

In₂O₃ nanowires as chemical sensors

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We present an approach to use individual In₂O₃ nanowire transistors as chemical sensors working at room temperature. Upon exposure to a small amount of NO₂ or NH₃, the nanowire transistors showed a decrease in conductance up to six or five orders of magnitude and also substantial shifts in the threshold gate voltage. These devices exhibited significantly improved chemical sensing performance compared to existing solid-state sensors in many aspects, such as the sensitivity, the selectivity, the response time, and the lowest detectable concentrations. Furthermore, the recovery time of our devices can be shortened to just 30 s by illuminating the devices with UV light in vacuum. © 2003 American Institute of Physics. [DOI: 10.1063/1.1559438]

Semiconducting metal oxides as chemical sensing materials have been extensively studied for a long time due to their advantageous features, such as good sensitivity to the ambient conditions and simplicity in fabrication.^{1–3} Among them, In₂O₃ has been found to have a pronounced sensitivity to such gases as O₃, Cl₂, NO₂, NH₃, CO, H₂, and other species.^{4–7} Nevertheless, there are some critical limitations difficult to overcome for thin-film-based sensing devices. First of all, such devices have a limited maximum sensitivity due to the limited surface-to-volume ratios for thin films.⁴ Secondly, most of the In₂O₃ thin film devices are operated at high temperatures (200–600 °C) in order to achieve enhanced chemical reactivity between the sensor materials and the surrounding gases, which brings significant inconvenience for practical applications. In contrast to thin-film-based devices, devices based on one-dimensional nanostructures have great potential to overcome these fundamental limitations due to their ultrahigh surface-to-volume ratios.^{8–11}

Here, we report our studies on using In₂O₃ nanowire transistors to work as chemical sensors for NO₂ and NH₃ at room temperature. Our devices exhibited far superior performance compared to previously reported results. For instance, our devices exhibited sensitivities (defined as the resistance after exposure divided by the resistance before exposure) of 10⁶ for NO₂ and 10⁵ for NH₃, which are four or five orders of magnitude better than results obtained with thin-film-based sensors.⁵ Response times (defined as time duration for resistance change by one order of magnitude) as short as 5 s for 100-ppm NO₂ and 10 s for 1% NH₃ have also been achieved. Furthermore, careful characterization has revealed the lowest detectable gas concentrations to be 0.5 ppm for NO₂ and 0.02% for NH₃ using our In₂O₃ nanowire transistors. In addition, we found that UV illumination of our devices can dramatically enhance the surface molecular desorption kinetics and thus lead to substantially reduced recovery time.

Single-crystalline In₂O₃ nanowires were synthesized by a laser ablation method, details of which can be found in our

previous publication.¹² This method produced In₂O₃ nanowires with diameters ~ 10 nm and lengths ~ 5 μ m. Devices with a single In₂O₃ nanowire between the source and drain electrodes were fabricated using the silicon substrate as a back gate. These as-fabricated In₂O₃ nanowire devices exhibited typical *n*-type transistor characteristics¹³ and were used in our nanowire chemical sensing measurements. The devices were mounted in a small chamber with electrical feed-through. The system was usually pumped to vacuum first to clean the surface of the nanowires, and then the conductance of the nanowires was monitored while flowing diluted NO₂ (0.5 to 100 ppm) or NH₃ (0.02% to 1%) in Ar or dry air.

Figure 1(a) inset shows a scanning electron microscope

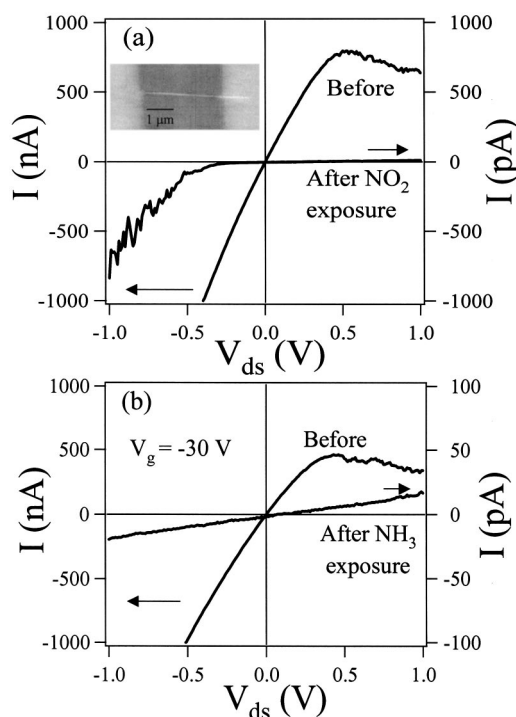


FIG. 1. (a) I - V curves measured before and after exposure to 100-ppm NO₂. Inset: SEM image of a metal / In₂O₃-nanowire / metal device used for this study. The diameter of the In₂O₃ nanowire is 10 nm and the length between two Ti/Au electrodes is 3 μ m. (b) I - V curves measured before and after exposure to 1% NH₃ with $V_g = -30$ V. The arrows inside indicate different scales used for the curves.

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(SEM) image of the In_2O_3 nanowire device used in the following measurements, where a single nanowire bridging the source and drain electrodes can be clearly seen. Figure 1(a) shows I - V curves recorded before and after exposing the nanowire device to 100-ppm NO_2 in Ar for 5 min with 0 V applied to the gate electrode. Different scales (left axis for the curve before the exposure and right axis for the curve after the exposure) were used to elucidate the change in the current magnitude. The I - V curve recorded before the exposure is typical of our In_2O_3 nanowire field-effect transistors (FETs), with a well-defined linear regime and a saturation regime under the positive bias. The asymmetry in the I - V curve is due to the local gating effect, similar to the pinch-off effect of conventional silicon-based FETs. A slight decrease in current was observed for $V_{\text{ds}} > 0.5$ V, leading to an intriguing negative differential resistance. This feature is tentatively attributed to a mobility degradation under high V_{ds} , as a high V_{ds} leads to the pinch-off effect, in which the carrier distribution takes a triangular shape in the nanowire, with a high percentage of carriers drifting along the sidewall of the nanowire.¹⁴ This leads to a lower average mobility for higher V_{ds} as electrons close to the sidewall experience more scattering with the surface. The zero-bias resistance for this device was 580 k Ω . After the exposure, the device showed a reduction in conductance around six orders of magnitude for $V_{\text{ds}} = 0.3$ V, as manifested by the data shown in Fig. 1(a). We have also found that within the NO_2 concentrations (0.5 to 100 ppm) we tested, the conductance of the nanowire transistor always decreased after the exposure and eventually saturated at a level similar to the curve shown in Fig. 1(a), although longer response time was observed for lower concentrations. After each exposure, the system was pumped to vacuum, followed by UV illumination to desorb the NO_2 molecules. The device fully recovered to its initial status immediately after the UV was turned on. Careful analysis of the response of the device under UV illumination reveals a recovery time less than 30 s. The underlying physics is that UV exposure generates electron and hole pairs in the nanowire, and the adsorbed NO_2 molecules undergo the transition from NO_2^- to NO_2 by taking one hole and leaving the nanowire surface. This recovery mechanism works for all sorts of adsorbed species, such as NO_2 , NH_3 , O_2 and moisture, and we have used it throughout this study to bring the device to its initial state after every exposure.

Figure 1(b) shows two curves recorded before and after the NH_3 exposure with the gate bias maintained at -30 V, and a reduction in conductance for five orders of magnitude for $V_{\text{ds}} = -0.3$ V was obtained. Our sensitivity values (10^6 for NO_2 and 10^5 for NH_3) are significantly higher than previously reported for NO_2 and NH_3 sensing.^{5,8,11} The enhanced sensitivity with our devices is primarily attributed to the enhanced surface-to-volume ratio due to the small diameter (10 nm) of our nanowires. An additional reason is related to the nature of the In_2O_3 nanowire surface, which can readily react with ambient species, as compared to the inert sidewall of carbon nanotubes.⁸

The sensing properties of our devices can also be studied by monitoring the current dependence on the gate bias, rendering a significant advantage over thin-film-based devices.⁵ Figure 2(a) shows two I - V_g curves recorded before and after

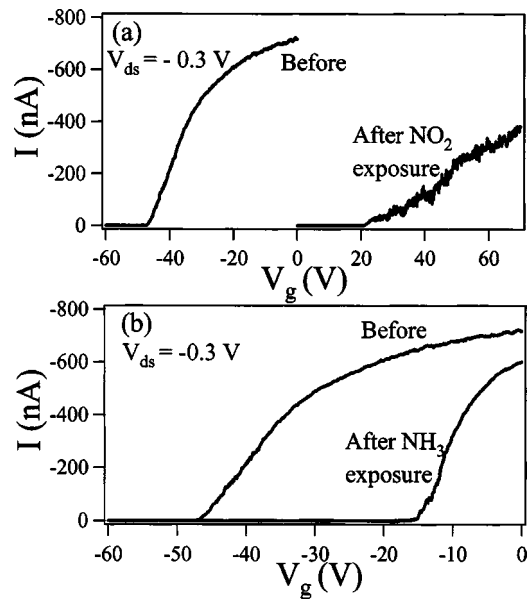


FIG. 2. (a) I - V_g curves before and after exposure to 100-ppm NO_2 with $V_{\text{ds}} = -0.3$ V. (b) I - V_g curves before and after exposure to 1% NH_3 with $V_{\text{ds}} = -0.3$ V.

exposure to 100 ppm NO_2 in argon with a constant $V_{\text{ds}} = -0.3$ V. Both curves confirm In_2O_3 nanowires are n -type doped semiconductors, as manifested by the reduced conductance under negatively increasing gate bias; however, a striking feature in Fig. 2(a) is a pronounced shift in the threshold voltage from -48 V before the exposure to 20 V after the exposure. The response to NO_2 can be understood by considering the interaction between NO_2 and the n -type doped In_2O_3 nanowires. Adsorption of oxidizing gases (such as NO_2) reduces the number of free electrons in the material and thus reduces the conductivity. The change of carrier concentration after the NO_2 exposure can be estimated to be $C\Delta V_{g,t}/eL \sim 1.72 \times 10^8 \text{ cm}^{-1}$, where $\Delta V_{g,t}$ is the shift of the threshold voltage, C is the capacitance of nanowire, estimated to be 1.21×10^{-16} F, and L is the nanowire length ($\sim 3 \mu\text{m}$).¹⁵ This indicates adsorption of about 17 NO_2 molecules per nanometer, if we assume each adsorbed molecule takes one electron away from the nanowire. Our results further point out the possibility of single-molecule detection by using In_2O_3 devices with ultrashort channel length (\sim a few nanometers).

Figure 2(b) shows two I - V_g curves before and after exposing the device to diluted NH_3 in Ar with $V_{\text{ds}} = -0.3$ V. A significant shift in the threshold voltage from -48 V to -16 V was observed, with maximum sensitivity 10^5 around $V_g = -30$ V. Our results are qualitatively different from previously published results based on In_2O_3 thin films operating at elevated temperatures (450°C),⁵ where an enhancement of the conduction was observed. Since UV illumination was used in our study before the NH_3 exposure to desorb the attached molecules on the In_2O_3 nanowire surface, our results suggest that NH_3 might adsorb as electron-withdrawing species on clean n -type doped In_2O_3 nanowires. More experimental work, as well as theoretical investigations, is necessary for a better understanding. An important consequence of the gate-dependent measurements is that selectivity between different gas species can be achieved by comparing

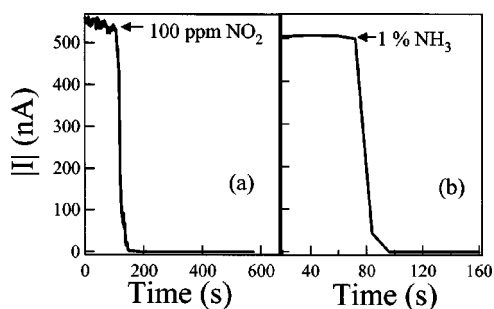


FIG. 3. Sensor electrical response to (a) 100-ppm NO_2 and (b) 1% NH_3 .

the shift of the threshold voltage. Our measurements have shown that NO_2 of various concentrations consistently shifted the threshold voltage to around 20 V, whereas NH_3 of various concentrations consistently shifted the threshold voltage to about -16 V. This can be understood since the final threshold voltage is directly related to the electron transfer between the nanowire and the adsorbed molecules, and thus can be used to pinpoint one chemical among similar species.

Besides the sensitivity, two other important parameters for chemical sensors are the response time and the minimum detectable concentrations for toxic species. The In_2O_3 nanowire sensors also showed advantages in these aspects. Figure 3(a) shows the response of the In_2O_3 nanowire device to 100-ppm NO_2 in Ar with $V_g = 0$ V and $V_{ds} = 0.3$ V. The current was observed to decrease sharply to almost zero within 50 s. Detailed analysis reveals a response time (defined as the time for the conductance to change by one order of magnitude) less than 5 s. This is significantly better than the response time of 50 s for thin-film-based semiconducting oxide sensors operating at elevated temperatures upon exposure to 100-ppm NO_2 .¹ Similar measurements were carried out to determine the response time to NH_3 , where we applied a gate voltage of -30 V with a constant source-drain bias of -0.3 V. The conductance of the In_2O_3 nanowire was observed to decrease by five orders of magnitude after exposure to 1% NH_3 within 30 s, as shown in Fig. 3(b). The response time corresponding to a tenfold decrease was determined to be less than 10 s. For comparison, the response times to 1% NH_3 for single-walled semiconducting carbon nanotubes is about 1–2 min, and the sensitivity is only 10–100.⁸ We have also carried out work to determine the lowest detectable concentrations for NO_2 and NH_3 . For NO_2 , concentrations of 20, 2, and 0.5 ppm led to response times of ~ 20 s, ~ 5 min, and ~ 10 –12 min, respectively, as shown in Fig. 4(a). The lowest concentration for NH_3 we have tested was 0.02%, where the limitation was imposed by the availability of highly diluted NH_3 in air or argon. Figure 4(b) shows a response time about 2 min for 0.02% NH_3 .

We have also used dry air instead of Ar in our sensing experiments, and similar results were observed. For instance, after flowing 100-ppm NO_2 mixed in air, the conductance of our nanowire transistor decreased by one order of magnitude within 30 s and the threshold gate voltage shifted by 50 V. Overall the oxygen molecules in the compressed air showed rather minor influence and the effects of NO_2 and NH_3 can be clearly distinguished.

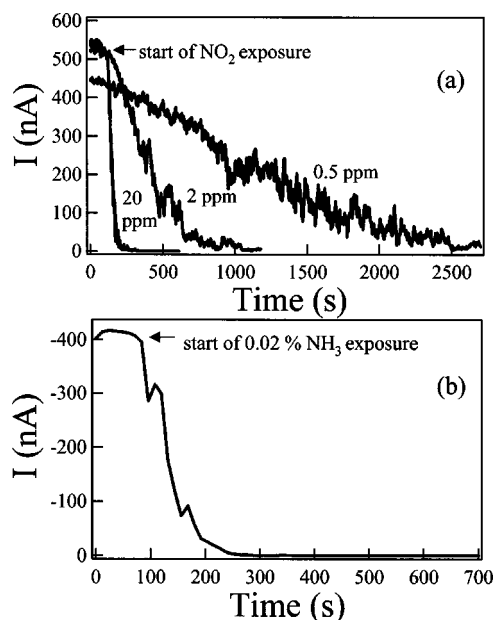


FIG. 4. Response of the In_2O_3 nanowire sensor to (a) various NO_2 concentrations and (b) 0.02% NH_3 .

In conclusion, In_2O_3 nanowires have been demonstrated to work as chemical sensors at room temperature. Our devices showed sensitivities as high as 10^6 for diluted NO_2 and 10^5 for diluted NH_3 . Substantial shifts in the threshold voltage were also observed and can be used to distinguish different gas species. The response times have been determined to be 5 s for 100-ppm NO_2 and 10 s for 1% NH_3 , and the lowest detectable concentrations are 0.5 ppm for NO_2 and 0.02% for NH_3 . Our work clearly demonstrates the advantages of nanowire chemical sensors and may lead to single-molecule detection in the near future.

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- ¹ Y. Shimizu and M. Egashira, *MRS Bull.* **24**, 18 (1999).
- ² D. E. Williams, *Sens. Actuators B* **57**, 1 (1999).
- ³ S. Strassler and A. Reis, *Sens. Actuators* **4**, 465 (1983).
- ⁴ W. Y. Chung, G. Sakai, K. Shimanoe, N. Miura, D. D. Lee, and N. Yamazoe, *Sens. Actuators B* **46**, 139 (1998).
- ⁵ M. Liess, *Thin Solid Films* **40**, 183 (2002).
- ⁶ J. Tamaki, C. Naruo, Y. Yamanoto, and M. Matsuoka, *Sens. Actuators B* **83**, 190 (2002).
- ⁷ G. Kiriakidis, M. Bender, N. Kataarakis, E. Gagaoudakis, E. Hourdakakis, E. Douloufakis, and V. Cimalla, *Phys. Status Solidi A* **185**, 27 (2001).
- ⁸ J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. Dai, *Science* **287**, 622 (2000).
- ⁹ J. Kong, M. G. Chapline, and H. Dai, *Adv. Mater.* **13**, 1384 (2001).
- ¹⁰ M. Law, H. Kind, B. Messer, F. Kim, and P. Yang, *Angew. Chem. Int. Ed. Engl.* **41**, 2405 (2002).
- ¹¹ E. Comini, G. Faglia, G. Sberveglieri, Z. Pan, and Z. Wang, *Appl. Phys. Lett.* **81**, 1869 (2002).
- ¹² C. Li, D. Zhang, S. Han, X. Liu, T. Tang, and C. Zhou, *Adv. Mater.* **15**, 143 (2003).
- ¹³ D. Zhang, C. Li, S. Han, X. Liu, T. Tang, W. Jin, and C. Zhou, *Appl. Phys. Lett.* **82**, 112 (2003).
- ¹⁴ S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).
- ¹⁵ C. Zhou, J. Kong, E. Yenilmez, and H. Dai, *Science* **290**, 1552 (2000).