

where \(h\), \(c\), \(q\), and \(\lambda\) are the Plank constant, speed of light, electronic charge, and the photon wavelength, respectively.
Figure 2-1. Photodetection Principle. A) Schematic of UV photodetector structure. B) Photodetection principles
Figure 2-2. Schematic structure of different semiconductor photodetectors
Figure 2-3. Typical J-V curves of photodetectors in dark and under illumination.
CHAPTER 3
EXPERIMENTAL DETAILS

3.1 NiO Solution

The NiO solution was prepared from a precursor, in which nickel acetate tetrahydrate were dissolved in ethanol. Ethanolamine was added to the precursor as a stabilizer in equal molar concentration to nickel acetate tetrahydrate.

3.2 ZnO NPs Solution

We used ZnO NPs (3–5 nm in size), which were synthesized through a sol-gel process using precursors of zinc acetate and tetramethylammonium hydroxide (TMAH). For a typical process, the ZnO NPs were synthesized by slowly dropwise addition of a stoichiometric amount of TMAH dissolved in ethanol (0.5M) to zinc acetate dehydrate (0.1M) dissolved in dimethyl sulfoxide (DMSO), followed by stirring for an hour. After that, add ethyl acetate and heptanes to obtain ZnO particles use centrifuge, the ZnO NPs were dissolved in ethanol and stored under ambient conditions. All solutions were filtered with a 0.45 μm filter.

3.3 UV Detectors Fabrication

All UV photodetectors were fabricated on pre-patterned ITO glass substrates with a sheet resistance of 20 Ω per square. The four ITO glass substrates were first cleaned with acetone and isopropanol in an ultrasonic cleaner for 15 minutes each. And then blown dry with N2 gas, and subsequently treated with UV ozone for 15 minutes. For p-type layer, a 130nm thick NiO layer was spin coated on the ITO glass substrates and the film was subsequently annealed at 270°C, 350°C, 450°C, 540°C for 40 minutes respectively. After shortly, four samples need to be cool down until 50°C. After that, for n-type layer, a 70nm thick ZnO layer was spin coated on the four ITO substrates and
the film was subsequently baked at 100°C for 10min. ZnO film also need to be cool down until 50°C. To finish this UV detector fabrication, a 80nm Al was thermally evaporated on top of ZnO layer as an electrode. This layer was deposited in a vacuum chamber with a base pressure of 1 × 10−6 torr. The deposition rate was 2 Å/s for Al. The active area of the devices used in this study was 0.04 cm2. ITO electrode was always ground and the Al electrode was applied by negative bias. In addition, the device is also fabricated on quartz substrate glass. ITO was sputtered on quartz substrate for 15min. The devices were tested in air without encapsulation. Figure 3-1 shows Schematic diagrams of UV photodetectors fabrication. The current-voltage (I – V) characteristics of the devices were measured with a Keithley 4200 semiconductor parameter analyzer. The devices were irradiated with monochromatic light from a Newport monochromator using an Oriel solar simulator as a source. Illumination between 300 and 400 nm were irradiated on the devices with different power intensities (35.6 μWcm−2 and 139μWcm−2, respectively). The illumination intensities at different wavelengths were measured using two calibrated Newport 918D photodiodes. The EL spectra were collected using an Ocean Optics HR4000 high-resolution spectrometer. The spectral response was also used to calculate the spectral detectivity of the devices across the UV wavelengths. To study the stability of the devices, the unencapsulated photodetectors were exposed to ambient conditions. The X-ray photoelectron spectroscopy (XPS) investigations were done on a Perkin Elmer 5100 XPS for NiO film analysis.
Figure 3-1. Schematic diagrams of UV photodetectors fabrication
CHAPTER 4
RESULTS AND DISCUSSIONS

As shown at Figure 4-1, the schematic energy band diagram of such a photodetector with pn-junction. A thin layer of NiO is used for p-type layer and ZnO is used for n-type layer. The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of a NiO were 1.8 eV and 5.5 eV, respectively and ZnO were 4.2 eV and 7.6 eV respectively and work functions of an ITO and a Al also were 4.8 eV and 4.3 eV, respectively.

Figure 4-2 shows that the device demonstrates a clear diode like rectifying behavior at bias voltages from +0.5 to -1.5V. The dark current densities in Figure 4-3 (A) were 36 nA/cm², 9.2 nA/cm², 6.8 nA/cm², and 0.7 nA/cm² at -1V, respectively. Also, photo current densities as Figure 4-3 (B) were 8.2 uA/cm², 1.8 uA/cm², 1.2 uA/cm², and 62 nA/cm² at -1V, respectively. The net photo generated current density, the difference of photo current densities and dark current densities decrease gradually with increased NiO annealing temperature. That is, the number of charge carriers flowing through the device under the light illumination. The 350 nm incident UV light with the intensity 0.115mW/cm² was irradiated on the UV photodetector under applied reverse bias.

The changes in dark current and photocurrent led to External Quantum Efficiency (EQE) and detectivity. The EQE and detectivity of the UV photodetector are shown in Figure 4-4 with annealed NiO at 270°C, 350°C, 450°C, and 540°C, respectively and UV photodetector at a reverse bias of -1V. The highest EQE and detectivity are obtained at 270°C annealed NiO UV photodetector, whereas the lowest EQE and detectivity are obtained at 540°C annealed NiO UV photodetector. The EQE reaches 25291%, 5743%, 3796% and 189% with 270°C, 350°C, 450°C, and 540°C NiO UV photodetector,
respectively. Also, detectivity (Jones) $2 \times 10^{13}$, $9.4 \times 10^{12}$, $7.2 \times 10^{12}$, and $1.11 \times 10^{12}$ were obtained.

Figure 4-5 illustrates the room-temperature spectral detectivity of UV detector with NiO annealed at 270°C under -1V applied bias. The spectra show the active range between 320-365nm. It indicates that this UV detector is visible blindness range. It also can be seen that cutoff occurred at 320nm due to absorption either ITO and glass substrate. As shown at Figure 4-6, life time was measured every week for a month. This UV detector is oxygen based device so the performance of EQE and detectivity for a month is very stable.

To measure rise time and fall time, the temporal responses of the four detectors were measured by shutting on/off the light at the wavelength of 350nm under a -1V applied bias in Figure 4-7. The four detectors exhibited totally different responses. It is well known that photogenerated electrons will circulate through the external circuit many times before recombining with hole if those photogenerated holes were trapped by the surface state at the interface. Consequently, the temporal photocurrent would not drop sharply when the UV light was turned off like Figure 4-7 (A). This point will discuss later. As increasing NiO annealing temperature, rise time and fall time is getting be fast in Figure 4-8.

As can be seen from the above, phot current multiplication occurred at four UV detectors. At this time, we would like to demonstrate that the photocurrent multiplication or gain mechanism to be controllable by annealing temperature. Each NiO different annealing films were measured by X-ray photoelectron spectroscopy (XPS). Figure 4-9 illustrates Ni2p$_{3/2}$ XPS spectra of each NiO film. For Ni2p$_{3/2}$ spectra three clearly
separated peaks can be detected, which correspond to the binding states of peak NiO state, peak Ni(OH)$_2$ state and shake-up peak. Red (853.4 eV), green (855.2eV), and blue peak (860eV) indicate NiO, Ni(OH)$_2$ and shake-up peak, respectively. It can be seen clearly, that the portion of Ni2p$^{3/2}$ from Ni(OH)$_2$ is decreasing with the higher NiO annealing temperature. Ni(OH)$_2$ come from excess of oxygen in surface of NiO film. As can be seen from Figure 4-10, O1s XPS spectra of each NiO film also show two peaks such as NiO (528.9eV) and Ni(OH)$_2$. This Figure also shows that Ni(OH)$_2$ peak is decreasing with the increasing NiO annealing temperature.

It is a well-known fact that NiO that is closely stoichiometric appears green like nickel oxide solution, whereas material that has an excess of oxygen tends more toward a black appearance [21]. To illustrate in a quantitative way the nature of this color change on NiO films picture that were shown in figure 4-11, 270°C NiO film is the darkest film and 540°C film is the lightest film. Nonstoichiometric NiO (540°C) is the darkest due to the presence of a lot of Ni$^{3+}$ ions resulting from the appearance of nickel vacancies and/or interstitial oxygen in NiO films and have intrinsically p-type conduction [22, 23]. Nam et al also observed more defective nickel oxide materials containing more Ni$^{3+}$ ion states [24]. Moreover, Lee at al proposed that nonstoichiometric nickel oxide of Ni$^{3+}$ ions (directly related to hole concentration) increases with increasing excess of oxygen, which corresponds to the quantity of Ni$^{2+}$ ions decreases resulting in a reduced number of reaction sites for OH$^-$ insertion [25].

Now, we can propose why dark current and photo current decrease with increasing NiO annealing temperature. It has been suggested that the oxidation and reduction reactions of preexisting Ni$^{3+}$ ions participate in the storage of charge [26]. It
means that Ni$^{3+}$ ions can be act as traps of the UV photodetector. Therefore, there can be a lot of energy level of hole traps near valance band in NiO films. When revere bias is applied to the device, electrons in valance band can be moved to higher energy band which is hole traps by thermal excitation. Then holes generated by thermal excitation are collected by the applied reverse bias, which correspond to increasing dark current.

For the explanation of photocurrent multiplication, the schematic band diagram as depicted in figure 4-12 illustrate the condition when the UV detector is under reverse bias and under UV illumination. The photogenerated holes at ITO / NiO interface are accumulated [27]. In addition, the accumulation of photogenerated holes near the interface brings the amount of electrons injected by tunneling barrier under UV illumination from the ITO electrode occurs.

As can be seen from Figure 4-13, UV photodetector was fabricated on quarts substrate with same procedure to compare between the device with glass substrate and the device with quartz substrate. The spectral EQE and detectivity were shown in Figure 4-14. The response range is similar to the UV photodetector on glass substrate. However, we can clearly observe that peak of EQE and detectivity within range between 300nm-400nm is located 345nm. The peak of detectivity is little shifted from the UV detector on glass substrate due to its transmittance. Sharp cut off after 320nm is limited by ITO electrode. Therefore, UV photodetector response can be wider if electrode is replaced with shorter absorption such as Ag nanowire.
Figure 4-1. Schematic diagram showing energy level of the device
Figure 4-2. Rectifying behavior of I-V characteristic

Figure 4-3. I-V characteristics of UV photodetector. A) Dark current. B) Photo current under illumination at room temperature
Figure 4-4. Annealing NiO temperature dependence versus EQE and detectivity

Figure 4-5. Spectral detectivity of the UV detector under -1V applied bias
Figure 4-6. Life time with EQE and detectivity. A) EQE B) Detectivity

Figure 4-7. Transient response of the UV detector with UV illumination on/off. A) 270°C, B) 350°C, C) 450°C, D) 540°C
Figure 4-8. Temperature dependence with rise and fall time

Figure 4-9. XPS Ni2p spectra of each different NiO films. A) 270°C  B) 350°C  C) 450°C  D) 540°C
Figure 4-10. XPS O1s spectra of each different NiO films. A) 270°C  B) 350°C  C) 450°C  D) 540°C

Figure 4-11. Picture of different NiO annealing film on ITO substrate
Figure 4-12. Proposed band structure for the high gain photodetector. A) Dark current mechanism, B) Photo current mechanism

Figure 4-13. Schematic of UV photodetector on Quartz substrate
Figure 4-14. I-V characteristics of UV detector in the dark and under illumination at room temperature

Figure 4-15. Spectral EQE and detectivity of the UV detector under -1V applied bias. A) EQE B) Detectivity
Figure 4-16. Transmittance of ITO, NiO and ZnO on quartz substrate
CHAPTER 5
CONCLUSIONS

This thesis has investigated the solution processed p-n junction ultraviolet photodetectors using p-type NiO and n-type ZnO Nanoparticle layer. The four UV detectors annealed NiO film different temperature exhibits clear rectifying current-voltage characteristics under the applied bias from +1V to -2V. Photocurrent multiplication phenomenon at NiO/ITO interface was proposed with X-ray photoelectron analysis. High external quantum efficiency and detectivity were obtained with NiO 270°C annealing temperature of UV detector.
LIST OF REFERENCES

BIOGRAPHICAL SKETCH

Ryu, Jiho was born in 1983, in Inje, Republic of Korea. He was curious about how the images of people were projected on the screen when he watched television as a student. He eventually looked it up in a children’s encyclopedia. With an incomplete answer to his question, his curiosity and interest continued to grow from this point. By the time he was in high school the cellular phone was invented, he wondered how the liquid crystal display could fit into such a small machine and move around. To answer this question, he went to Korea Polytechnic University and majored in advanced materials engineering (2001 – 2008). He concentrated in the field of display, which has decided his career path. After graduation with B.S. degree, he joined the Department of Materials Science and Engineering at University of Florida, and completed his M.S. thesis under the advisory of Dr. Franky So in August 2012. He will start to work for LG Display as a researcher on September in 2012.