Ultraviolet Photodetector Fabricated From Multiwalled Carbon Nanotubes/Zinc-Oxide Nanowires/p-GaN Composite Structure

Dali Shao, Mingpeng Yu, Jie Lian, and Shayla M. L. Sawyer

***Abstract*— An ultraviolet (UV) heterojunction photodetector was fabricated from multiwalled carbon nanotubes (MWCNTs)/zinc-oxide nanowires (NWs)/p-GaN composite structure. The photodetector demonstrated significant rectifying characteristics and relative fast transient response with response time on the order of milliseconds. Under back illumination, the photodetector exhibited a narrow bandpass photoresponse spectrum (13-nm full-width at half-maximum) centered at 375 nm with a maximum responsivity of 6 mA/W. The good performance of this heterojunction photodetector is attributed to improved carrier transport and collection efficiency through the MWCNTs network deposited on top of the ZnO NWs.**

***Index Terms*— Gallium nitride (GaN), heterojunction, ultraviolet photodetector, zinc oxide (ZnO) nanowires.**

I. INTRODUCTION

ZINC oxide (ZnO) is a promising candidate for ultraviolet (UV) photodetector applications because of its unique optical and electrical properties including direct wide bandgap (3.37 eV), large exciton binding energy (60 meV), high chemical stability, and strong resistance to high-energy proton irradiation [1], [2]. Currently, the most prominent issue hindering the development of ZnO p-n junction UV photodetectors is the lack of a reproducible p-ZnO material [3]. As an alternative, n-ZnO has been used to combine with other available p-type semiconductor materials, such as Si, 6 H-SiC, and NiO to form p-n heterojunctions [4]–[7]. In particular, UV photodetectors fabricated from n-ZnO and p-GaN can achieve high-quality heterojunctions because of the small lattice mismatch between the two materials [8]. In addition, the strong radiation hardness of both ZnO and GaN makes their combination high potential for space applications. In recent literature, UV photodetectors were fabricated from ZnO epitaxial layers and nanowires (NWs) grown on p-GaN via molecular beam epitaxy (MBE) and vapor-liquid-solid (VLS) growth methods, respectively [9], [10].

In this letter, a heterojunction UV photodetector was fabricated from multiwalled carbon nanotubes (MWCNTs)/ZnO NWs/p-GaN composite structure. Under back illumination, the photodetector exhibited a narrow bandpass photoresponse spectrum with only 13-nm full-width at half-maximum (FWHM). This may have high potential for identification of DNA, protein, and bacteria through detection of their intrinsic UV fluorescence [11]. In addition, both a fast transient response (<6 ms) and high responsivity (~6 mA/W under back illumination) was demonstrated, which is attributed to improved carrier transport and collection efficiency through MWCNTs network. The results presented in this letter may stimulate interests of further investigation of UV photodetectors that fabricated from TiO_2/p-GaN and WO_3/p-GaN heterojunctions.

II. EXPERIMENT

The p-GaN substrate (Sensor Electronic Technology) consists of a 0.5 μm epitaxial GaN layer doped with magnesium (3×10^{17} cm^{-3}) grown on the top of a 3 μm semi-insulating GaN buffer layer and a 330 μm double side polished c-plane sapphire wafer. The ZnO NWs were grown on p-GaN substrate using hydrothermal method. Ammonium hydroxide (28 wt%) was added dropwise into 0.1 M zinc chloride solution until the pH was 10–11 and the solution was clear. Subsequently, the transparent solution was transferred to a teflon-lined autoclave (Parr, USA) and the p-GaN substrate with ZnO nanoparticles as a seed layer was suspended in the solution at 95 °C for 3 h in a regular laboratory oven. Then the growth solution was cooled down to room temperature naturally. The resulting substrate was thoroughly washed with deionized water and absolute ethanol for several times and dried in air at room temperature. After the growth of ZnO NWs, MWCNTs with carboxyl functionalized group were dissolved in dimethylformamide and deposited onto the top of ZnO NWs to form the MWCNTs network. Then aluminium contact with thickness of 300 nm and Au contact with thickness of 150 nm were deposited using E-beam evaporator through shadow masks. Finally, the photodetector was packaged and wire bonded using Epo-Tek H20E conductive epoxy.

Manuscript received June 7, 2013; revised July 9, 2013; accepted July 10, 2013. Date of publication August 6, 2013; date of current version August 21, 2013. This work was supported in part by the National Security Technologies through National Science Foundation (NSF) Industry/University Cooperative Research Center Connection One, the NSF Smart Lighting Engineering Research Center under Grant EEC-0812056, and NSF Career Award DMR 1151028. The review of this letter was arranged by Editor J.-M. Liu.

D. Shao and S. M. L. Sawyer are with the Department of Electrical, Computer, and System Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180 USA (e-mail: shaod@rpi.edu).

M. Yu and J. Lian are with the Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180 USA.

Color versions of one or more of the figures in this letter are available online at http://ieeexplore.ieee.org.

Digital Object Identifier 10.1109/LED.2013.2273351

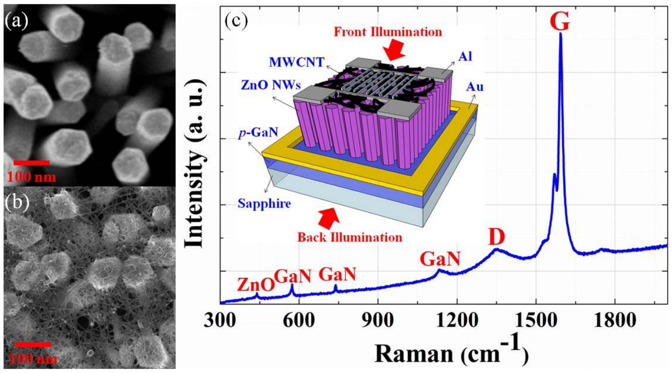

Fig. 1. (a) High-resolution SEM images showing the morphology of the ZnO NWs before deposition of MWCNTs network and (b) with MWCNTs network on the top. (c) Raman spectrum of the MWCNT/ZnO NWs/p-GaN composite structure. Inset: schematic view of the heterojunction photodetector.

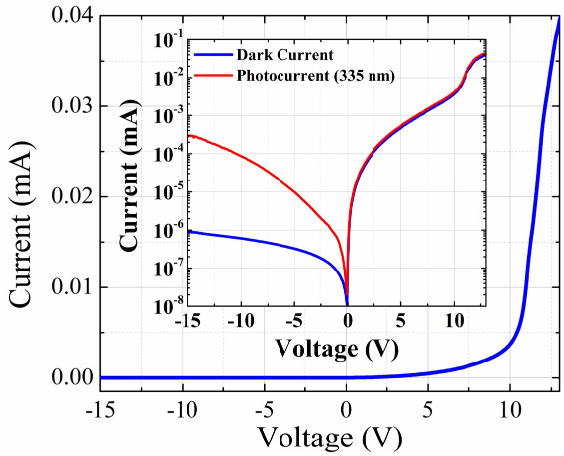

Fig. 2. *I–V* curve of the heterojunction photodetector measured under dark environment. Inset: log scale plot of the *I–V* curve measured under dark and under illumination by a 335-nm UV LED.

III. RESULTS AND DISCUSSION

The high-resolution scanning electron microscopy (SEM) images of the ZnO NWs before and after the deposition of MWCNTs are shown in Fig. 1(a) and (b), respectively. The average diameter of the ZnO NWs is 110 nm. The Raman spectrum of the MWCNTs/ZnO NWs/p-GaN composite structure is shown in Fig. 1(c) and the inset illustrates the schematic view of the heterojunction UV photodetector. The Raman spectrum shown in Fig. 1(c) confirmed the good quality of the MWCNT network, in which the relative intensity of the disorder D-band at 1347 cm^{-1} to the crystalline G-band at 1590 cm^{-1} is around 0.29. The sheet resistance of the MWCNTs network was measured using a similar MWCNTs network deposited on glass, which was determined to be 27 Ω/square.

The *I–V* characteristic of the photodetector measured under dark environment displayed significant rectification characteristics, as shown in Fig. 2. A rectification ratio of 511 was observed when biased at ±2 V, which is much larger than that of the MBE grown ZnO/p-GaN heterojunction photodetector reported in [9] (<10). This indicates the good electrical property of our hydrothermally synthesized heterojunction. The threshold voltage and reverse saturation current were determined to be 4.3 V and 0.33 nA (at -5 V), respectively. The dark current under forward bias increases exponentially following the equation, $I \sim \exp(\alpha V)$, which is usually observed in wide bandgap p-n diodes because of a recombination-tunneling mechanism [12], [13]. The constant α was evaluated to be 0.97 V^{-1} by fitting the experimental data in Fig. 2, which falls in the range 0.45–1.50 V^{-1} for the semiconductor junctions, as suggested in [12]. The inset of Fig. 2 is the log scale plot of the dark current and photocurrent measured under illumination by a 335-nm UV LED with intensity of 31.65 mW/cm^2. The ON-OFF ratio at -15 V is about 300, which is 19 times higher than that of the ZnO NWs/p-GaN photodetector grown by VLS method [10].

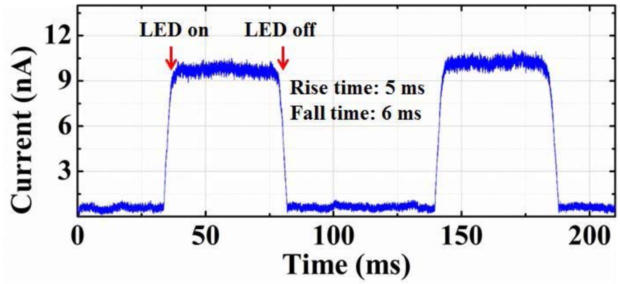

Fig. 3. Transient response of the heterojunction photodetector measured by turning ON and OFF a 335-nm UV LED.

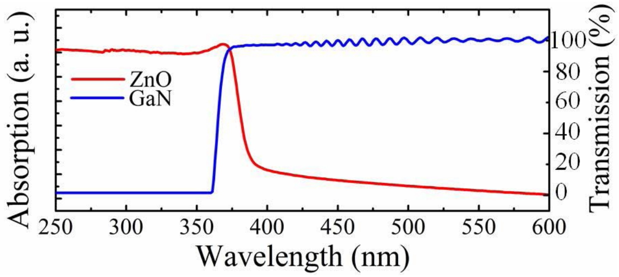

Fig. 4. Transmission spectrum of GaN layer (blue line) and absorption spectrum of ZnO NWs (red line).

The transient response of photodetector is shown in Fig. 3. The rise time and fall time of the photodetector were measured to be ~5 and ~6 ms, respectively, which is around 1000 times faster than the ZnO NWs/p-GaN heterojunction photodetector fabricated via VLS growth method [10]. The fast transient response of the photodetector in this letter is attributed to improved carrier transport and collection efficiency through the MWCNTs, which has been discussed detailed in our previous work [5]. It is worth to mention that Girolami *et al.* [14] reported a diamond UV detector with response time on the orders of nanoseconds, demonstrated diamond as a competing material for ultrafast UV detector applications.

Fig. 4 shows the transmission and absorption spectra of the p-GaN layer and ZnO NWs, respectively. It is clear from the spectra that the GaN layer has a sharp transmission edge at 360 nm and the absorption of the ZnO NWs shows a cutoff at 385 nm. The transmission of GaN and the absorption of

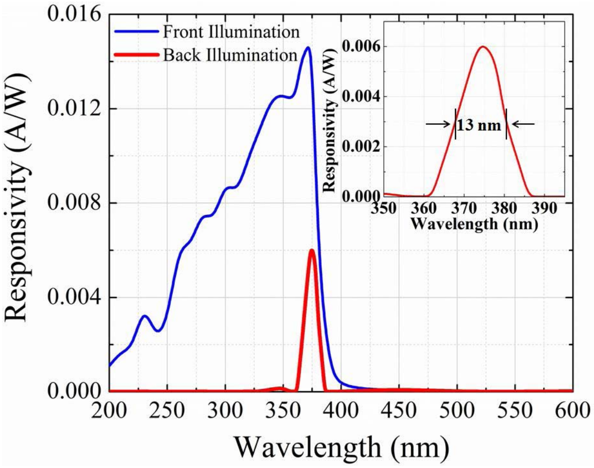

Fig. 5. Room-temperature responsivity spectra of the heterojunction photodetector measured under front and back illuminations when biased at 0 V. Inset: enlarged view of the responsivity spectrum under back illumination at 0 V.

ZnO have an overlap in the region from 360 to 385 nm. This narrow window ensures high spectrum selectivity when back illuminated from the GaN side.

Fig. 5 shows the room-temperature responsivity spectra of the heterojunction photodetector under back and front illumination with 0 V bias. The spectrum under back illumination (red line) shows a narrow band centered at 375 nm with a maximum responsivity of 6 mA/W, which is almost 600 times higher than that of the ZnO/p-GaN heterojunction grown by MBE method [9]. The high responsivity of the photodetector in this letter as compared with other n-ZnO/p-GaN-based photodetectors is attributed to the improved carrier transport and collection efficiency as a result of improved device integrity by applying MWCNTs network. From the inset of Fig. 5, we can see that the responsivity spectrum under back illumination have a FWHM of only 13 nm, indicating that the responsivity of the photodetector is highly selective. To the contrary, the photoresponsivity spectrum of the photodetector under front illumination (blue line) shows a broad response with high-energy tail. This is due to the lack of a GaN filter and therefore photons with energy above the bandgap of ZnO NWs and MWCNTs can be absorbed.

IV. CONCLUSION

In conclusion, an UV heterojunction photodetector was fabricated from MWCNTs/ZnO NWs/p-GaN composite structure. Compared with ZnO/p-GaN photodiodes fabricated through MBE and VLS methods, the photodetector in this letter exhibits not only fast transient response, but also greatly improved photoresponsivity. In addition, a narrow bandpass photoresponse spectrum with FWHM of 13 nm was realized by taking advantage of the GaN substrate as a filter. The enhanced device performance is attributed to improved carrier transport and collection efficiency through MWCNTs network.

REFERENCES

[1] C.-Y. Chang, F.-C. Tsao, C.-J. Pan, *et al.*, "Electroluminescence from ZnO nanowire/polymer composite *p-n* junction," *Appl. Phys. Lett.*, vol. 88, no. 17, pp. 173503-1–173503-3, Apr. 2006.

[2] D. C. Look, C. Coskun, B. Claflin, *et al.*, "Electrical and optical properties of defects and impurities in ZnO," *Phys. B, Condensed Matter*, vols. 340–342, pp. 32–38, Dec. 2003.

[3] G. D. Yuan, W. J. Zhang, J. S. Jie, *et al.*, "p-Type ZnO nanowire arrays," *Nano Lett.*, vol. 8, no. 8, pp. 2591–2597, Jul. 2008.

[4] D. Shao, M. Yu, J. Lian, *et al.*, "Heterojunction photodiode fabricated from hydrogen treated ZnO nanowires grown on p-silicon substrate," *Appl. Phys. Lett.*, vol. 101, no. 21, pp. 211103-1–211103-4, Nov. 2012.

[5] D. Shao, M. Yu, J. Lian, *et al.*, "Heterojunction photodiode fabricated from multiwalled carbon nanotube/ZnO nanowire/p-silicon composite structure," *Appl. Phys. Lett.*, vol. 102, no. 2, pp. 021107-1–021107-3, Jan. 2013.

[6] Y. I. Alivov, Ü. Özgür, S. Doğan, *et al.*, "Photoresponse of n-ZnO/p-SiC heterojunction diodes grown by plasma-assisted molecular-beam epitaxy," *Appl. Phys. Lett.*, vol. 86, no. 24, pp. 241108-1–241108-3, Jun. 2005.

[7] S.-Y. Tsai, M.-H. Hon, and Y.-M. Lu, "Fabrication of transparent p-NiO/n-ZnO heterojunction devices for ultraviolet photodetectors," *Solid-State Electron.*, vol. 63, no. 1, pp. 37–41, Sep. 2011.

[8] X. Wei, R. Zhao, M. Shao, *et al.*, "Fabrication and properties of ZnO/GaN heterostructure nanocolumnar thin film on Si (111) substrate," *Nanoscale Res. Lett.*, vol. 8, no. 112, pp. 1–7, Feb. 2013.

[9] H. Zhu, C. X. Shan, B. Yao, *et al.*, "High spectrum selectivity ultraviolet photodetector fabricated from an n-ZnO/p-GaN heterojunction," *J. Phys. Chem. C*, vol. 112, no. 51, pp. 20546–20548, Nov. 2008.

[10] C.-H. Chen, S.-J. Chang, S.-P. Chang, *et al.*, "Novel fabrication of UV photodetector based on ZnO nanowire/p-GaN heterojunction," *Chem. Phys. Lett.*, vol. 476, nos. 1–3, pp. 69–72, Jul. 2009.

[11] P. J. Hargis, T. J. Sobering, G. C. Tisone, *et al.*, "Ultraviolet fluorescence identification of protein, DNA, and bacteria," *Proc. SPIE*, vol. 2366, pp. 147–153, Feb. 1995.

[12] J. B. Fedison, T. P. Chow, H. Lu, *et al.*, "Electrical characteristics of magnesium-doped gallium nitride junction diodes," *Appl. Phys. Lett.*, vol. 72, no. 22, pp. 2841–2843, Mar. 1998.

[13] R. Ghosh and D. Basak, "Electrical and ultraviolet photoresponse properties of quasialigned ZnO nanowires/p-Si heterojunction," *Appl. Phys. Lett.*, vol. 90, no. 24, pp. 243106-1–243106-3, Jun. 2007.

[14] M. Girolami, P. Allegrini, G. Conte, *et al.*, "Diamond detectors for UV and X-ray source imaging," *IEEE Electron Device Lett.*, vol. 33, no. 2, pp. 224–226, Feb. 2012.