Gigantic enhancement in response and reset time of ZnO UV nanosensor by utilizing Schottky contact and surface functionalization

Jun Zhou,[1,2] Yudong Gu,[1,3] Youfan Hu,[1] Wenjie Mai,[1] Ping-Hung Yeh,[1] Gang Bao,[2] Ashok K. Sood,[4] Dennis L. Polla,[5] and Zhong Lin Wang[1,a]

[1]*School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA*
[2]*Department of Biomedical Engineering, Emory University, Atlanta, Georgia 30332, USA*
[3]*Department of Advanced Materials and Nanotechnology, College of Engineering, Peking University, 100084 Beijing, China*
[4]*Magnolia Optical Technologies, Inc., 52-B Cummings Park, Woburn, Massachusetts 01801, USA*
[5]*DARPA/MTO, 3701 North Fairfax Dr., Arlington, Virginia 22203-1714, USA*

UV response of ZnO nanowire nanosensor has been studied under ambient condition. By utilizing Schottky contact instead of Ohmic contact in device fabrication, the UV sensitivity of the nanosensor has been improved by four orders of magnitude, and the reset time has been drastically reduced from ~417 to ~0.8 s. By further surface functionalization with function polymers, the reset time has been reduced to ~20 ms even without correcting the electronic response of the measurement system. These results demonstrate an effective approach for building high response and fast reset UV detectors. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3133358]

Ultraviolet (UV) photon detectors have a wide range of applications from environmental monitoring, missile launching detection, space research, high temperature flame detection to optical communications.[1] For these applications, fast response time, fast reset time, high selectivity, high responsivity, and good signal-to-noise ratio are commonly desired characteristics.[2] For UV photon detector based on polycrystalline ZnO thin film, a slow response time ranging from a few minutes to several hours is commonly observed.[3,4] Due to large surface-to-volume ratio and reduced dimensionality of the active area, ZnO nanostructures are expected to have high photon conductance.[5] Kind *et al.*[6] reported the photon response of a single ZnO nanowire (NW) under UV illumination, which has also been studied by other groups.[7–9] Most of the studies have been focused on the mechanism investigation[10,11] and improving the sensitivity.[9,12] For example, Lao *et al.*[9] have improved the sensitivity of the ZnO NW UV nanosensor (NS) for five orders of magnitude by functionalizing the surface of ZnO nanobelts using polymers that have a high absorption at the UV range. However, little attention has been paid on improving the response and recovery time[13] especially the reset time (defined as the time need to recovery to $1/e$ (37%) of the maximum photocurrent).

In this letter, we demonstrate effective ways for improving both the sensitivity and reset time of ZnO NW NSs. By fabricating Schottky type (ST) devices instead of Ohmic type (OT) devices, the UV sensitivity of ZnO NW NS has been improved for four orders of magnitude, and the reset time has been decreased from ~417 to ~0.8 s. By further surface coating with positive charged poly(diallydimethylammonium chloride) (PDADMAC) and negative charged poly(sodium 4-styrenesulfonate) (PSS), the reset time has been decreased to ~20 ms even without correcting the electronic response of the measurement system.

The ZnO NWs for the NS fabrication were synthesized by thermal evaporation of ZnO powders without using any catalyst.[14] UV response of our devices was characterized by a portable UV lamp (Spectroline, Model ENF-280C, 365 nm). The photon-response spectrum measurement was carried out in a PTI QuantaMaster Luminescence (QM 3PH) system. All of the measurements were carried out at room temperature in ambient condition.

We first studied the performance of an Ohmic-contact ZnO NW NS. The "metal-semiconductor-metal" (M-S-M) device structure is depicted in Fig. 1(a). To make an Ohmic contact, Ti/Au electrodes were deposit on a single ZnO NW through shadow mask technology. The high linear *I-V* characteristic [black curve in the inset of Fig. 1(b)] of the device in dark indicated that the device is Ohmic as expected. By illuminating the device using a 365 nm UV source at a power density of ~30 μW/cm², the photon conductance was improved for only ~15%. After ~260 s continuous illumination, the current was still unsaturated. More importantly, the reset time of the sensor was ~417 s, and the current could not recover to its initial state even after ~2500 s [Fig. 1(b)].

The slow UV response and recovery of the Ohmic ZnO NW NS may be attributed to the oxygen adsorption and desorption process.[4–7] In dark, oxygen molecules adsorb on the ZnO NW surface by capturing free electrons from the *n*-type ZnO $[O_2(g)+e^-{\rightarrow}O_2^-(ad)]$, thereby creating a depletion layer with low conductivity near the surface. Upon UV illumination at photon energies above ZnO band gap, electron-hole pairs are generated $[h\nu{\rightarrow}e^-+h^+]$. Photon-generated holes migrate to the surface and discharge the adsorbed oxygen ions $[O_2^-(ad)+h^+{\rightarrow}O_2(g)]$ to photon-desorbed oxygen from the surfaces. The unpaired electrons accumulate gradually with time until desorption and readsorption of O_2 reach an equilibrium state, resulting in a gradual current rise until saturation during UV illumination. Although holes recombine quickly with electrons upon turning off UV light, there are still a lot of electrons left in the ZnO. O_2 molecules gradually readsorb on the surface and capture these electrons, which results in a slow current decay.

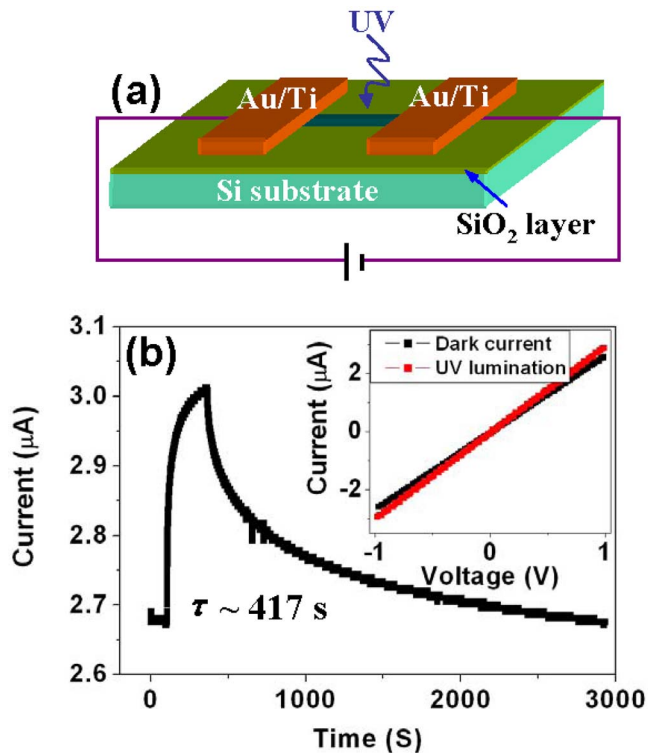a)Author to whom correspondence should be addressed. Electronic mail: zlwang@gatech.edu.

FIG. 1. (Color online) (a) Schematic of a ZnO NW UV NS device structure with Ohmic contacts. (b) Photon response of a ZnO NW UV NS, made using Ti/Au electrodes and at a bias of 1 V, when illuminated by ~30 μW/cm^2 365 nm UV source. The inset shows the corresponding *I-V* characteristics in dark or under UV illumination.
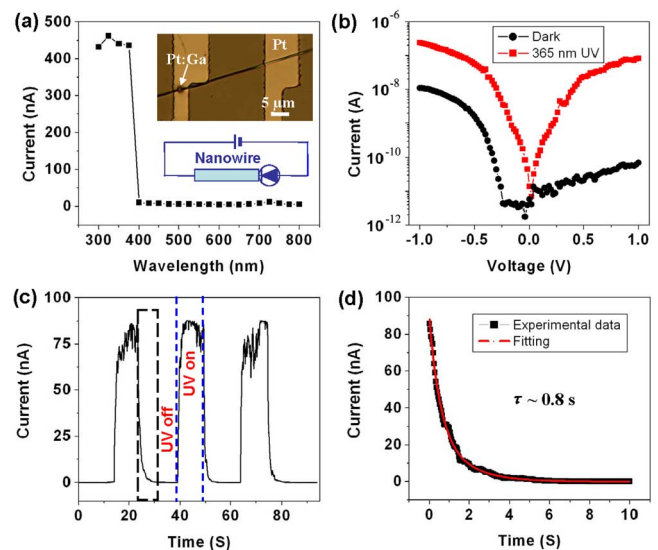

FIG. 2. (Color online) (a) Photon-response spectrum of the ZnO NW UV NS as a function of wavelength of incident light. Upper inset is an optical image of ST ZnO NW NS device. Lower inset shows the schematic structure of the device. (b) *I-V* characteristics of a sensor device both in the dark (black cycle) and under 365 nm UV illumination (red rectangle). (c) Time dependence of the photocurrent growth and decay under periodic illumination of the 365 nm UV light on the device. The bias on the device is 1 V. (d) Experimental curve (black) and fitted curve (red) of the photocurrent decay process.

Although the sensitivity of OT ZnO NW UV NS can be improved by using small size NWs, however the reset time is still in the order of few hundred second or even longer.[15] Such a performance is not adequate for sensor application especially used for UV detection purpose at a high frequency, thus we developed ST NS device which is expected to have fast response and high sensitivity.[4] The ST ZnO NW NSs were fabricated by the following process. First, patterned Pt microelectrode arrays were fabricated on SiO$_2$/Si substrate by UV lithography and e-beam evaporation process. Second, single ZnO NW was placed on the electrodes by dry printing process.[16] Finally, focus ion beam microscopy was used to deposit Pt:Ga electrode on one end of ZnO NW to make a good Ohmic contact, and left another end as Schottky contact. The typical optical image of a ST ZnO NW NS device is shown in upper inset of Fig. 2(a), in which the white arrow head indicates the Pt:Ga electrode. The schematic structure of the device can be considered as a single ZnO NW connected with a Schottky barrier (SB), which is shown in the lower inset of Fig. 2(a). Figure 2(a) shows a photon-response spectrum of the device under the modulated illumination of light with wavelength ranging from 300 to 800 nm. The photon response shows a sharp onset from 380 to 400 nm, corresponding to the ZnO band gap. Above the band gap energy, the photon response is almost constant, while little photon response is found from 400 to 800 nm. The high wavelength selectivity suggests that the device is intrinsically "visible-blind."

Figure 2(b) shows typical *I-V* characteristics of ST ZnO NW NS both in the dark (black curve) and upon ~30 μW/cm^2 365 nm UV light illumination (red curve). It reveals that the NS was more sensitive when the SB was reversely biased. The response behavior of the device were characterized by measuring the current under fixed bias of 1 V (the SB was reversely biased) as a function of time when the device was periodically exposed to the UV light, which is shown in Fig. 2(c). The current increases from 0.04 to 60 nA within 0.6 s, which is nearly a 1500-fold enhancement in response. When the UV light was turned off, the current decreased to reach its initial state within 6 s with a reset time of 0.8 s, which is shown in Fig. 2(d). The decay time of the photon response follows a second-order exponential decay function, with estimated time constant of $\tau_{d1}=0.52$ s and $\tau_{d2}=1.47$ s, and relative weight factors of 64% and 36%, respectively. The differences in device performances between the two types of NSs can therefore attribute to the SB at the ZnO/Pt interface.

It is well known that metal Pt (work function of ~6.1 eV) and *n*-type ZnO (work function of ~5.1 eV) can form a Schottky contact, and the adsorbed oxygen at the metal/semiconductor interface can significant modify the SB.[17] Normally, the presence of a SB at the metal/semiconductor interface plays a crucial role in determining the electrical transport property of the M-S-M structure.[17] At a fixed bias voltage, the voltage drop occurs mainly at the reversely biased SB.[18] When the reverse-biased Schottky contact is illuminated by 365 nm UV, photon-generated electrons and holes in the interface region are separated by the strong local electric field, thus reduce the electron-hole recombination rates and increase the carrier lifetime, resulting in an increase in free carrier density. The photon-desorption of oxygen at the ZnO/Pt interface modifies the density of defects states and, hence, alters the SB. Both of the two processes may lower the height and narrow the width of the SB, thus electrons may transit over the lowered height of the SB or tunnel through the narrowed width of the SB. This mechanism accounts for the enhanced UV response. The
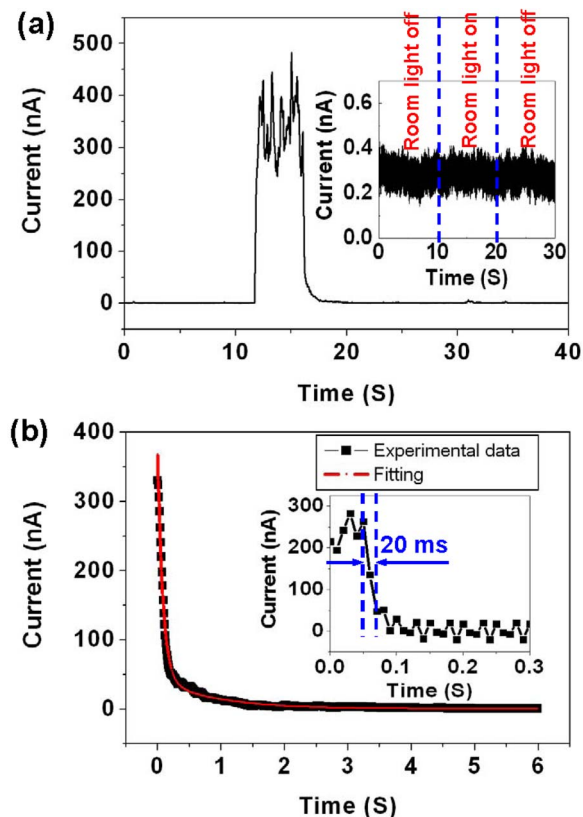
FIG. 3. (Color online) (a) Photocurrent of a surface functionalized ST ZnO NW NS when illuminated by UV with ∼30 μW/cm^2 at 365 nm and a bias of 5 V. The inset shows the response of the device when room light was turning on and off. (b) Experimental curve (black) and fitted curve (red) of the photocurrent decay process as the response time of the measurement system was 100 ms. The inset shows the photocurrent decay process as the response time of the measurement system was 10 ms.

more rapid photocurrent decay in the ST device is mostly dictated by the electrical transport property of the SB. Upon turning off the UV light, the photon-generated electrons and holes in the interface region decreased dramatically, and the oxygen is only required to be readsorbed close to the interface to modify the SB height. It should be noted that, as the SB can be modified by many effects (such as surface absorption, strain, etc.), the long time performance stability and reliability of the ST type device may be affected, but surface passivation may protect the device.

The response speed of the ST ZnO NW NS can be further enhanced by surface functionalization. Positive charged PDADMAC and negative charged PSS layers were sequent coated on the device by a layer-by-layer self-assembly method.[9] The polymer coated device has no response to visible light, as shown in the inset of Fig. 3(a). However, a sharp response was detected when the device was exposed to 365 nm UV light [Fig. 3(a)], indicating that the ST ZnO NW NS is still UV selective after surface coating. The current increased from 0.3 to 200 nA within 120 ms under ∼30 μW/cm^2 UV illumination. When the UV light was turned off, the current decreased to 37% of its initial photocurrent within 110 ms. The decay time of the photon response follows a second-order exponential decay function, with estimated time constant of $\tau_{d1} = 0.084$ s and $\tau_{d2} = 0.88$ s, and relative weight factors of 88% and 12%, respectively [Fig. 3(b)]. It should be noted that the response time of the measurement system itself was set at 100 ms,

thus the real reset time the device should be much shorter than 110 ms. We measured the reset time of the device by setting the response time as 10 ms, the result is shown in the inset of the Fig. 3(b). Although the noise level was high, the photon-current decreased from ∼270 to ∼50 nA in 20 ms, indicating that the real reset time of the device is less than 20 ms in the order of a few milliseconds.

The mechanism for giant improvement of the UV response speed by surface coating is not fully understood yet. The polymer molecules may largely occupy the sites at which the adsorbed and ionized oxygen tend to occupy. Thus the UV response of device was dominated by the photon-generated electrons and holes, the recombination of which in the ZnO/Pt interface region is rather fast. But the oxygen adsorption and desorption process are usually slow.[7]

In summary, utilizing of Schottky contacts and surface functionalization has been demonstrated as effective ways for improving response speed especially the reset time of ZnO NW UV NSs. The fast UV response speed, high spectrum selectivity combined with high photosensitivity suggest the possibility of using ZnO NWs as visible-blind UV sensors for commercial, military, and space applications. Beside the UV sensors, we believe that the performance of gas sensors, strain sensors and biosensors can also be improved dramatically by the Schottky contacts introduced in device fabrication, which is distinctly different from the conventionally designed devices with Ohmic contacts.

[1] E. Monroy, F. Omnes, and F. Calle, Semicond. Sci. Technol. **18**, R33 (2003).
[2] L. Luo, Y. F. Zhang, S. S. Mao, and L. W. Lin, Sens. Actuators, A **127**, 201 (2006).
[3] P. Sharma, K. Sreenivas, and K. V. Rao, J. Appl. Phys. **93**, 3963 (2003).
[4] Y. Z. Jin, H. P. Wang, B. Q. Sun, J. C. Blakesley, and N. C. Greenham, Nano Lett. **8**, 1649 (2008).
[5] C. Soci, A. Zhang, B. Xiang, S. A. Dayeh, D. P. R. Aplin, J. Park, X. Y. Bao, Y. H. Lo, and D. Wang, Nano Lett. **7**, 1003 (2007).
[6] B. H. Kind, H. Yan, B. Messer, M. Law, and P. Yang, Adv. Mater. (Weinheim, Ger.) **14**, 158 (2002).
[7] K. Keem, H. Kim, G. T. Kim, J. S. Lee, B. Min, K. Cho, M. Y. Sung, and S. Kim, Appl. Phys. Lett. **84**, 4376 (2004).
[8] Y. Y. Lin, C. W. Chen, W. C. Yen, W. F. Su, C. H. Ku, and J. J. Wu, Appl. Phys. Lett. **92**, 233301 (2008).
[9] C. S. Lao, M. C. Park, Q. Kuang, Y. Deng, A. K. Sood, D. L. Polla, and Z. L. Wang, J. Am. Chem. Soc. **129**, 12096 (2007).
[10] S. E. Ahn, H. J. Ji, K. Kim, G. T. Kim, C. H. Bae, S. M. Park, Y. K. Kim, and J. S. Ha, Appl. Phys. Lett. **90**, 153106 (2007).
[11] Y. B. Li, F. D. Valle, M. Simonnet, I. Yamada, and J. J. Delaunay, Appl. Phys. Lett. **94**, 023110 (2009).
[12] R. S. Aga, D. Jowhar, A. Ueda, Z. Pan, W. E. Collins, R. Mu, K. D. Singer, and J. Shen, Appl. Phys. Lett. **91**, 232108 (2007).
[13] J. B. K. Law and J. T. L. Thong, Appl. Phys. Lett. **88**, 133114 (2006).
[14] Z. W. Pan, Z. R. Dai, Z. L. Wang, Science **291**, 1947 (2001).
[15] Q. H. Li, T. Gao, Y. G. Wang, and T. H. Wang, Appl. Phys. Lett. **86**, 123117 (2005).
[16] Z. Y. Fan, J. C. Ho, Z. A. Jacobson, R. Yerushalmi, R. L. Alley, H. Razavi, and A. Javey, Appl. Phys. Lett. **8**, 20 (2008).
[17] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981) p. 281.
[18] Z. Y. Fan and J. G. Lu, Appl. Phys. Lett. **86**, 032111 (2005).