Ultraviolet photodetectors with ZnO nanowires prepared on ZnO:Ga/glass templates

Chien-Yuan Lu, Shoou-Jinn Chang,[a] Sheng-Po Chang, Ching-Ting Lee, Che-Fu Kuo, and Hong-Ming Chang
Institute of Microelectronics, Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan 70101, Taiwan Department of Electrical Engineering, Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan 70101, Taiwan

Yu-Zung Chiou
Department of Electronic Engineering, Southern Taiwan University of Technology, Tainan 710, Taiwan

Cheng-Liang Hsu
Department of Electronic Engineering, National University of Tainan, Tainan 700, Taiwan

I-Cherng Chen
Micro Systems Technology Center, Industrial Technology Research Institute South, Tainan 709, Taiwan

(Received 5 April 2006; accepted 29 August 2006; published online 9 October 2006)

Vertically well-aligned ZnO nanowire ultraviolet (UV) photodetectors were fabricated by spin-on-glass technology on ZnO:Ga/glass templates. With 2 V applied bias, it was found that dark current density of the fabricated device was only 2.0×10^{-7} A/cm^2. It was also found that UV-to-visible rejection ratio and quantum efficiency of the fabricated ZnO nanowire photodetectors were more than 1000 and 12.6%, respectively. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2360219]

In recent years, ZnO has attracted much attention for optoelectronic applications. ZnO is a *n*-type semiconductor with a large exciton binding energy of 60 meV and wide band gap energy of 3.37 eV at room temperature.[1,2] These properties make it a potentially useful photonic material for ultraviolet (UV) photodetectors[3,4] and other optoelectronic applications.[5,6] Further, ZnO nanowires are regarded as one of the most promising materials for nanoscale UV photodetector, UV laser diode, and optical switch applications.[6–9] Very recently, we reported the growth of vertically well-aligned ZnO nanowires on ZnO:Ga/glass templates by self-catalyzed vapor-liquid-solid (VLS) method.[10–13] We also demonstrated ZnO nanowire UV photodetectors by flipping the sample so that tips of the vertical ZnO nanowires were contacted directly with another indium tin oxide (ITO)/glass substrate.[11] However, such a simple scheme is not suitable for practical applications since tips of the vertical ZnO nanowires were contacted softly with the underneath ITO/glass. Thus, detector response was very sensitive to vibration. For feasible detectors, it is necessary to solidly connect electrical contact pads to both ends of the nanowires. Previously, it has been shown that one can either disperse the nanowires onto precoated electrodes or use electron beam lithography to fabricate electrodes on top of the nanowires.[14–19] Using these methods, Kind *et al.* have successfully fabricated photoconductive devices with horizontal ZnO nanowires.[8] In this work, we report the fabrication of UV photodetectors using vertical ZnO nanowires. Properties of the fabricated photodetectors will also be discussed.

The well-aligned vertical ZnO nanowires used in this study were grown on ZnO:Ga/glass templates. Detailed growth procedures could be found elsewhere.[10–13] Figure 1 shows cross-sectional field emission surface electron microscopy (FESEM) images with 30° title angle of the as-grown ZnO nanowires prepared on ZnO/glass template. It can be seen clearly that high density well-aligned ZnO nanowires with uniform length and diameter were selectively grown.[10] From x-ray diffraction and photoluminescence measurements, it was found that the ZnO nanowires were preferred oriented in the (002) *c*-axis direction with good crystal quality.[10–13] For the fabrication of photodetectors, we coated a thin spin-on-glass (SOG) film onto the as-grown ZnO nanowires followed by 90 °C thermal treatment for 30 min. Figure 2 shows top-view SEM picture of the ZnO nanowires coated with insulating SOG. With proper spin coating condition, we can control the SOG thickness so that only sharp tips of the ZnO nanowires were exposed.

To solidly connect electrical contact pads to the tips of these nanowires, we thermally evaporated 200-nm-thick Au

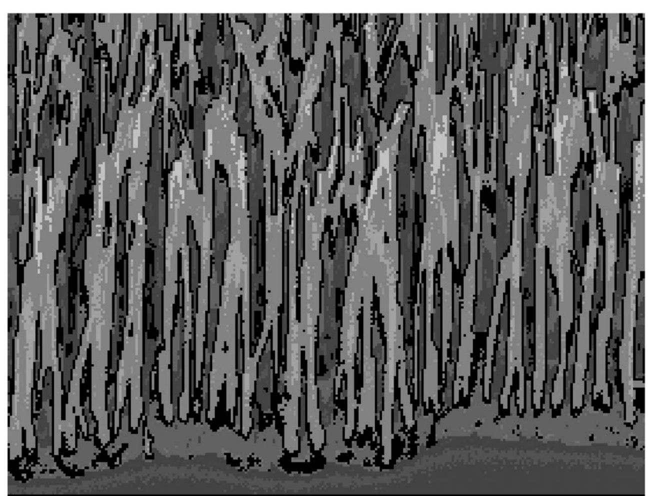

FIG. 1. Cross-sectional FESEM images with 30° title angle of the as-grown ZnO nanowires prepared on ZnO/glass template.

[a]Electronic mail: changsj@mail.ncku.edu.tw

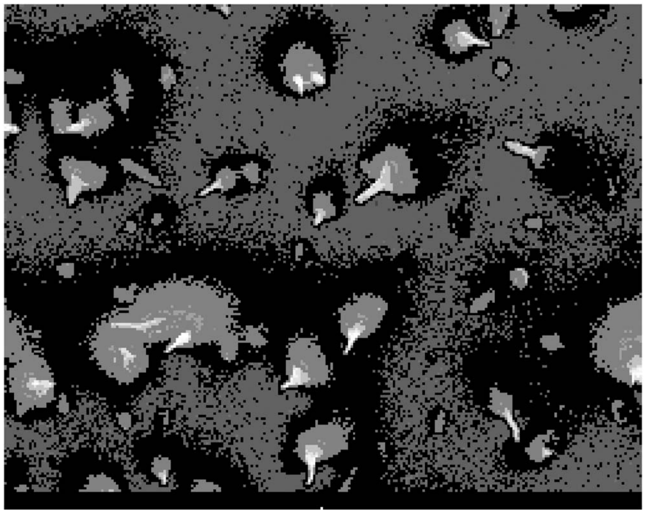

FIG. 2. Top-view SEM picture of the ZnO nanowires coated with insulating SOG.

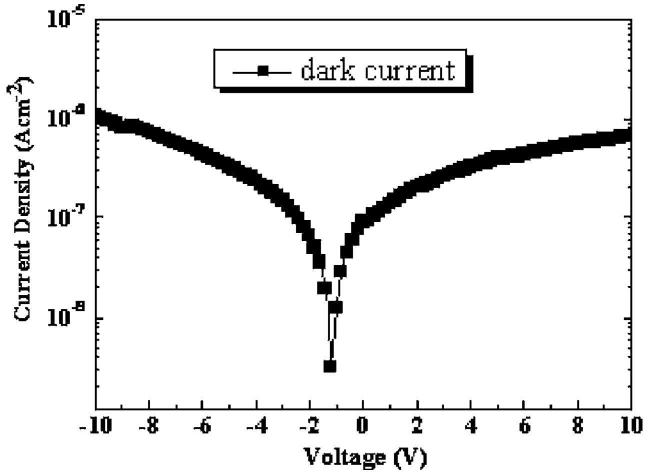

FIG. 4. Measured dark *I-V* characteristics of the fabricated device.

film through shadow mask onto the samples, as shown in Fig. 3. Current-voltage (*I-V*) characteristic of the fabricated device was then measured. Spectral responsivity measurements of the fabricated photodetectors were also performed by Jobin-Yvon Spex system with a 300 W xenon arc lamp light source (Perkinelmer PE300BUV) and a standard synchronous detection scheme measured at 300 Hz. Figure 4 shows measured dark *I-V* characteristics of the fabricated device. With 1 V applied bias, it was found that dark current density of the device was only 1.37×10^{-7} A/cm^2. The extremely small dark current should be attributed to the highly resistive nature of the undoped ZnO nanowires.

Figure 5 shows measured transient response of the photodetector. As we turned off the UV lamp, it was found that photocurrent decreased rapidly followed by a much slower decrease. The slow transient can be described by a stretched-exponential function as often reported for persistent photocurrent I_{ppc} in crystalline semiconductors.[20–22]

$$I_{ppc}(t) = I_0(t)\exp\left[-\left(\frac{t_x}{\tau}\right)^{\beta}\right], \quad (1)$$

where $I_0(t)$ is the current when the light excitation is removed, τ is a decay time constant, and β is a decay exponent. Using the exponential fit, it was found that the decay exponent β and time constant τ of the nanowire photodetector were around 1 and 0.44 ms, respectively. Previously, it has been shown that photoconduction of ZnO nanowire is governed by desorption and adsorption of oxygen.[23–25] In the dark, oxygen molecules among the nanowires surface carried the negative charges by capturing the free electrons from the *n*-type ZnO. Thereby, it creates a depletion layer with low conductivity near the nanowires surface. Under UV illumination, photogenerated holes oxidize the adsorbed negatively charged oxygen species on the surface while the electrons in the conduction band increase the conductivity.[26,27] It has been pointed out that transient response of ZnO nanowires will also be affected by the recovery of the modified surface chemistry.[14] To fully understand these phenomena, we need to perform more experiments, such as measurement of transit response in different oxygen concentrations and different temperatures. These experiments are underway and the results will be reported separately. It should be noted that the 0.44 ms time constant observed in this study was much smaller than that reported from ZnO-based metal-oxide-metal photodetectors.[28] The increased surface area to volume ratio of the ZnO nanowires should also provide us a large photocurrent to dark current contrast ratio.

Figure 6 shows measured spectra response of the ZnO nanowire photodetector biased at 1 V. It can be seen that peak responsivity occurred at around 365 nm. Here, we define UV-to-visible rejection ratio as the responsivity measured at 365 nm divided by the responsivity measured at 425 nm. With such a definition, it was found that we achieved a UV-to-visible rejection ratio of around 1000. We

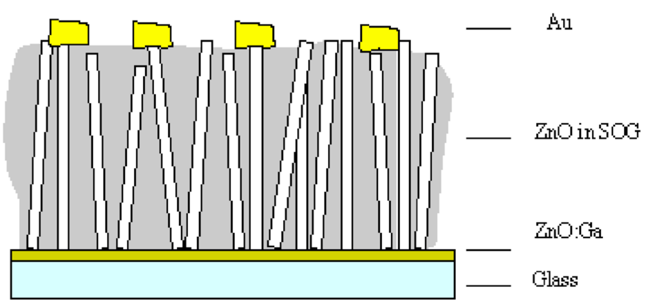

FIG. 3. (Color online) Schematic diagram of the fabricated ZnO nanowire photodetectors.

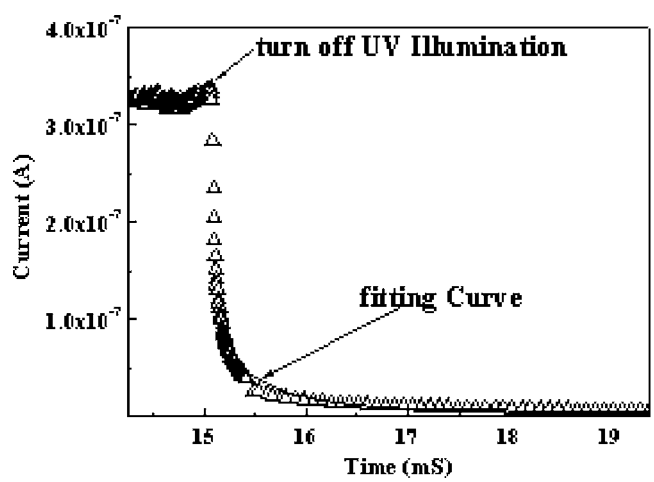

FIG. 5. Measured transient response of the fabricated photodetector as we switched off the UV lamp.

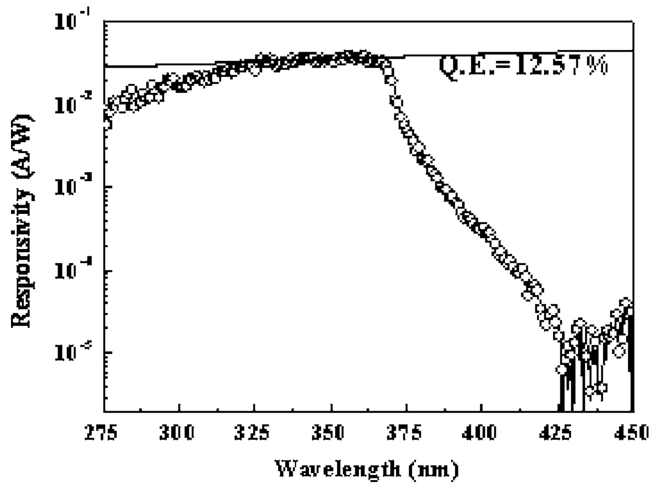

FIG. 6. Measured spectra response of the ZnO nanowire photodetector biased at 1 V.

also calculated quantum efficiency of the photodetector from the measured response. With an incident wavelength of 365 nm, it was found that quantum efficiency of the ZnO nanowire UV photodetector could reach 12.6%.

In summary, vertically well-aligned ZnO nanowire UV photodetectors were fabricated by spin-on-glass technology on ZnO:Ga/glass templates. It was found that time constant of the fabricated photodetectors was 0.44 ms. It was also found that we could achieve low dark current, high UV-to-visible rejection ratio, and high quantum efficiency from the fabricated devices.

[1] J. Chen, Y. Zhang, B. J. Skromme, K. Akimoto, and S. J. Pachuta, J. Appl. Phys. **78**, 5109 (1995).
[2] H. Kato, M. Sano, K. Miyamoto, and T. Yao, Jpn. J. Appl. Phys., Part 2 **42**, L1002 (2003).
[3] W. I. Park, Y. H. Jjun, S. W. Jung, and G. C. Yi, Appl. Phys. Lett. **82**, 964 (2003).
[4] L. B. K. Law and J. T. L. Thong, Appl. Phys. Lett. **88**, 133114 (2006).
[5] L. Vayssieres, K. Keis, A. Hagfeldt, and S. E. Lindquist, Chem. Mater. **13**, 4386 (2001).
[6] J. C. Johnson, H. Q. Yan, P. Yang, and R. J. Saykally, J. Phys. Chem. B **107**, 8816 (2003).
[7] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, Science **292**, 1897 (2001).
[8] H. Kind, H. Yan, B. Messer, M. Law, and P. Yang, Adv. Mater. (Weinheim, Ger.) **14**, 158 (2002).
[9] H. Yan, J. Johnson, M. Law, R. He, K. Knutsen, J. R. McKinney, J. Pham, R. Saykally, and P. Yang, Adv. Mater. (Weinheim, Ger.) **15**, 1907 (2003).
[10] C. L. Hsu, S. J. Chang, H. C. Hung, Y. R. Lin, C. J. Huang, Y. K. Tseng, and I. C. Chen, IEEE Trans. Nanotechnol. **4**, 649 (2005).
[11] C. L. Hsu, Y. R. Lin, S. J. Chang, T. S. Lin, S. Y. Tsai, and I. C. Chen, Chem. Phys. Lett. **411**, 221 (2005).
[12] Y. K. Tseng, C. J. Huang, H. M. Cheng, I. N. Lin, K. S. Liu, and I. C. Chen, Adv. Funct. Mater. **13**, 811 (2003).
[13] Y. K. Tseng, H. C. Hsu, W. F. Hsieh, K. S. Liu, and I. C. Chen, J. Mater. Res. **18**, 2837 (2003).
[14] M. S. Arnold, Ph. Avouris, Z. W. Pan, and Z. L. Wang, J. Phys. Chem. B **107**, 659 (2003).
[15] W. I. Park, G. C. Yi, W. I. Kim, and S. M. Park, Appl. Phys. Lett. **82**, 4358 (2003).
[16] S. C. Lyu, Y. Zhang, H. Ruh, H. J. Lee, H. W. Shim, E. K. Suh, and C. J. Lee, Chem. Phys. Lett. **363**, 134 (2002).
[17] B. J. Jin, S. H. Bae, S. Y. Lee, and S. Im, Mater. Sci. Eng., B **71**, 301 (2000).
[18] H. J. Egelhaaf and D. Oelkrug, J. Cryst. Growth **161**, 190 (1996).
[19] R. Konenkamp, R. Word, and C. Schlegel, Appl. Phys. Lett. **24**, 6004 (2004).
[20] J. T. Xu, D. You, Y. W. Tang, Y. Kang, X. Li, X. Y. Li, and H. M. Gong, Appl. Phys. Lett. **88**, 072106 (2006).
[21] M. Salis, A. Anedda, F. Quarati, A. J. Blue, and W. J. Cunningham, J. Appl. Phys. **97**, 033709 (2005).
[22] B. Poti, A. Passaseo, M. Lomascolo, R. Cingolani, and M. De Vittorio, Appl. Phys. Lett. **85**, 6083 (2004).
[23] Q. H. Li, T. Gao, Y. G. Wang, and T. H. Wang, Appl. Phys. Lett. **86**, 123117 (2005).
[24] Y. W. Heo, B. S. Kang, L. C. Tien, D. P. Norton, F. Ren, J. R. LaRoche, and S. J. Pearton, Appl. Phys. A: Mater. Sci. Process. **80**, 497 (2005).
[25] O. Harnack, C. Pacholski, H. Weller, A. Yasuda, and J. M. Wessels, Nano Lett. **3**, 1097 (2003).
[26] S. J. Baik, J. H. Jang, C. H. Lee, W. Y. Cho, and K. S. Lim, Appl. Phys. Lett. **70**, 3516 (1997).
[27] Q. H. Li, Q. Wan, Y. X. Liang, and T. H. Wang, Appl. Phys. Lett. **84**, 4556 (2004).
[28] T. K. Lin, S. J. Chang, Y. K. Su, B. R. Huang, M. Fujita, and Y. Horikoshi, J. Cryst. Growth **281**, 513 (2005).