Ultraviolet photodetectors based on doped ZnO films

Z N Ng¹ and K Y Chan¹,²*¹
¹Centre for Advanced Devices and Systems, Faculty of Engineering, Multimedia University, 63100 Cyberjaya, Selangor, Malaysia
²Research Institute for Digital Lifestyle, Multimedia University, 63100 Cyberjaya, Selangor, Malaysia

*kychan@mmu.edu.my

Abstract. In this paper, we report the realization of ultraviolet (UV) photodetector based on doped ZnO films. The ZnO p-n junction was fabricated on indium tin oxide (ITO) coated glass, which consists of n-type and p-type layers based on Ga-doped (2 at.%) and N-doped (20 at.%) ZnO films, respectively. The current-voltage (IV) characteristics, photosensitivity, photoresponsivity, and photocurrent gain were derived to determine the performance of the device. At 5 V reverse bias, the ZnO-based UV photodetector exhibits photosensitivity of 10.9, photoresponsivity of $2.1 \times 10^{-2}$ AW⁻¹, and photocurrent gain of $7.2 \times 10^{-2}$.

1. Introduction

Semiconductor-based ultraviolet (UV) photodetector has evolved from Si-based to wide bandgap semiconductors such as gallium nitride (GaN), nickel oxide (NiO), and zinc oxide (ZnO). Wide bandgap-based photodetectors are more stable and have been utilized in several critical applications such as chemical sensing and flame detection [1]. The designs of the photodetector are usually based on Schottky junction [2], p–n [3], p–i–n [4], and metal–semiconductor–metal (MSM) [5] structures. ZnO-based photodetectors have recently attracted more research interest due to their wide bandgap, abundance, and non-toxicity. However, it is undisputable that ZnO-based photodetectors usually undergo a rather complicated fabrication process, especially devices that involve the growth of surface nanostructures, which faces a challenge in terms of precise control of diameter and surface states of the final product. As a result, the performance of the device is usually different from one another, resulting in reproducibility and reliability issues of fabricated devices [6]. Furthermore, the challenge toward reliable ZnO-based optoelectronic devices remains due to the challenge of achieving p-type conductivity [7]. As a result, many opt to employ heterojunction structure based on n-type ZnO (n-ZnO) with other p-type materials such as p-Si [8]. P-type ZnO (p-ZnO) has been attempted with single-doping of group V compounds and co-doping of III-V compounds [9–12]. The reliability of p-type ZnO may lead to issues such as high leakage currents, large turn-on voltages, poor rectification on ZnO homojunction devices [13]. Hence, these issues have constituted the main bottleneck for the practical application of ZnO-based photodetectors. Therefore, more studies should be conducted to address such issues.

In this work, we attempt to realize UV photodetector based on ZnO p-n junction, using low cost sol-gel spin coating process for the growth of n-type gallium-doped ZnO (ZnO:Ga) and p-type nitrogen-doped ZnO (ZnO:N) films on indium tin oxide (ITO) coated glass, followed by chemical etching to complete the fabrication of the device.
2. Experimental
The experiment begins with the preparation of ZnO precursor solution, which consists of zinc acetate dihydrate as a precursor, isopropanol (IPA) as a solvent, and monoethanolamine (MEA) as a stabiliser. Ammonium acetate and gallium (III) nitrate hydrate were added into separate ZnO precursor solutions as the supplies of nitrogen and gallium dopants for p-type and n-type doping, respectively. The percentage of N and Ga doping level was optimized to their best electrical properties as demonstrated and reported by our group previously [14,15]. The transparent and homogeneous solutions were stirred and heated at 60 °C for 2 hours and aged for another 22 hours at room temperature before proceeding to the coating process. Prior to the coating of ZnO films, the ITO coated glass was cleaned in an ultrasonic bath, wiped with cleanroom grade lint-free wipers, and dried with nitrogen nozzle. The fabrication of the photodetector device starts with the coating of ZnO:N film on the ITO coated glass, followed by the coating of ZnO:Ga film on top of ZnO:N film. The solutions were spin-coated and cured on a hot-plate to evaporate the solvent and remove residuals. The process of spin coating and baking was repeated several times to achieve the desired film thickness with 10 layers of coating for each ZnO:N and ZnO:Ga films. Finally, the sample was taken into a furnace and annealed at 450 °C for 1 h. To complete the fabrication of the photodetector device, a diluted hydrochloric acid solution was prepared to perform wet etching process on the annealed sample. Figure 1 shows the patterned mesa structure and schematic illustration of the ZnO p-n photodetector. Using current-voltage (I-V) measurement system, the I-V characteristic and time-dependent photoresponse of the device at room temperature can be measured. Voltage sweep between -5 to 5 V was performed to obtain the I-V plot. The device was injected with several reverse bias voltage (1–5 V) and illuminated by an UV light emitting diode (LED) that emits a 365 nm wavelength at a fixed on/off time for about 40 seconds (s).

![Figure 1](image_url)

**Figure 1.** UV detecting ZnO-based photodetector.

3. Result and discussions
A surface profilometer was used to determine the thickness of the ZnO:Ga and ZnO:N films. The 10 layer ZnO:Ga is approximately 425 nm, the same goes to that of ZnO:N films. Figure 2 shows the I-V characteristics of the device in the dark and under UV light illumination at room temperature in ambient atmosphere with voltage sweep between -5 to 5 V. Under dark condition, current of approximately -0.28 mA flowed in the device at reverse bias of 5 V, corresponding to a resistance of 17.9 kΩ. Under UV light illumination, the current increase to -3.05 mA at the same reverse bias, corresponding to lower resistance of 1.6 kΩ. The increment in current magnitude indicates that the device is UV sensitive and response to the UV light illumination with an increase of photoconduction and photocurrent. With the values of dark current (I_d) and photocurrent (I_ph), the photosensitivity (S) can be calculated with equation (1) [16].
\[ S = \frac{l_{ph}}{l_d} \] (1)

In this case, the photosensitivity of this photodetector is 10.9 at reverse bias of 5 V. These results are superior in comparison with MSM type photodetector based on fluorine-doped tin oxide, aluminum doped ZnO, and silver contact by Chongsri et al. [17], where the highest photoilluminated current is only 11.64 µA at 10 V bias voltage. The illumination of UV (365 nm) light on the ZnO photodetector causes the absorbed photons to generate electron-hole (e-h) pairs in the depletion region, as the energy of UV is greater than that of ZnO’s bandgap. As a result, the photo-generated electrons will migrate to the n-ZnO layer and photo-generated holes will migrate to the p-ZnO layer, therefore enhancing the reverse photocurrent [18].

![IV characteristics of ZnO-based photodetector.](image)

**Figure 2.** IV characteristics of ZnO-based photodetector.

In addition, it is important to look at the photoresponse of UV photodetector. Figure 3 shows the time-dependent photocurrent of the ZnO-based photodetector in response to turn-on and turn-off of UV illumination for about 40 s. The increase of reverse bias voltage from 1 to 5 V has increases the photocurrent, also translates to higher the on-off ratio with higher reverse bias voltage. Next, the photoresponsivity (2) and photoconductive gain (3) were calculated to evaluate the device performance, by using the following formulas:

\[ R = \frac{l_{ph} - l_d}{P_{opt}} \] (2)

\[ G = R \frac{hc}{nq\lambda} \] (3)

where R is the photoresponsivity, G is the photoconductive gain, \( P_{opt} \) is the power of the light that is illuminated on the device (50 mW/cm²), η is the quantum efficiency (~ 1 for convenience), q is the absolute value of electron charge (1.6×10⁻¹⁹ Coulombs), \( \lambda \) is the wavelength of illuminated light (365 nm), h is the Planck’s constant (6.626×10⁻³⁴ Js), and c is the velocity of light (3×10⁸ m/s). As reverse bias voltage increases from 1 to 5 V, the photoresponsivity of the device increases from \( 3.9 \times 10^{-3} \) to \( 2.1 \times 10^{-2} \) AW⁻¹, while photoconductive gain increases from \( 1.3 \times 10^{-5} \) to \( 7.2 \times 10^{-5} \), as plotted in figure 4.
The photoresponsivity obtained here is higher compared to the work of Patel et al. [19], where their NiO/ZnO heterojunction achieved a photoresponsivity of $1 \times 10^{-3}$ A W$^{-1}$.

**Figure 3.** Cyclical photoresponse of device with different biases under UV with on and off light.

ZnO based photodetector’s response to UV is consistent with the absorption curve at UV region as reported before [14,20]. The shorter wavelength in UV has higher energy and the absorption of high-energy photons occurs at the surface region of the ZnO, generating the electron-holes near the surface and contributes to the photocurrent. Under UV illumination in reverse bias, the carriers are swept apart due to a built-in electric field. As photo-generated electrons traveled from n-ZnO layer to the cathode, the photo-generated holes are displaced in the p-ZnO layer. Some holes may move from p-ZnO layer to the ITO anode, but some may be trapped in the defect sites of p-ZnO layer. These trapped holes will then shift the valence band edge of the p-ZnO film upwards, aligning its Fermi energy closer to that of ITO anode, leading to electron tunnelling effect at the barrier of ITO/p-ZnO interface [21]. Visible light with wavelengths at 400 nm and above has lower energy that is insufficient to excite the electrons from the valence band to the conduction band, and therefore, visible light does not affect to the photocurrent [6].
4. Conclusion
In this study, ZnO p-n photodetector is successfully fabricated on ITO coated glass substrate by using low cost sol-gel processing method. The thickness of the ZnO films are 425nm, as measured with a surface profilometer. The prepared UV photodetector was characterized by I-V measurement system and the photoresponse of the device was also captured. At 5 V reverse bias, the ZnO-based UV photodetector exhibits photosensitivity of 10.9, photoresponsivity of $2.1 \times 10^{-2}$ AW$^{-1}$, and photoconductive gain of $7.2 \times 10^{-2}$.

Acknowledgement
The authors would like to acknowledge Multimedia University for providing the necessary facilities for this research. The authors would also like to acknowledge Telekom Research & Development Sdn. Bhd. (TM R&D) for providing financial sponsorship to facilitate this research project under TM R&D Research Grant 2017 (Project Code: MMUE/170011).

References
[1] Rana V S Rajput J K Pathak T K and Purohit L P 2018 Multilayer MgZnO/ZnO thin films for UV photodetectors J. Alloys Compd. 764, p. 724–729.
[2] Zhou X Jiang D Yang X Duan Y Zhang W Zhao M Liang Q Gao S Hou J and Zheng T 2018 Voltage-dependent responsivity of ZnO Schottky UV photodetectors with different electrode spacings Sensors Actuat. A Phys. 284, p. 12-16.
[3] Liu J L Xiu F X Mandalapu L J and Yang Z 2006 P-type ZnO by Sb doping for PN-junction photodetectors Proc. Of SPIE. 6122, p. 61220H.
[4] Singh K J Singh C A Singh T J Chettri D and Sarkar S K 2017 ZnO based homojunction p-i-n solar cell to self-power UV detector 2017 Int. Conf. on Inventive Communication and Computational Technologies (IEEE) p. 304–307.
[5] Ahmed A A Devarajan M and Afzal N 2017 Fabrication and characterization of high performance MSM UV photodetector based on NiO film Sensors Actuat. A Phys. 262, p. 78–86.
[6] Zhang T F Wu G A Wang J Z Yu Y Q Zhang D Y Wang D D Jiang J B Wang J M and Luo L B 2017 A Sensitive ultraviolet light photodiode based on graphene-on-zinc oxide Schottky junction Nanophotonics. 6, p. 1073–1081.
[7] Fan J C Sreekanth K M Xie Z Chang S L and Rao K V 2013 P-Type ZnO materials: Theory, growth, properties and devices Prog. Mater. Sci. 58, p. 874–985.

[8] Jeong I S Kim J H and Im S 2003 Ultraviolet-enhanced photodiode employing n-ZnO/p-si structure Appl. Phys. Lett. 83, p. 2946–2948.

[9] Zhao Y Peng X Li Z Zhou M Liang X Wang J Min J Wang L and Shi W 2012 The photoluminescence characterization of the N-doped ZnO films produced by wet chemical deposition Appl. Phys. A Mater. Sci. Process. 107, p. 959–963.

[10] Xiu F X Yang Z Mandalapu L J Liu J L and Beyermann W P 2006 P-type ZnO films with solid-source phosphorus doping by molecular-beam epitaxy Appl. Phys. Lett. 88, p. 1–3.

[11] Vaithianathan V Lee B-T Chang C-H Asokan K and Kim S S 2006 Characterization of As-doped, p-type ZnO by x-ray absorption near-edge structure spectroscopy Appl. Phys. Lett. 88 112103.

[12] Bu I Y Y 2015 Sol-gel synthesis of p-type zinc oxide using aluminium nitrate and ammonia J. Ind. Eng. Chem. 28, p. 91–96.

[13] Mandalapu L J Yang Z Xiu F X Zhao D T and Liu J L 2006 Homojunction photodiodes based on Sb-doped p-type ZnO for ultraviolet detection Appl. Phys. Lett. 88, 092103.

[14] Ng Z N Chan K Y Low C Y Kamaruddin S A and Sahdan M Z 2015 Al and Ga doped ZnO films prepared by a sol-gel spin coating technique Ceram. Int. 41, p. S254–258.

[15] Ng Z-N Chan K-Y Muslimin S and Knipp D 2018 P-Type Characteristic of Nitrogen-Doped ZnO Films J. Electron. Mater. 47, p. 5607–5613.

[16] Echresh A Echresh M Khranovskyy V Nur O and Willander M 2016 High photocurrent gain in NiO thin film/M-doped ZnO nanorods (M=Ag, Cd and Ni) heterojunction based ultraviolet photodiodes J. Lumin. 178, p. 324–330.

[17] Chongsri K and Pecharapa W 2014 UV photodetector based on al-doped zno nanocrystalline sol-gel derived thin films Energy Procedia. 56, p. 554–559.

[18] Amiruddin R and Santhosh Kumar M C 2016 Role of p-NiO electron blocking layers in fabrication of (P-N):ZnO/Al:ZnO UV photodiodes Curr. Appl. Phys. 16, p. 1052–1061.

[19] Patel M and Kim J 2017 Transparent NiO/ZnO heterojunction for ultra-performing zero-bias ultraviolet photodetector on plastic substrate J. Alloys Compd. 729, p. 796–801.

[20] Ng Z-N Chan K-Y Sin Y-K Yam F-K and Knipp D 2017 Sol–Gel Derived Al–Ga Co-Doped ZnO Thin Films Embedded with Microrods J. Nanosci. Nanotechnol. 17, p. 348–353.

[21] Kim D Y Ryu J Manders J Lee J and So F 2014 Air-stable, solution-processed oxide p-n heterojunction ultraviolet Photodetector ACS Appl. Mater. Interfaces. 6, p. 1370–1374.