# Schottky-Gated Probe-Free ZnO Nanowire Biosensor

By *Ping-Hung Yeh, Zhou Li,* and *Zhong Lin Wang**

One-dimensional nanostructures have been demonstrated as outstanding materials for fabricating ultrasensitive nanosensors because of their large surface-to-volume ratio. Using a nanowire (NW)[1–6] or nanotube (NT)[7–14] as a fundamental unit and bonding its two ends on a solid substrate will form a field-effect transistor (FET), which is the most typical configuration for gas, chemical, and biochemical sensors. The contacts at the two ends are mostly chosen to be ohmic in order to enhance the surface effect of the NW/NT on the measured change in conductance. The mechanisms for these nanosensors with ohmic contacts have been suggested to arise from various sources. First, surface-adsorbed charged molecules may change the NW conductance by modification of the surface charge and states.[1–5] Second, biomolecules may lead to a change in device conductance by disturbing the gate potential, which is referred to as the electrostatic gating effect.[6–9] Third, the local workfunction and thus the band alignment are changed when biomolecules are adsorbed onto the surface, which is denoted as the interfacial contact effect.[7,9–12] Fourth, a change in gate coupling is possible due to the low permittivity ε of biomolecules in comparison to that of the electrolyte.[7,13] Finally, biomolecules can slightly reduce the carrier mobility of NTs.[7,14] Moreover, these nanodevices usually use a bioprobe to recognize the molecules that are to be detected, such as antibody to antigen and virus, enzyme to substrate.[15,16]

In the work reported in this Communication, we deliberately introduced a nonsymmetrical Schottky contact at one end of a ZnO NW nanodevice and studied its response to biomolecules. The results show its much-enhanced sensitivity in comparison to ZnO NWs with ohmic contacts. The operation of the nanosensor is largely determined by the behavior at the Schottky junction and it can clearly differentiate between positively and negatively charged molecules; this is a major difference from nanosensors' characteristics as reported in the literature. The electrical response comes from the variation of the Schottky barrier height (SBH) and barrier width as a result of biomolecule adsorption at the Schottky contact. Such a nanosensor is probe-free, and there is no need to introduce antibody–antigen interaction to enhance its sensitivity. This introduces a new methodology in the design of nanosensors.

[*] Prof. Z. L. Wang, Dr. P.-H. Yeh, Z. Li
School of Materials Science and Engineering
Georgia Institute of Technology
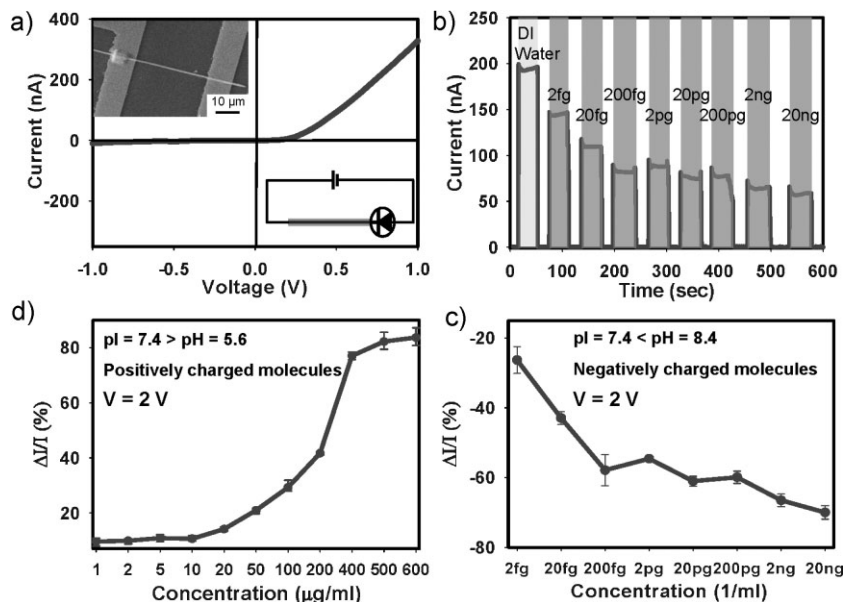Atlanta, GA 30332 (USA)
E-mail: zlwang@gatech.edu
Z. Li
Department of Advanced Materials and Nanotechnology
College of Engineering
Peking University
100084 Beijing (P. R. China)

Our nanosensors were fabricated using ZnO NWs grown by a vapor–solid process.[17] For comparison purposes, we fabricated an ohmic contact device (OCD) and a Schottky-gated device (SGD) using the same type of NWs. For the OCD, a single-crystal ZnO NW was placed on a Pt electrode pattern, and then Pt-Ga was deposited on both ends of the NW to form ohmic contacts using a focused ion beam (FIB) system. The length of the NW was sufficiently long to minimize the effect from FIB contamination. The mechanism of the OCD is to detect molecules by measuring the variation of the conductance. A sketch and a typical ohmically contacted *I–V* curve of the OCD are given in Figure 1a. The response of the OCD is shown in Figure 1b. We used hemoglobin as our sensing molecules; the pH was adjusted to control the electrical properties of the molecules. When the positively or negatively charged molecules were introduced at a concentration
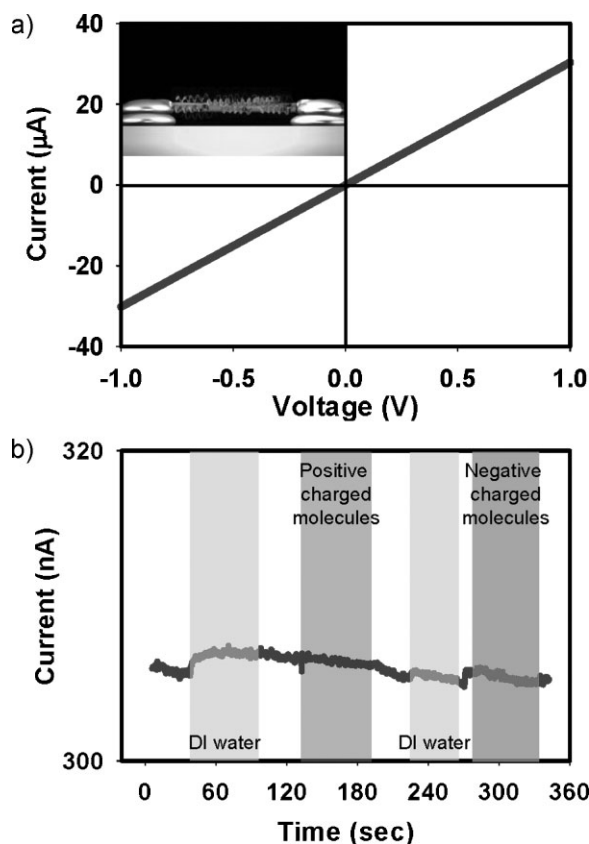
Figure 1. The OCD was fabricated using a single-crystal ZnO NW that shows little response to the biomolecules. a) Pt-Ga was deposited by FIB on both ends of the NW to form ohmic contacts (inset), as proven by its corresponding *I–V* curve. b) When either positively charged molecules or negatively charged molecules are introduced, the electrical signal of the device shows little change.

© 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
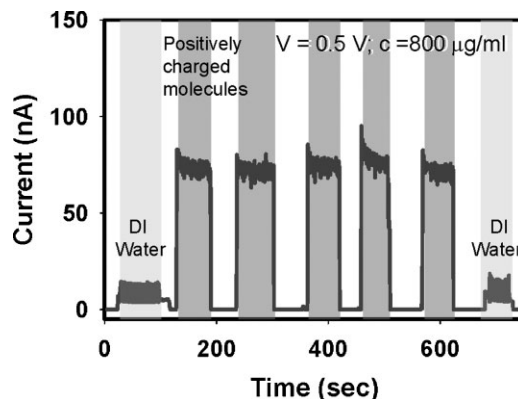
WILEY
InterScience®
DISCOVER SOMETHING GREAT

of 800 µg mL^{-1}, the electrical signals of the device showed little change. This was possibly because the conductance of the ZnO NW was rather high, so that the introduction of surface-adsorbed molecules did not change the conductance to any appreciable degree.

In order to enhance the sensitivity of the sensor, we deliberately introduced the nonsymmetrical Schottky contact in the device fabrication. For the SGD, a ZnO NW was placed on a Pt electrode pattern, the natural contacts of which are mainly Schottky type. By using a FIB to deposit Pt-Ga at a localized region at one end, a local ohmic contact is achieved. A scanning electron microscopy (SEM) image of a Schottky-gated biosensor device is shown in the upper-left inset of Figure 2a. A home-built microfluidic cell was placed over the SGD to control the liquid environment. A typical Schottky-contacted I–V curve of the SGD is shown in Figure 2a and the effective circuit diagram in the lower-right inset. This SGD uses the molecules to alter the Schottky barrier height (SBH); the device was operated under reverse bias to enhance the sensitivity. This is because only a few molecules are needed to change the SBH. The fast reaction and distinct current variations can be seen in Figure 2b. Because the molecules were dispersed in deionized (DI) water in different concentrations, the devices were also immersed in DI water, under which the baseline of the device was calibrated.

The electrical response of a SGD was characterized for a series of concentrations of charged molecules. The response of the DI water was taken as the reference line for measuring the conductance. For hemoglobin with an isoelectric point (pI) of 7.4, the molecules are negatively charged at pH 8.4 (pI < pH), and

Figure 3. Repeated detection of positively charged molecules at a concentration of $c = 800$ µg mL^{-1} under an applied reverse bias of 0.5 V.

the corresponding measurement result is shown in Figure 2b. The negatively charged molecules resulted in a decrease in conductance, as shown in Figure 2c; the detection range is from 2 fg mL^{-1} to 20 ng mL^{-1}. In contrast, when the molecules are positively charged (pH 5.6, pI > pH), an increase in conductance resulted, as presented in Figure 2d, although the trend is nonlinear due to the Schottky contact. The lower detection limit is 10–20 µg mL^{-1}, and the upper detection limit is ca. 500 µg mL^{-1}. Both measurements are under a reverse bias of 2 V.

It is apparent that, as for the ZnO NW-based sensors, the response of the SGD is much larger than that of the OCD. The results of the SGD were reproduced many times. Figure 3 shows repeated detection of the positively charged molecules at a fixed concentration of $c = 800$ µg mL^{-1} under an applied reverse bias of 0.5 V. The positively charged molecules increase the conductance with reference to DI water. The repeatedly congruent results show the stability of the sensor. A response factor of around 800% has been achieved.

When the molecules were negatively charged, the electric signal at a reverse bias of 0.5 V was too small to be detected. Therefore, we increased the bias to 2 V; repeated detection by the sensor is shown in Figure 4. Again the current is reduced for the negatively charged molecules and the consistent measurements show the stability of the device.

The response of the SGD to charged molecules can be explained from its band diagram in the area of the metal–NW contact (Fig. 5a). Once negatively charged molecules begin to adsorb at the junction region, the local Schottky barrier height (ϕ_{SB}) and width increase (by Δ') owing to the local build up of negative molecules (Fig. 5b). In such a case, the conductance of the device drops as more negatively charged molecules are adsorbed at the junction region, and thus the magnitude of the transported current drops with reference

Figure 2. A SGD uses the charged molecules to alter the SBH; the device is operated under reverse bias to enhance its sensitivity. a) By depositing Pt-Ga by FIB in a localized region, a local ohmic contact is achieved at one end. A SEM image of a Schottky-gated biosensor device is shown in the upper-left inset. The I–V curve shows a typical Schottky characteristic. b) A fast response and distinct current variations can be seen when the sensor is exposed to a series of concentrations of negatively charged molecules (pI 7.4 < pH 8.4). c) The negatively charged molecules result in a decrease in conductance. d) When the molecules are positively charged (pI 7.4 > pH 5.6), the conductance of the device increases.
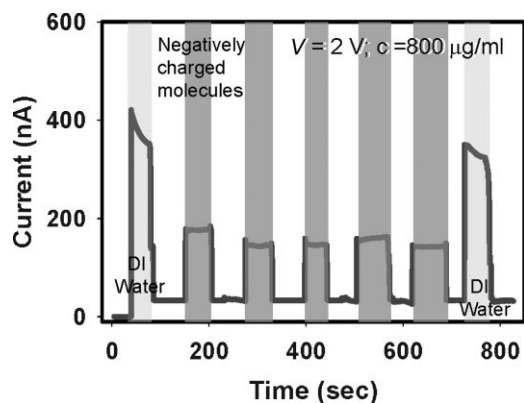
COMMUNICATION

Figure 4. Repeated detection of negatively charged molecules at a concentration of $c = 800\,\mu g\,mL^{-1}$ under an applied reverse bias of 2 V.

to the DI water case, consistent with the data shown in Figure 2b. On the other hand, when positively charged molecules are introduced into the solution, the positively charged molecules lower the SBH (by Δ) at the contact region. Although that may increase the barrier width (Fig. 5c), it is the height of the barrier that matters for charge transport at room temperature. The
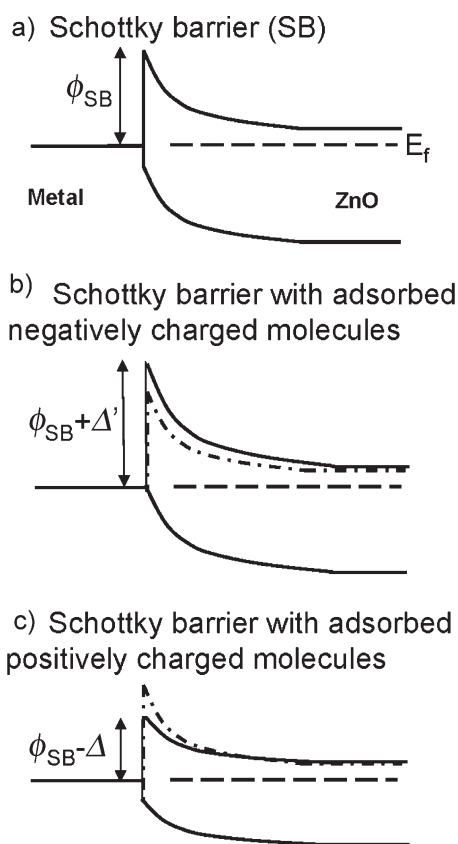
Figure 5. A possible explanation of the response of the Schottky-gated device to the charged molecules. The dash-dotted line represents the Schottky barrier at the contact when the device is immersed in DI water. The solid line represents the Schottky barrier when the charged molecules are present at the junction.

conductance of the junction increases dramatically, resulting in an increase in the transported current, as shown experimentally in Figure 2d and 3.

It is necessary to point out that the stability of ZnO NWs in biofluid is a concern. The device is only good for a few hours in such a solution,[18,19] and the biosolution tends to dissolve the ZnO NWs. Approaches are being developed to improve the stability of the NWs, but the principle demonstrated here is rather general.

In summary, we have demonstrated probe-free and highly sensitive NW-based nanosensors for detecting biologically and chemically charged molecules. The core of the device relies on the nonsymmetrical Schottky contact under reverse bias. The SGD has several merits in comparison to the conventional ohmically contacted devices. First, it does not need a bioprobe to detect molecules; rather, it depends on the attraction of the charged molecules to the junction region. Thus, the device has the potential of proactively detecting charged molecules. Second, for the same type of NWs, for example ZnO, the sensitivity of the SGD is much higher than that of the OCD because a few molecules at the junction region can change the "gate" that effectively tunes the conductance. Third, owing to the nature of the charge and potential profile at the junction region, the SGD is likely to have some selectivity in detecting positively charged molecules versus negatively charged molecules. A low detection limit of $2\,fg\,mL^{-1}$ has been demonstrated. The approach demonstrated here can serve as a guideline for designing more practical chemical and biochemical sensors.

Experimental

The ZnO NWs were grown using a vapor–solid process. ZnO powder was used as the source material and loaded in an alumina boat located at the center of an alumina tube (75 cm), which was placed in a single-zone horizontal tube furnace. Argon gas was used as carrier gas at a flow rate of 50 standard cubic centimeters per minute (sccm) throughout the experiment. An alumina substrate with length of 10 cm was loaded 20 cm downstream from the source material. The furnace was heated to 1475 °C and held at that temperature for 4.5 h under a pressure of ca. 250 mbar. Then the furnace was turned off, and the tube was cooled down to room temperature under an argon flow.

An ohmic contact device (OCD) and a Schottky-gated device (SGD) were fabricated using the same type of NWs. For the OCD, a single-crystal ZnO NW was placed on a Pt electrode pattern, and then Pt-Ga was deposited on both sides of the NW to form ohmic contacts using a FIB system (FEI Nova Nanolab 200 FIB/SEM). The length of the NW was sufficiently long to minimize the effect from FIB contamination. For the SGD, a ZnO NW was placed on a Pt electrode pattern, the natural contacts of which are mainly Schottky type. By depositing Pt-Ga using the FIB at a localized region at one end, a local ohmic contact is achieved. Electrical-signal measurements were carried out using a semiconductor characterization system (Keithley Instruments 4200). A home-built microfluidic cell was placed over all biosensor devices to control the liquid environment.

Acknowledgements

COMMUNICATION

[1] Y. Cui, Q. Wei, H. Park, C. M. Lieber, *Science* **2001**, *293*, 1289.

[2] C. M. Lieber, *MRS Bull.* **2003**, *28*, 486.

[3] G. F. Zheng, F. Patolsky, Y. Cui, W. U. Wang, C. M. Lieber, *Nat. Biotechnol.* **2005**, *23*, 1294.

[4] F. Patolsky, C. M. Lieber, *Mater. Today* **2005**, *8*, 20.

[5] M. Curreli, C. Li, Y. Sun, B. Lei, M. A. Gundersen, M. E. Thompson, C. Zhou, *J. Am. Chem. Soc.* **2005**, *127*, 6922.

[6] J. H. He, Y. Y. Zhang, J. Liu, D. Moore, G. Bao, Z. L. Wang, *J. Phys. Chem. C* **2007**, *111*, 12152.

[7] I. Heller, A. M. Janssens, J. Männik, E. D. Minot, S. G. Lemay, C. Dekker, *Nano Lett.* **2008**, *8*, 591.

[8] A. B. Artyukhin, M. Stadermann, R. W. Friddle, P. Stroeve, O. Bakajin, A. Noy, *Nano Lett.* **2006**, *6*, 2080.

[9] E. L. Gui, L. J. Li, K. Zhang, Y. Xu, X. Dong, X. Ho, P. S. Lee, J. Kasim, Z. X. Shen, J. A. Rogers, S. G. Mhaisalkar, *J. Am. Chem. Soc.* **2007**, *129*, 14427.

[10] R. J. Chen, H. C. Choi, S. Bangsaruntip, E. Yenilmez, X. Tang, Q. Wang, Y. L. Chang, H. Dai, *J. Am. Chem. Soc.* **2004**, *126*, 1563.

[11] H. R. Byon, H. C. Choi, *J. Am. Chem. Soc.* **2006**, *128*, 2188.

[12] X. Tang, S. Bansaruntip, N. Nakayama, E. Yenilmez, Y. L. Chang, Q. Wang, *Nano Lett.* **2006**, *6*, 1632.

[13] K. Besteman, J. O. Lee, F. G. M. Wiertz, H. A. Heering, C. Dekker, *Nano Lett.* **2003**, *3*, 727.

[14] A. Maroto, K. Balasubramanian, M. Burghard, K. Kern, *ChemPhysChem* **2007**, *8*, 220.

[15] Z. W. Pan, Z. R. Dai, Z. L. Wang, *Science* **2001**, *291*, 1947.

[16] K. Maehashi, T. Katsura, K. Kerman, Y. Takamura, K. Matsumoto, E. Tamiya, *Anal. Chem.* **2007**, *79*, 782.

[17] F. Patolsky, G. F. Zheng, O. Hayden, M. Lakadamyali, X. Wei, Zhuang, C. M. Lieber, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 14017.

[18] J. Zhou, N. S. Xu, Z. L. Wang, *Adv. Mater.* **2006**, *18*, 2432.

[19] Z. Li, R. S. Yang, M. Yu, F. Bai, C. Li, Z. L. Wang, *J. Phys. Chem. C* **2009**, *112*, 20114.