Large enhancement in photon detection sensitivity via Schottky-gated CdS nanowire nanosensors

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The Schottky contact based photon detection was demonstrated using CdS (visible light responsive), silicon (indirect n-type oxygen-non-adsorbing), and CuO (indirect p-type oxygen-adsorbing) nanowire nanosensors. With changing one of the two nanowire-electrode contacts from ohmic to Schottky, detection sensitivities as high as 10⁵% were achieved by the CdS nanowire nanosensor operated at the reverse bias mode of −8 V, which was 58 times higher than that of the corresponding ohmic contact device. The reset time was also significantly reduced. In addition, originally light nonresponsive silicon and CuO nanowires became light responsive when fabricated as a Schottky contact device. These improvements in photon detection can be attributed to the Schottky gating effect realized in the present nanosensor system by introducing a Schottky contact. © 2010 American Institute of Physics. [doi:10.1063/1.3285178]

Photon detection, in ultraviolet (UV)^{1,2} or visible light regime, ^{3,4} finds a wide range of applications in environment, space research, and optical communication.⁵ Nanowires (NWs) are the functioning element in nanosized photon detection sensors owing to their large surface-to-volume ratios and demonstrated high sensitivities.^{6,7} For photon detection applications, fast response time, fast reset time, and high sensitivity are desired.⁸ In traditional design of NW nanosensors, maintaining a good ohmic contact state at the two contact ends of the NW is critical for the device performance. The purpose is to minimize the contact resistance and emphasize the effect from the changes in the surface state of the NW. To create a good ohmic contact with NWs of semiconductors like ZnO, SnO, etc., one often dopes Ga into the Pt electrode. For such ohmic contact based devices (OCD), the main mechanism of detection is based on the changes of the intrinsic conductance of the whole NW. Recently, our group demonstrated a design of NW nanosensors in which one end of the NW is purposely made Schottky contact. Such Schottky contact based devices (SCD) exhibited unusually high sensitivities and short response and reset times, attributable to the gating effect of the Schottky barrier modulated by the local adsorption of the analyzed species at the contact, which have shown gigantic enhancements in sensitivity as well as response and reset times in strain sensor, UV, bio, and gas nanosensors. 10-14

In this letter, the concept of SCD is extended to other types of semiconductor NWs, including visible light responsive CdS, indirect p-type oxygen-adsorbing CuO, and indirect n-type oxygen nonadsorbing silicon NWs. Larger enhancements were achieved with white light illumination for CdS NWs, and originally light nonresponsive CuO and silicon NWs turned light responsive. These phenomena can all

be related to the gating effect of the Schottky contact.

The CdS NWs were synthesized by a PVD process, ^{15,16} the silicon NWs by a vapor transport and condensation method, ^{17,18} and the CuO NWs by oxidation of copper substrates. ¹⁹ The fabricated photon detectors were characterized by using light sources of white light (equipped in an optical microscope), green light (laser pointer), and ultraviolet (UV) lamp (Spectroline, Model ENF-280C, 254 and 365 nm). The I-V curves were recorded with a semiconductor characterization system (Keithley Instruments 4200).

The inset of Fig. 1(a) shows the optical microscopy (OM) image of the CdS NW based OCD. The dark potion is the gap between the two Pt electrodes, and the two small

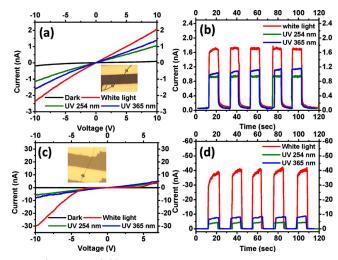


FIG. 1. (Color online) (a) I-V characteristics of CdS NW based OCD under four different light illumination conditions. The inset shows the OM image of the OCD. (b) The response curves of the OCD under illumination of three different light sources. (c) I-V characteristics of CdS NW based SCD under four different light illumination conditions. The inset shows the OM image of the SCD. (d) The response curves of the SCD under illumination of three different light sources.

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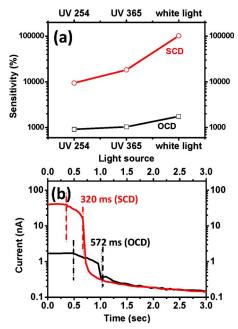


FIG. 2. (Color online) (a) Sensitivity vs illumination light source for CdS NW based OCD and SCD. (b) The reset process of CdS NW based OCD and SCD.

rectangles present in the two Pt electrodes are where Ga is doped. The doping of Ga was carried out by using a focused ion beam (FIB) microscopy and the resulting Pt/Ga formed an ohmic contact with all three kinds of NWs had been investigated. Figure 1(a) shows the I-V curves of the CdS NW based OCD recorded at room temperature and under four different illumination conditions as follows: dark, white light, UV 254 nm, and UV 365 nm. Because of the low conductance of the CdS NW, the resulting current under dark condition was as low as 100 pA.²⁰ The current was increased significantly upon light illumination because of the photon generated photocurrent and desorption of oxygen at the surface. 21 Part of the originally adsorbed, negatively charged oxygen ions combined with the holes generated from the optical absorption and subsequently desorbed, reducing the electron depletion layer thickness to increase the electron flow channel width and thus the conductance. The current response curves recorded under the three different light sources with the device operated at the forward bias mode of 8 V are shown in Fig. 1(b). The current values were near zero when the light was off and jumped to a steady higher value once the light was on. The current dropped off when the light was turned off but in a much slower rate exhibiting an apparent tailing. Evidently, the response was much faster than the reset in the present OCDs, consistent with the phenomenon observed for the ZnO NW based OCD. In addition, the reproducibility of the response pattern is excellent. The sensitivity of the OCD, defined as $(I_{light}-I_{dark})/I_{dark}$ in percentage, under white light, UV 254 nm, and UV 365 nm illumination were found to be 1755, 915, and 1034%, respectively, as determined from Fig. 2(a).

The inset of Fig. 1(c) shows the OM image of the CdS NW based SCD. The lower Pt electrode was deposited Ga to form an ohmic contact with the NW, whereas the NW was let in natural contact with the upper Pt electrode to form a Schottky contact. Platinum is a well-know high work function material and a Schottky contact forms when Pt is in contact with most semiconductor materials unless Pt is

doped to reduce its work function value.²² Figure 1(c) shows the I-V curves of the SCD under the four different light illumination conditions. The currents of the SCD under dark condition were about one order of magnitude lower than those of the OCD at the reverse bias mode due to the Schottky barrier effect (data cannot be read out from the figure). The current response curves recorded under the three different light sources with the device operated at the reverse bias mode of -8 V were shown in Fig. 1(d). The large enhancements in current pick-up upon light illumination for the SCD over the corresponding OCD are evident from the comparison of Figs. 1(b) and 1(d) in the scale of the vertical axis. Also evident to note is the sharp drop of the current at reset, implying much shortened reset times. The sensitivities under white light, UV 254 nm, and 365 nm illumination at the reverse bias mode of -8 V were determined to be 101, 975, 9448, and 18 296%, which were 58, 10, and 17 times higher than those of the corresponding OCDs, respectively. These data were presented in Figs. 2(a). Note that the white light illumination gave the largest enhancement ratio.

Figures 2(b) shows a typical comparison for the reset times of the OCD and SCD under white light illumination. The reset time is defined as the time needed to achieve a 37% deviation from the initial state, from which one can judge the rate of the reset process. Evidently, the reset time of the SCD (320 ms) was significantly shorter than that of the OCD (572 ms) under white light illumination. As for the UV illumination cases, the same trend persists, with 57 versus 343 ms for the UV 254 nm case and 380 versus 640 ms for the UV 365 nm case (data not shown here).

When operated at the reverse bias mode, the electron would flow from the Pt electrode to the CdS NW, overcoming or tunneling through the Schottky barrier, provided a large enough bias voltage is applied. In addition, the oxygen of the air atmosphere adsorbed not only on the surface of the CdS NW but also at the Schottky contact. When the device was illuminated with light of sufficient energy, there were electron-hole pairs generated via the optical absorption and the photon-generated electron-hole pairs were separated by the strong local electrical field existing at the Pt-NW interface. Part of the adsorbed, negatively charged oxygen ions combined with the holes and subsequently desorbed. This process not only reduced the electron depletion layer thickness of the CdS NW to increase the electron flow channel width but also lowered the Schottky barrier height (SBH) and thinned the Schottky barrier width (SBW) to enable easier electron crossing and tunneling. Both effects increased the conductance of the system, with the Schottky gating effect being the dominant one, leading to drastic increase in electron flow. As for the corresponding OCD, the much more capable Schottky gating effect was absent and only the electron flow channel widening showed its effect. The large enhancement in sensitivities was thus observed for the SCD because of the presence of the Schottky contact. Also, when operated at the reverse bias mode, the starting Schottky barrier is higher in SBH and wider in SBW, and thus leaves more room for possible improvement upon light illumina-

To further explore the potential merits of the SCD, we also investigated the SCDs constructed using silicon and CuO NWs as the functioning element. Both silicon and CuO are indirect band gap semiconductors, with silicon being n-type and non-oxygen-adsorbing whereas CuO p-type and

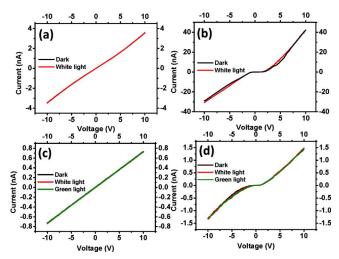


FIG. 3. (Color online) (a) The I-V characteristics of silicon NW based OCD under dark and white light illumination. (b) The I-V characteristics of silicon NW based SCD under dark and white light illumination. (c) The I-V characteristics of CuO NW based OCD under three different illumination conditions. (d) The I-V characteristics of CuO NW based SCD under three different illumination conditions.

oxygen-adsorbing. It is interesting to study how materials characteristics affect the performance of SCD. Figures 3(a) and 3(b) show the I-V curves for the silicon NW based OCD and SCD, respectively, under dark and white light illumination conditions. For the OCD case, both I-V curves exhibited a good ohmic contact behavior and there were no appreciable changes in currents, indicating the idleness of the silicon NW based nanosensors toward light exposure. As to the SCD case, both I-V curves showed Schottky contact characteristics, and slight current changes were obtained at some bias voltage regions upon white light illumination. When the bias voltage was set at -8 V, the current pick-up was about 2 nA, corresponding to a sensitivity of 8%. Note here that silicon is non-oxygen-adsorbing, and thus lacks the electron flow modulation ability both in electron flow channel width and Schottky barrier characteristics (SBH and SBW), through oxygen adsorption-desorption. Consequently, the silicon NW based OCD appeared practically light nonresponsive. The slight sensitivity of the SCD came from the increasing charge carrier density resulted from the strong local electrical field existing at the NW-Pt interface. The originally light nonresponsive silicon based NW nanosensor turned slightly light responsive because of the introduction of the Schottky contact.

For the CuO NW based devices, Figs. 3(c) and 3(d) show the I-V curves for the OCD and SCD, respectively, under the following three illumination conditions: dark, white light, and green light. For the OCD case, all three I-V curves exhibited an excellent ohmic contact behavior and completely overlapped, indicating nonresponsiveness of the device toward light exposure. As to the SCD case, all three I-V curves showed Schottky contact characteristics, and slight current changes were obtained in a bias voltage window centering around -3 V both upon white and green light illumination. When the bias voltage was set at -3 V, the current pick-ups were about 42 and 73 pA, corresponding to sensitivities of 30% and 52%, respectively for white and green light illumination. Here, CuO is a p-type semiconduc-

tor and thus a hole conducting material with holes as the major charge carrier. Although CuO is oxygen-adsorbing, the excess amount of holes already existing in the NW, making the variation in oxygen adsorption amount acquired upon light illumination negligible, leading to the light nonresponsiveness of the CuO NW based OCD. And since the mobility of hole is much smaller than that of electron, the resulting currents are much smaller in values, as can be seen from the scales of the vertical axis of Figs. 3(c) and 3(d). Again, the slight sensitivity of the CuO NW based SCD came from the increasing charge carrier density resulted from the strong local electrical field existing at the NW-Pt interface. The originally light nonresponsive CuO based NW nanosensor turned slightly light responsive because of the introduction of the Schottky contact.

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¹C. 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).

²H. Kind, H. Yan, B. Messer, M. Law, and P. Yang, Adv. Mater. **14**, 158 (2002).

³Q. H. Li, T. Gao, Y. G. Wang, and T. H. Wang, Appl. Phys. Lett. **86**, 123117 (2005).

⁴R. Yang, Y. L. Chueh, J. R. Morber, R. Snyder, L. J. Chou, and Z. L. Wang, Nano Lett. **7**, 269 (2007).

⁵E. Monroy, F. Omnes, and F. Calle, Semicond. Sci. Technol. **18**, R33 (2003).

⁶C. 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).

⁷M. S. Arnold, P. Avouris, Z. W. Pan, and Z. L. Wang, J. Phys. Chem. B 107, 659 (2003).

⁸L. Luo, Y. F. Zhang, S. S. Mao, and L. W. Lin, Sens. Actuators, A 127, 201 (2006).

⁹J. H. He, Y. H. Lin, M. E. McConney, V. V. Tsukruk, Z. L. Wang, and G. Bao, J. Appl. Phys. **102**, 084303 (2007).

¹⁰J. Zhou, Y. Gu, Y. Hu, W. Mai, P. H. Yeh, G. Bao, A. K. Sood, D. L. Polla, and Z. L. Wang, Appl. Phys. Lett. **94**, 191103 (2009).

¹¹P. H. Yeh, Z. Li, and Z. L. Wang, Adv. Mater. **21**, 4975 (2009).

¹²T. Y. Wei, P. H. Yeh, S. Y. Lu, and Z. L. Wang, J. Am. Chem. Soc. **131**, 17690 (2009).

¹³X. D. Wang, J. Zhou, J. Song, J. Liu, N. Xu, and Z. L. Wang, Nano Lett. 6, 2768 (2006).

¹⁴J. Zhou, Y. Gu, P. Fei, W. Mai, Y. Gao, R. Yang, G. Bao, and Z. L. Wang, Nano Lett. 8, 3035 (2008).

¹⁵Y. F. Lin, J. Song, Y. Ding, S. Y. Lu, and Z. L. Wang, Appl. Phys. Lett. **92**,

022105 (2008).

16Y. F. Lin, J. Song, Y. Ding, S. Y. Lu, and Z. L. Wang, Adv. Mater. 20,

3127 (2008). ¹⁷C. T. Huang, C. L. Hsin, K. W. Huang, C. Y. Lee, P. H. Yeh, U. S. Chen,

and L. J. Chen, Appl. Phys. Lett. **91**, 093133 (2007). ¹⁸W. F. Lee, C. Y. Lee, M. L. Ho, C. T. Huang, C. H. Lai, H. Y. Hsieh, P. T.

W. F. Lee, C. Y. Lee, M. L. Ho, C. T. Huang, C. H. Lai, H. Y. Hsieh, P. T. Chou, and L. J. Chen, Appl. Phys. Lett. **94**, 263117 (2009).

¹⁹B. J. Hansen, G. Lu and J. Chen, J. Nanomater. **2008**, 830474 (2008).

²⁰Y. Gu, E. S. Kwak, J. L. Lensch, J. E. Allen, T. W. Odom, and L. J. Lauhon, Appl. Phys. Lett. 87, 043111 (2005).

²¹A. Many, J. Shappir, and U. Shaked, Surf. Sci. **14**, 156 (1969).

²²S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).