Ultraviolet Photodetection Based on ZnO Colloidal Nanoparticles Made by Top-down Wet-chemistry Synthesis Process

Liqiao Qin, Christopher Shing, Shayla Sawyer
Electrical, Computer, and Systems Engineering Department
Rensselaer Polytechnic Institute
Troy, NY 12180, USA
qinl@rpi.edu

***Abstract*—ZnO bulk material (bandgap 3.26 eV) was reduced in size via a top-down wet-chemistry synthesis process into colloidal nanoparticles that were then coated with polyvinyl-alcohol (PVA). When the nanoparticles were excited at 340 nm, strong UV emission at 377 nm was observed, and parasitic green emission (510 nm) which normally appears in ZnO nano-material was suppressed. Quantum confinement effects of the nanoparticles were observed by a 5 nm blue shift from ZnO bulk material (380 nm) in the absorption spectrum. The same characteristics held true when the particles were deposited onto substrates to form a photoconductive detector. Point contact current-voltage characteristics of the detector were measured under darkness and 340 nm UV LED. The ratio of the UV photogenerated current to dark current was as high as 10^5. Spectral response of the detector demonstrates a sharp cut-off wavelength at 375 nm, with a UV responsivity equivalent to twice that of a commercial UV enhanced Si-based photodetector. The time response indicated the rise and fall time were 22s and 11s respectively. The results confirm that top-down wet-chemistry synthesized ZnO nanoparticles are suitable for small signal visible blind UV detection.**

Keywords-ZnO colloidal nanoparticles, top-down wet-chemistry, photodetector, AlGaN, PVA

I. INTRODUCTION

Photodetectors based on wide band gap materials, including ZnO, AlGaN, and GaN can provide improved sensitivity in the ultraviolet (UV) spectral region. These detectors are poised to compete with photomultiplier tube (PMT) technology for applications that require visible blind operation, low power consumption, ruggedness, and compact size. In some cases, these factors reduce the impact of the high current gain (~10^6) of a PMT [1]. Benefiting from the maturity of Si-processing technology, the semiconductor alternative to PMT technology for UV light detection is based on Silicon (Si). UV-enhanced silicon photodiodes address most of the above characteristics but these photodetectors exhibit some inherent limitations: the requirement of filters to block out visible and infrared photons and the degradation of the devices on exposure to intense UV light energies. Also, for blue/UV detection with high-responsivity in Si, methods must be employed to enhance this detection, including ion implantation and cooling to reduce dark current [2]. As such, alternative wide bandgap materials, including ZnO, AlGaN, and GaN, are better matched for detecting UV.

ZnO is a direct wide bandgap semiconductor material (documented values range from 3.2 to 3.4 eV), with attractive characteristics including large exciton binding energy (60 meV), high radiation hardness, and relatively low growth temperature [3-7]. These characteristics have prompted its use for transparent conducting electrodes (TCOs) [8, 9], varistors [10], sensors [11], UV photodetector [3-7, 12], light emitting diodes (LEDs) [13], transistors [14], solar cells [15], magnetic [16], biological applications [17] and catalysis [18]. Nanoparticles, especially colloidal nanoparticles, are attractive as they take advantage of three dimensional quantum confinement effects, are easy to fabricate, can have a large active area, and are relatively low cost [19]. Currently, the methods of manufacturing colloidal ZnO can be classified into two groups: bottom-up and top-down. Photodetectors based on ZnO colloidal nanoparticles made by the bottom-up chemistry process exhibited good UV performance [3, 19,]. But devices based on the ZnO colloidal nanoparticles produced by a top-down chemistry method, especially a multi-layer heterostructure comprised of colloidal nanoparticles embedded in GaN-based semiconductor substrates to our knowledge have not been investigated. These devices could be potentially integrated with GaN-based heterojunction field effect transistors (HFETs). In addition, ZnO materials usually exhibit strong parasitic green photoluminescence which is caused by excess Zn^{2+} ions and oxygen deficiencies [20-23]. Many researchers seek to suppress the green emission by surface passivation thus to increase the UV performance of ZnO.

In this paper, a photodetector based on ZnO colloidal nanoparticles with PVA coating created by top-down wet-chemical means are demonstrated on AlGaN substrate. The fabrication and measurement setup will be described. Materials characterization results including high resolution SEM, photoluminescence and absorbance will follow. Point contact current-voltage characteristics of the samples measured under darkness and 340 nm UV LED sources are also demonstrated. Finally, the spectral response and time response results are examined. Results and analysis demonstrate the conclusion that a visible-blind UV detector based on ZnO nanoparticles made by top-down wet-chemistry and coated with PVA deposited on a

978-1-4244-4964-4/10/$25.00 ©2010 IEEE

semiconductor substrate is achieved with higher responsivity in the UV region than a commercial Si based UV-enhanced detector. PVA acts as an effective surface passivation agent, contributing to the high responsivity.

II. EXPERIMENT

ZnO bulk material was reduced in size by a top-down wet-chemistry synthesis process into nanoparticles which were then coated with polyvinyl-alcohol (PVA) [24]. Then the nanoparticles were dispersed into ethanol to form a 30mg/ml suspension. For material characterization, including SEM, photoluminescence and absorbance measurements, the solutions were spin-cast onto quartz substrates and annealed in air at 150℃ for 5 minutes. After the performance of material was confirmed, the solutions were spin-cast onto an AlGaN substrate, whose cut-off wavelength is 300 nm, and annealed in air at 150℃ for 5 minutes. Two irregular 100 nm Aluminium (Al) contacts were deposited by E-beam lithography through a foil mask to fabricate a photoconductive UV detector. Wires were bonded by a conductive epoxy to the Al contacts. Absorbance characteristics were measured using a Shimadzu UV-Vis 2550 spectrophotometer. Photoluminescence was characterized by a SLM8100 fluorometer. Point contacts current-voltage characteristics of samples were measured using a HP4155B semiconductor parameter analyzer under darkness and 340 nm UV LED illumination. The spectral response was measured utilizing a Keithley 6487 high resolution pico-Amps sourcemeter, a Shimadzu UV-Vis 2550 spectrophotometer, and a Newport 1928-C optical power meter. The spectrophotometer provided the scanning wavelengths from 200 to 520 nm, and the light intensities were monitored by the optical meter. Time response was measured using a Tektronix TDS 2022B Oscilloscope, Agilent 3320A wave function generator, and a Keithley 2430 as a 20V bias power supply. The wave function generator drove a 340 nm UV LED at a 200 second period. The oscilloscope monitored the output wave and the generated current through a 10M ohms resistance. All measurements were performed at room temperature in air.

III. RESULTS AND DISCUSSIONS

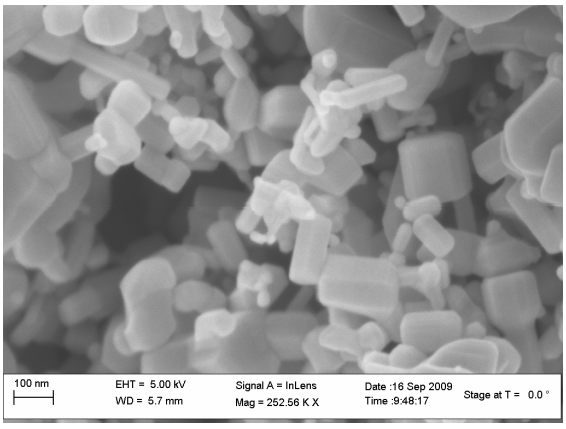


Figure 1. High resolution SEM results of ZnO coated with PVA dispersed in ethanol and then spin-cast on quartz plates.

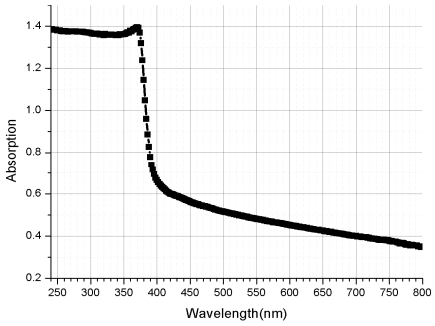


Figure 2. Absorption spectra of ZnO coated with PVA dispersed in ethanol and then spin-cast on quartz plates.

Fig. 1 is a high resolution (100 nm scale) SEM image of ZnO nanoparticles coated with PVA dispersed in ethanol and then spin-casted on quartz plate. This image reveals that the nanoparticles' sizes are not uniform and range from 10 to 100 nm. This non-uniform size distribution is caused by the limited ability of the top-down wet-chemistry synthesis process to control particle size. Despite this, the optical and electrical performance of the ZnO nanoparticles demonstrates their good UV detection quality.

The absorption spectrum in Fig. 2 demonstrates a strong UV absorption and a weak visible light absorption. As indicated, the cut-off wavelength is 375 nm, 5 nm blue shift in comparison comparing with the ZnO bulk material whose bandgap is 3.26 eV (380 nm). This shift corresponds to the quantum confinement effects of nanoparticles [21-24].

The photoluminescence measurements of ZnO nanoparticles with and without PVA dispersed in ethanol and spin-cast onto a quartz plate are depicted in Fig. 3, where the excitation wavelength is fixed at 340 nm and the detector is scanned from 350 to 620 nm. The results directly indicate that there is a strong UV emission peak at 377 nm from the ZnO nanoparticles, the band edge emission of the nanoparticles. The visible emission of the ZnO nanoparticles coated with PVA is very small and the strong parasitic green emission often found in ZnO nano-materials has vanished. But the green emission dominates the emissions from the ZnO nanoparticles without PVA. It is reported that the green emission is caused by excess Zn^{2+} ions and oxygen deficiency, which can be weakened by surface passivation [21-24]. This severely reduced green emission from our ZnO nanoparticles demonstrates that PVA acts as a surface passivation agent, interacting with Zn^{2+} and thus contributing to the good quality ZnO nanoparticles. The same characteristics holds true when the particles were deposited onto other substrates to form photoconductive detector.

Fig.4 is I-V plots of ZnO nanoparticles in ethanol deposited onto intrinsic AlGaN with irregular Al contacts deposited on them. I-V measurements are taken under darkness and under 340 nm UV LED. The dark current is on the order of tens to hundreds of pico-Amps. Large UV generated currents are detected under 340 nm UV LED illumination. The ratio of photo-generated current to dark current (on/off ratio) is as high as 10^5 when the bias is ±20V. The significant UV photocurrents prove the strong UV detection ability of PVA coated ZnO nanoparticles.

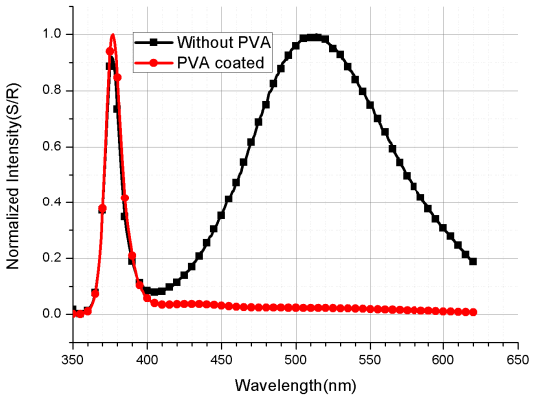


Figure 3. Emission spectra of ZnO coated with/without PVA dispersed in ethanol and then spin-cast on quartz plates (excited at 340 nm).

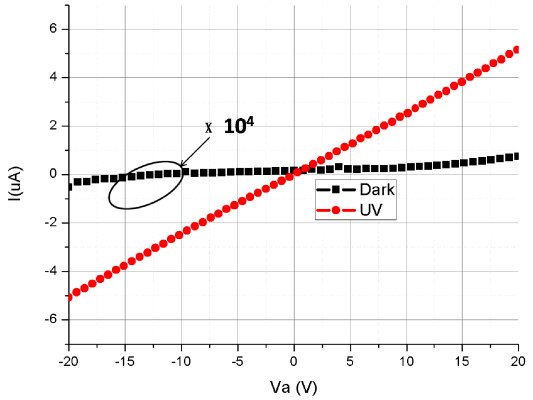
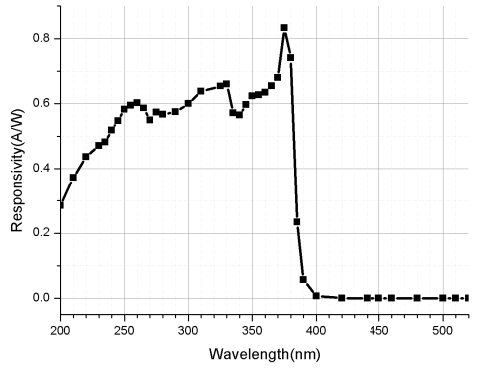
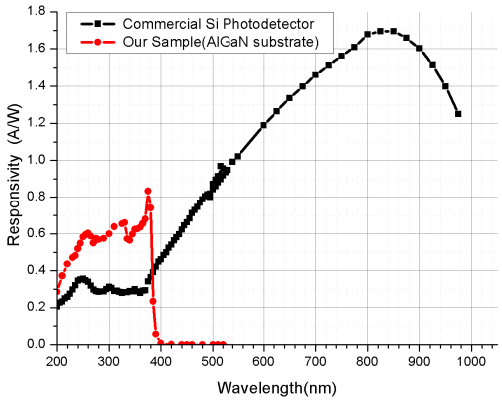


Figure 4. I-V plot of ZnO coated with PVA dispersed in ethanol and then spin-cast on AlGaN

Based on the work function of Al (4.08 eV) and electron affinity of ZnO (4.5 eV), Al is expected to form ohmic contacts with intrinsic ZnO, a material that usually exhibits n-type semiconductor performance. This is verified by the UV generated current in Fig. 4. Yet, as the dark current in Fig. 4 demonstrates, sometimes the ZnO nanoparticle photodetectors appears to make Schottky contacts with Al. It is reported that ZnO and gold formed ohmic contacts due to different surface impurities and defects of ZnO, even though ZnO and gold should typically form Schottky contacts [9]. ZnO and Al can form two types of contacts based on different surface impurities and defects in ZnO, but the ohmic contacts will dominate.



(a)



(b)

Figure 5. Spectral response (a) of ZnO coated with PVA dispersed in ethanol and then spin-cast on AlGaN substrate, and comparison with commerce Si based UV enhanced photodiode (b).

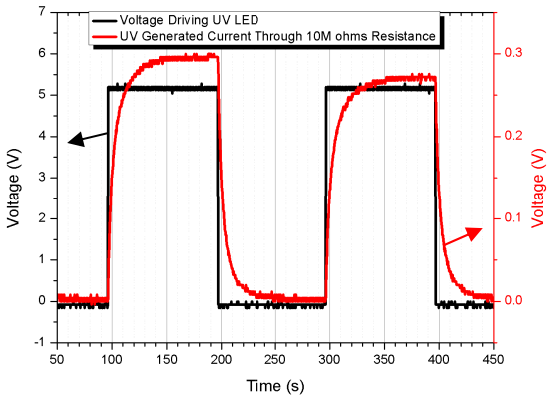


Figure 6. Time response of ZnO coated with PVA dispersed in ethanol and then spin-cast on AlGaN substrate

Fig. 5 shows that the spectral response of PVA coated ZnO nanoparticles spin-casted on AlGaN. It demonstrates that this photodetector reaches a sharp cut-off wavelength at 375 nm. The optical power used in the spectral measurement in the UV region was between 10 to 30 nW confirming ability of the ZnO nanoparticle photodetector to sense small UV signals.

As the wavelength decreases, the absorption coefficient will increase and the penetration depth of UV light will become more shallow. Thus, the concentration of carriers near the surface of the film increases. As a result, the lifetime of the photo-generated carriers will decrease and lead to a drop in the current [3].

Compared with the commercial UV enhanced Si-based photodetector, this ZnO-nanoparticles based photodetector has an UV responsivity approximately twice as high and is visible-blind. UV detection can be conveniently measured under normal environment conditions without any filters.

Time response of the photodetector was measured under a 340 nm UV LED driven by a square wave signal with a 200 second period. Both the square wave signal and the UV generated current across a 10M ohms resistor were measured through an oscilloscope. The result is shown in Fig. 6. The

rise time (from 10% to 90%) and fall time (from 90% to 10%) of the photodetector can be extracted from this figure. The results are 22s and 11s respectively, which are consistent with the results found in literature [9]. Further analysis via successive I-V measurements without the conductive epoxy used for wire bonding demonstrated the photo-generated current decreases to dark current immediately after the LED is turned off, a number contrary to the previous results. Our interpretation is without the conductive epoxy used for wire bonding, the time response of the photodetector should be faster than the response time indicated in Fig. 6. This indicates that the conductive epoxy has a negative impact on the photodetector's response time. Further quantitative analysis of the epoxy-device interaction and studies towards decreasing the response time to make the photodetector suitable for high speed application are being researched.

IV. CONCLUSIONS

The strong UV emission and severely diminished visible emission demonstrate that the PVA coated ZnO nanoparticles in this paper have good UV emission quality. This may be caused by the surface passivation of PVA. Also, quantum confinement effects of the nanoparticles were observed with a 5 nm blue shift of the cut-off wavelength. Photoconductive detectors based on ZnO nanoparticles were fabricated and, under 340 nm UV LED and biased at ±20V, had a ratio of photo-generated current to dark current as high as 10^5. The responsivity spectrum showed a sharp cut-off wavelength at 375 nm, with a UV responsvity about twice of a commercial UV enhanced Si-based photodetector when the incident UV light is in ten nano-Watt order. The time response indicated the rise and fall time were 22s and 11s respectively. These results indicate that low cost PVA coated ZnO nanoparticles could be applied in, large area, planar fabrication, and high sensitive and visible-blind UV photodetection with GaN-based semiconductor substrates.

ACKNOWLEDGMENT

The authors gratefully acknowledge support from NSF Industry/University Cooperative Research Center Connection One. They also want to thank Professor Partha Dutta in Electrical, Computer and Systems Engineering Department at Rensselaer Polytechnic Institute for providing ZnO samples. Finally, the authors would like to thank National Security Technologies for their support.

REFERENCES

[1] J.B. Limb, D. Yoo, J.H.Ryou, W.Lee, S.C.Shen and R.D. Dupuis, "GaN ultraviolet avalanche photodiodes with optical gain greater than 1000 grown on GaN substrates by metal-organic chemical vapor deposition", Appl. Phys. Lett., Vol. 89, 011112, 2006.

[2] S. M. Sze and Kwok K. Ng, "Physics of semiconductor devices (3rd edition)", Wiley, 2007.

[3] Y. Jin, J. Wang, B. Sun, J. Blakesley, and N. Greenham, "Solution-processed ultraviolet photodetectors based on colloidal ZnO nanoparticles", Nano Lett., Vol. 8, pp. 1649-1653, June, 2008.

[4] Z. Bi, J. Zhang, X. Bian, D. Wang, X. Zhang, W. Zhang and Z. Hou, "A high-performance ultraviolet photoconductive detector based on a ZnO film grown by RF sputtering", J. Electron. Mater., Vol. 37, pp. 760-763, May, 2008.

[5] S.J. Young, L.W. Ji, S.J. Chang, S.H. Liang, K.T. Lam, T.H. Fang, K.J. Chen, X.L. Du, Q.K. Xue, "ZnO-based MIS photodetector", Sens. Act. A, Vol. 141, pp. 225-229 , 2008.

[6] Y. Lin, C. Chen, W. Yen, W. Su, C. K, and J. Wu, "Near-ultraviolet photodetector based on hybrid polymer/zinc oxide nanorods by low-temperature solution processes", Appl. Phys. Lett., Vol. 92, 233301, 2008.

[7] G. Cheng, Z. Li, S. Wang, G. Gong, K. Cheng, X. Jiang, S. Zhou, Z. Du, T. Cui, and G. Zou, "The unsaturated photocurrent controlled by two-dimensional barrier geometry of a single ZnO nanowire Schottky photodiode", Appl. Phys. Lett., Vol. 93, 123103, 2008.

[8] J. K. Sheu, M.M. Lee, C.J.Tun and S.W.Lin, "Ultraviolet band-pass Schottky barrier photodetectors formed by Al-doped ZnO contacts to n-GaN", Appl. Phys. Lett., Vol. 88, 043506, 2006.

[9] V. Bhosle, J. T. Prater, F. Yang, D. Burk, and J. Narayan, "Gallium-doped zinc oxide films as transparent electrodes for organic solar cell applications", J. Appl. Phys., Vol.102, 023501, 2007.

[10] P. Dura´n, F. Capel, J. Tartaj, C. Moure, "A strategic two-stage lowtemperature thermal processing leading to fully dense and fine-grained doped-ZnO varistors", Adv. Mater. Vol.14 , pp.137-141, 2002.

[11] S. Pearton, W. T Lim, J. S Wright, R.Khanna, L. Voss, L. Stafford, L. c Tien, H. S Kim, D. P Norton, J. J Chen, H. T Wang, B. S Kang, F. Ren, J. Jun and J. Lin, "Development of thin film and nanorod ZnO-based LEDs and sensors", MRS, symposium K, 2006.

[12] D. Lin, H. Wu, W. Zhang, He. Li, and W. Pan, "Enhanced UV photoresponse from heterostructured Ag-ZnO nanowires", Appl. Phys. Lett., Vol. 94, 172103, 2009.

[13] E. Neshataeva, T. Kümmell,G. Bacher, and A. Ebbers, "All-inorganic light emitting device based on ZnO nanoparticles", Appl. Phys. Lett., Vol. 94, 091115, 2009.

[14] S. Lee, Y. Jeong, S. Jeong, J. Lee, M. Jeon,J. Moon, "Solution-processed ZnO nanoparticle-based semiconductor oxide thin-film transistors", Superlatt. Microstruc., Vol. 44, pp.761-769, 2008.

[15] M. Wang, Y. Lian, X. Wang, "PPV/PVA/ZnO nanocomposite prepared by complex precursormethod and its photovoltaic application", Curr. Appl. Phys. Vol. 9, pp.189-194, 2009.

[16] S. A. Chambers, "Electron mediated ferromagnetism in epitaxial co-doped ZnO", OPTO, 2007 Integrated Optoelectronic Devices, 6474-49, Session 12.

[17] X. Zhua, I. Yurib, X. Gana, I. Suzukib and G. Lia, "Electrochemical study of the effect of nano-zinc oxide on microperoxidase and its application to more sensitive hydrogen peroxide biosensor preparation", Biosens. Bioelectron., Vol. 22, pp. 1600-1604, March, 2007.

[18] Y. Janga, C. Simera and T. Ohm, "Comparison of zinc oxide nanoparticles and its nano-crystalline particles on the photocatalytic degradation of methylene blue", Mater. Res. Bull., Vol. 41, pp. 67-77, January, 2006.

[19] J. Jun, H. Seong, K. Cho, B. Moon, S. Kim, "Ultraviolet photodetectors based on ZnO nanoparticles", Ceram. Int., doi:10.1016/ j.ceramint.2009.03.032 , 2009.

[20] S. Monticone, R. Tufeu, and A.V. Kanaev, "Complex nature of the UV and visible fluorescence of colloidal ZnO nanoparticles", J. Phys. Chem. B, Vol. 102, pp. 2854-2862, 1998.

[21] Y.L. Wu, A.I.Y. Tok, F.Y.C. Boey, X.T. Zeng, X.H. Zhang, "Surface modification of ZnO nanocrystals", Appl. Surf. Sci., Vol. 253, pp. 5473-5479, 2007.

[22] L. Wu , Y. Wu, X. Pan, and F. Kong, "Synthesis of ZnO nanorod and the annealing effect on its photoluminescence property", Opt. Mater., Vol. 28, pp. 418-422, 2006.

[23] K. Borgohain and S. Mahamuni, "Luminescence behaviour of chemically grown ZnO quantum dots", Semicond. Sci. Technol. Vol. 13, pp. 1154-1157, 1998.

[24] S. Sharma, A. Tran, O. Nalamasu, and P.S. Dutta, "Spin-coated ZnO thin films using ZnO nano-colloid", J. Electron. Mater., Vol. 35, pp. 1237, 2006.