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High-Sensitivity Humidity Sensor Based on a Single SnO_2 Nanowire

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Nanowires (NWs) and nanobelts (NBs) are considered as ideal building blocks for constructing nanosized devices due to high surface to volume ratio and their special physical and chemical properties resulting from the reduced sizes. Until now, many semiconductor NWs/NBs have been successfully applied in nanodevices, including nanolasers,[1] nanogenerators,[2] and various chemical and biological nanosensors.[3,4] Well-known humidity control is very important for many fields in technology and our daily life. In the past years, many detection techniques have been explored from old wet and dry bulb thermometry to modern capacitive, resistive, and thermal conductive moisture detectors. In order to further promote the sensitivity, selectivity, chemical and thermal stability, intensive efforts have been put in the exploration of a humidity sensor based on nanostructured materials such as carbon nanotubes,[5] metal oxide nanoparticles,[6] and NW films.[7]

Being an important n-type semiconductor with a wide band gap (E_g = 3.6 eV at 300 K), SnO_2 possesses many unique optical and electrical properties: remarkable receptivity variation in gaseous environment, high optical transparency in the visible range (up to 97%), low resistivity (10^{-4} to 10^6 $\Omega\cdot cm^{-1}$), and excellent chemical stability. These properties make SnO_2 NWs/NBs well suited for chemical sensors and transparent conducting electrodes. To date, many nanodevices based on SnO_2 NWs/NBs have been fabricated, including field effect transistors (FET),[8] field emissions,[9] UV sensors,[10] and gas sensors.[3a,11] In this communication, we present a new type of SnO_2 nanodevice, a humidity detector using a single SnO_2 NW as the sensing unit. This new type of SnO_2 NW-based sensor has fast and sensitive response to relative humidity (RH) in air from a wide range of environments at room temperature (30 °C). In addition, it has relatively good reproducibility, and its linear response to RH makes it to calibrate.

Single-crystalline SnO_2 NWs to be used as humidity sensors were synthesized by chemical vapor deposition (CVD) using Au nanoparticles as catalysts in a homemade synthetic apparatus.[12] Experimental details are available in Supporting Information. Figure 1a is a typical SEM image of as-synthesized NWs with high yield. The XRD pattern indicates that the NWs are rutile structured SnO_2 with a good crystallinity (Figure S1). The diameter of SnO_2 NWs ranges from 50 to 300 nm, and the length of SnO_2 NWs is up to tens of micrometers. Low-magnification TEM image (upper inset of Figure 1a) and corresponding EDS analysis (Figure S2) show that a Au nanoparticle exists at the tip of the SnO_2 NW, which is the representative characteristic of the vapor−liquid−solid (VLS) growth mechanism.[13] The selective area electron diffraction (SAED, lower inset of Figure 1a) pattern taken from the body of the SnO_2 NW reveals that the as-synthesized SnO_2 NW is single crystalline and grows along the [001] direction.

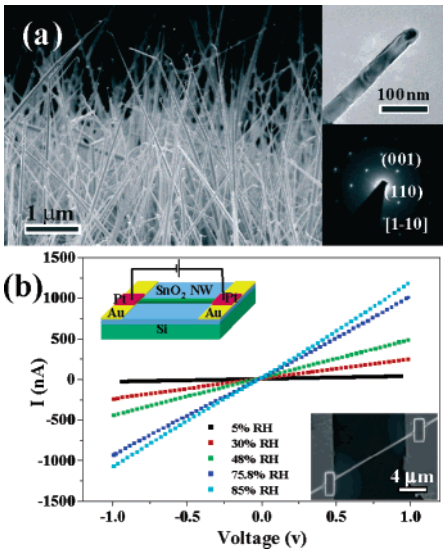

Figure 1. (a) Typical SEM image of SnO_2 NWs. Insets are corresponding TEM image (upper) and SAED pattern (lower) of a single SnO_2 NW. (b) $I-V$ curves of a single SnO_2 NW in different static RH atmosphere from dry air (5%) to 85% RH air at 30 °C. Insets are schematic illustration (upper) and corresponding SEM image (lower) of a SnO_2 NW-based nanodevice.

Cathodoluminescence (CL) analysis is a suitable technique to determine the crystalline quality and the presence of defect structure in nanocrystals. Room-temperature CL spectrum (Figure S3) of SnO_2 NWs indicates that there is a broad blue luminescent peak centered at around 470 nm (2.64 eV), but near band edge (NBE) emission (expected around 320 nm) was not detected. According to previous studies,[14] the luminescence in the range of 400−600 nm of SnO_2 is attributed to several possible luminescence centers, such as oxygen vacancies, defects in the surface, and/or impurities in the NWs. As for blue emission around 470 nm, the electron transition mediated by oxygen vacancies in the band gap is responsible, too.[14c]

The SnO_2 NW-based humidity sensor is based on a FET nanodevice. A single SnO_2 NW of 250 nm in diameter was placed between two Au electrodes of 100 nm thickness and deposited with Pt by focused ion beam (FIB) microscopy as the top electrode to improve contact (see inset of Figure 1b). In order to measure the current signals through the SnO_2 NW, two Au electrodes are connected with a support chip by a Au wire binding technique. Figure 1b shows the $I-V$ curves of the SnO_2 NW-based sensing element in different static air of 5−85% RH at 30 °C. In any RH atmospheres, $I-V$ curves of the device exhibit good linear behavior, which proves a good ohmic contact between the SnO_2 NW and Au electrodes. At the same time, it is clearly seen that the resistance of the SnO_2 NW decreases promptly with the increase of RH in air. The resistance of the SnO_2 NW in dry air (5%) is calculated to be about 2.80×10^7 Ω, which is 14 times that (2.00×10^6 Ω) in

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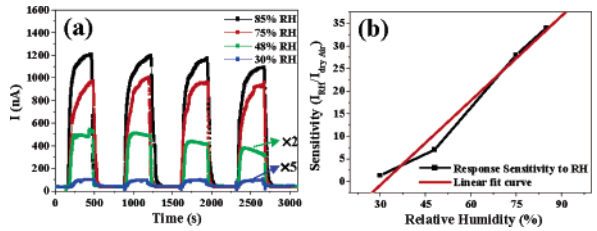

Figure 2. (a) Current response of a SnO_2 NW-based sensor to dynamic switches between dry air (5%) and different RH (30−85%) at 30 °C. (b) Linear dependence relation between current response sensitivity and relative humidity. Bias voltage of 1 V is applied during the test.

48% RH air and about 32 times that (8.59×10^5 Ω) in 85% RH air (see Table S1 in Supporting Information). Obviously, water vapor in air has a strong influence on the conductivity of SnO_2 NWs.

Further dynamic testing procedures were carried out, which provided more information on three of the most important parameters for a sensing device: sensitivity, response and recovery time, and reproducibility. Figure 2a shows a series of current response of the SnO_2 NW-based sensor to dynamic switches between dry air (5%) and different RH (30−85%) at 30 °C. When the sensor was exposed to the moist air of 85% RH in reference to dry air, the current through the SnO_2 NW promptly increased and then gradually reached a relatively stable value. When the sensor was switched to dry air again, the current abruptly decreased and rapidly reached a relatively stable value. The response time and recovery time (defined as the time required to reach 90% of the final equilibrium value) were 120−170 and 20−60 s, respectively. We note that the response sensitivity ($R_{RH}/R_{dry\ air}$, i.e., I_{RH}/I_{air} under constant voltage) of the SnO_2 NW-based humidity sensor presents a good linearity with RH in air, using response sensitivity as a function of RH in air (Figure 2b). At this point, our SnO_2 NW-based humidity sensor surpasses previous humidity sensors based on carbon nanotubes.[5] At the same time, the SnO_2 NW-based humidity sensor has relatively good reproducibility, although its response sensitivity decreases about 10% after four cycles of humidity switch between dry air and given RH air. Furthermore, when the sensor was kept in the moisture for about 1 h, the current still recovered to the original value (see Figure S4). This result indicates that the interaction between water vapor and the surface of the NW should be dominated by physisorption, while chemisorption plays a minor role.

The static and dynamic testing results presented above indicate that water vapor in air has a strong influence on the conductivity of SnO_2 NWs, and such conductivity change resulting from the fluctuation of RH in air is always reversible. In fact, the effect of water vapor in air on the conductivity of SnO_2 chemical sensors has been attracting significant attention because water vapor in air sometimes disturbs the response of a sensor to the detected gas.[15] A few mechanisms have been proposed for explaining the surface conductivity change in the presence of water vapor.[16,17] In general, water molecules can be adsorbed by physisorption or hydrogen bonding. At higher temperature (100−500 °C), water molecules can react with the Lewis acid site (Sn) and Lewis base site (O) on the SnO_2 surface and form ($Sn^+_{Sn}-OH^-$) and then release electrons (e^-).[16] As a result, the depletion layer becomes thin and promotes the surface conductivity of the SnO_2 NW. In our nanodevice, however, the working temperature of the SnO_2 NW-based humidity sensor is at room temperature so that dissociative adsorption should hardly take place. Therefore, a more reasonable explanation for the increase of the conductivity of the SnO_2 NW in moisture is that the pre-adsorbed oxygen on the surface of the SnO_2 NW has been displaced by competitive water physisorption.[17]

In summary, we have synthesized high-yield SnO_2 NWs via a Au catalytic VLS growth process. CL characterization results demonstrate that the as-synthesized SnO_2 NWs possess a large number of oxygen vacancies in the crystals. Hence, the surface of the SnO_2 NW is very sensitive to oxygen and water vapor in air. As inspired by this, we fabricated a new type of SnO_2 humidity sensor based on a single NW. Both static and dynamic testing proved that the SnO_2 NW-based humidity sensor has a fast response and high sensitivity to RH changes in air, and at the same time, its response sensitivity is linear with RH in air. Considering excellent chemical stability of SnO_2, this new type of SnO_2 NW-based humidity sensor is expected to have promising applications in various complicated moisture, including acid and alkali moist gas for fast detecting of humidity.

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Supporting Information Available: Experimental details, XRD pattern, EDS spectra and CL analysis of SnO_2 NWs, and the resistance of SnO_2 NW in different RH air. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Huang, M. H.; Mao, S.; Feick, H.; Yan, H. Q.; Wu, Y. Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. D. *Science* **2001**, *292*, 1897.
(2) Wang, Z. L.; Song, J. H. *Science* **2006**, *312*, 242.
(3) (a) Kolmakov, A.; Zhang, Y. X.; Cheng, G. S.; Moskovits, M. *Adv. Mater.* **2003**, *15*, 997. (b) Chen, Y.; Wang, X. H.; Erramilli, S.; Mohanty, P.; Kalinowski, A. *Appl. Phys. Lett.* **2006**, *89*, 223512.
(4) (a) Cui, Y.; Wei, Q. Q.; Park, H. K.; Lieber, C. M. *Science* **2001**, *293*, 1289. (b) Zheng, G. F.; Patolsky, F.; Cui, Y.; Wang, W. U.; Lieber, C. M. *Nat. Biotechnol.* **2005**, *23*, 1294.
(5) (a) Huang, X. J.; Sun, Y. F.; Wang, L. C.; Meng, F. L.; Liu, J. H. *Nanotechnology* **2004**, *15*, 1284. (b) Yeow, J. T. W.; She, J. P. M. *Nanotechnology* **2006**, *17*, 5441.
(6) Ahmad, M. M.; Makhlouf, Salah, A.; Khalil, K. M. S. *J. Appl. Phys.* **2006**, *100*, 094323.
(7) (a) Zhang, Y. S.; Yu, K.; Jiang, D. S.; Zhu, Z. Q.; Geng, H. R.; Luo, L. Q. *Appl. Surf. Sci.* **2005**, *242*, 212. (b) Wu, R. J.; Sun, Y. L.; Lin, C. C.; Chen, H. W.; Chavali, M. *Sens. Actuators, B* **2006**, *115*, 198. (c) Wang, G.; Wang, Q.; Lu, W.; Li, J. H. *J. Phys. Chem. B* **2006**, *110*, 22029.
(8) Cheng, Y.; Xiong, P.; Fields, L.; Zheng, J. P.; Yang, R. S.; Wang, Z. L. *Appl. Phys. Lett.* **2006**, *89*, 093114.
(9) Chen, Y. J.; Li, Q. H.; Liang, Y. X.; Wang, T. H.; Zhao, Q.; Yu, D. P. *Appl. Phys. Lett.* **2004**, *85*, 5682.
(10) Liu, Z. Q.; Zhang, D. H.; Han, S.; Li, C.; Tang, T.; Jin, W.; Liu, X. L.; Lei, B.; Zhou, C. W. *Adv. Mater.* **2003**, *15*, 1754.
(11) (a) Comini, E.; Faglia, G.; Sberveglieri, G.; Pan, Z. W.; Wang, Z. L. *Appl. Phys. Lett.* **2002**, *81*, 1869. (b) Wan, Q.; Wang, T. H. *Chem. Commun.* **2005**, *30*, 3841. (c) Chen, Y. J.; Nie, J.; Xue, X. Y.; Wang, Y. G.; Wang, T. H. *Appl. Phys. Lett.* **2006**, *88*, 083105.
(12) Kuang, Q.; Jiang, Z. Y.; Xie, Z. X.; Lin, S. C.; Lin, Z. W.; Xie, S. Y.; Huang, R. B.; Zheng, L. S. *J. Am. Chem. Soc.* **2005**, *127*, 11777.
(13) Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964**, *4*, 89.
(14) (a) Calestani, D.; Zha, M.; Zappettini, A.; Lazzarini, L.; Salviati, G.; Zanotti, L.; Sbervegieri, G. *Mater. Sci. Eng.* **2005**, *25*, 625. (b) Luo, S. H.; Chu, P. K.; Liu, W. L.; Zhang, M.; Lin, C. L. *Appl. Phys. Lett.* **2006**, *88*, 183112. (c) Her, Y. C.; Wu, J. Y.; Lin, Y. R.; Tsai, S. Y. *Appl. Phys. Lett.* **2006**, *89*, 043115.
(15) (a) Barsan, N.; Weimar, U. *J. Electroceram.* **2001**, *7*, 143. (b) Hahn, S. H.; Barsan, N.; Weimar, U.; Ejakov, S. G.; Visser, J. H.; Soltis, R. E. *Thin Solid Fims* **2003**, *436*, 17. (c) Pang, P. F.; Guo, Z. D.; Cai, Q. Y. *Talanta* **2005**, *65*, 1343.
(16) Heiland, G.; Kohl, D. *Chemical Sensor Technology*;Seiyama, T., Ed.; Kodansha: Tokyo, 1988; Vol. 1, Chapter 2, pp 15−38.
(17) Henrich, V. A.; Cox, P. A. *The Surface Science of Metal Oxides*; University Press: Cambridge, 1994; p 312.

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