Chemical gating of In_2O_3 nanowires by organic and biomolecules

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In_2O_3 nanowire transistors were used to investigate the chemical gating effect of organic molecules and biomolecules with amino or nitro groups. The nanowire conductance changed dramatically after adsorption of these molecules. Specifically, amino groups in organic molecules such as butylamine, donated electrons to In_2O_3 nanowires and thus led to enhanced carrier concentrations and conductance, whereas molecules with nitro groups such as butyl nitrite made In_2O_3 nanowires less conductive by withdrawing electrons. In addition, intrananowire junctions created by partial exposure of the nanowire device to butyl nitrite were investigated, and pronounced rectifying current–voltage characteristics were obtained. Furthermore, chemical gating by low-density lipoprotein cholesterol, the offending agent in coronary heart diseases, was also observed and attributed to the amino groups carried by the bio species. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1625421]

Over the past decade, the synthesis of various nanomaterials has attracted immense attention due to their potential to serve as building blocks for emerging nanoscale devices.[1–3] Among them, the electronic and sensing properties of nanowires and nanotubes have been widely studied because of their nanoscale dimensions and enormous surface-to-volume ratios.[4–9] For example, carbon nanotubes have been utilized to work as sensors for toxic gases[6] and small molecules.[7] Field-effect transistors (FETs) based on individual In_2O_3 nanowires have also been shown to offer superior performance as toxic gas sensors for NO_2 and NH_3, based on charge transfer between the toxic species and the nanowires.[9] These devices were further observed to exhibit doping-dependent NH_3 sensing characteristics, as reduced conduction was observed for heavily doped nanowires[9,10] and enhanced conduction was observed for lightly doped nanowires.[10] Inspired by the afore-mentioned results, we have explored using our In_2O_3 nanowires to investigate the chemical gating effect of small organic molecules with amine or nitro groups. The electron-donating capability of amine groups and electron-withdrawing capability of nitro groups were found to induce dramatic changes in the nanowire conductance as well as significant shifts in the gate threshold voltages, as a result of the carrier concentration variation. In addition, adsorption of the nitro compound on partial lengths of the nanowires led to modulated chemical gating and intrananowire junctions exhibiting prominent rectifying behavior. Furthermore, biosensors for species like low-density lipoprotein (LDL) cholesterol, which is the major carrier of cholesterol in blood and the offending agent in coronary heart disease,[11] have also been constructed based on the In_2O_3 nanowires.

Single-crystalline In_2O_3 nanowires with diameters around 10 nm were used in this study[12,13] and a schematic diagram is shown in Fig. 1(a). Figure 1(b) inset shows a scanning electron micrograph (SEM) of an In_2O_3 nanowire bridging the source/drain electrodes with a channel length of $\sim 3\,\mu$m. To avoid complications similar to the doping-dependent NH_3 sensing experiment,[10] only lightly doped In_2O_3 nanowires were used for the chemical and biomolecule gating experiments described later. Several compounds were used for chemical gating measurements, including tert-

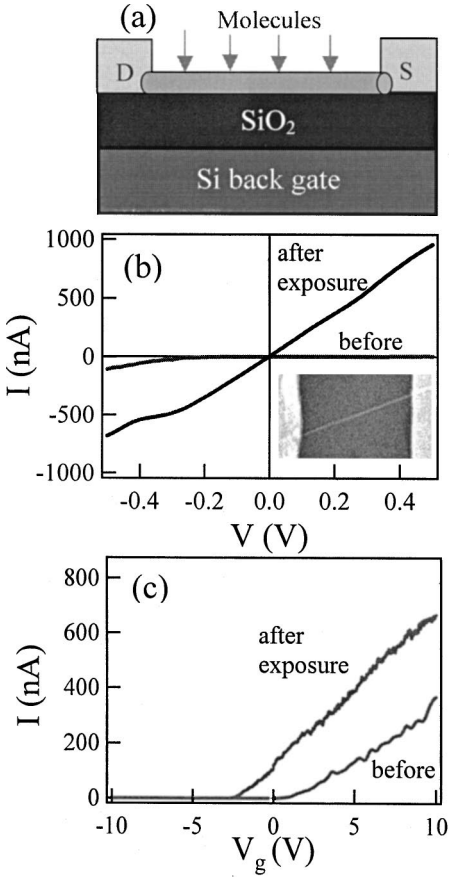

FIG. 1. (a) Scheme for molecular absorption on an In_2O_3 nanowire device. The thickness of the SiO_2 layer is 100 nm. (b) $I-V$ curves of an In_2O_3 device before and after exposure to butylamine. Inset: SEM image of the device. (c) $I-V_g$ curves recorded before and after molecular absorption with the drain–source bias $V=0.1$ V.

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butylamine [$CH_3(CH_2)_3NH_2$, 99.5% from Aldrich], 3′–(aminoprol) triethoxysilane [APTES, $NH_2(CH_2)_3Si(OEt)_3$, 99% from Aldrich] and butyl nitrite [$CH_3(CH_2)_3NO_2$, 99% from Aldrich]. The adsorption of the organic molecules was carried out by placing fully characterized In_2O_3 nanowire transistors facing the interior of a container with the organic compound for typically 5 min. The nanowires remained above the liquid organics and were exposed only to the molecular vapor. After the exposure, the device was dried with a stream of nitrogen. Electronic properties of the devices were characterized in ambient atmosphere and at room temperature both before and after the exposure.

Figure 1(b) shows two $I-V$ curves with the gate bias $V_g=0$ of an In_2O_3 nanowire transistor before and after exposure to butylamine. Before the chemical exposure, the device showed very little conduction with a zero-bias resistance of 250 MΩ. After exposure to butylamine, the device exhibited significantly enhanced conduction with a zero-bias resistance of 17 MΩ. In addition to the conductance variation, the sensing properties of our devices can also be studied by monitoring the current dependence on the gate bias. Figure 1(c) shows two $I-V_g$ curves recorded before and after exposure to butylamine with a constant drain–source bias $V=0.1$ V. Both curves confirm In_2O_3 nanowires are n-type-doped semiconductors, however, a -3 V shift in the threshold voltage (from 0.5 to -2.5 V) was observed after the exposure. This indicates an increase of electron concentration in the nanowire, which can be estimated to be 1.1×10^7 cm^{-1} following $C\Delta V_T/eL$, where C is the nanowire capacitance, ΔV_T is the shift in threshold voltage, e the electron charge, and L the channel length.[13] This increase in electron concentration and conductance is attributed to the chemical gating effect of the amino groups in butylamine, consistent with our previous observation that lightly doped nanowires exhibited enhanced conduction upon NH_3 exposure.[10] Similar results (not shown) were obtained with other In_2O_3 devices exposed to APTES, where a dramatic increase in conductance and a negative shift in the gate threshold voltage were consistently observed. This further confirms the electron-donating effect of the amino groups.

In sharp contrast to butylamine and APTES, our In_2O_3 nanowire devices exhibited a totally different behavior when exposed to butyl nitrite. Figure 2(a) shows two $I-V$ curves recorded before and after the butyl nitrite adsorption at a fixed gate bias $V_g=0$ V. This device was relatively conductive before the exposure; however, after the exposure, the device showed a reduction in conductance around five orders of magnitude for $V=0.3$ V. Furthermore, we also observed a significant positive shift in the gate threshold voltage from -0.6 V before the exposure [shown in Fig. 2(b) inset] to $\sim5-10$ V after the exposure [shown in Fig. 2(b)], indicating a decrease in the electron concentration. This can be understood as nitro groups are highly oxidative and are thus expected to withdraw electrons from our nanowires, subsequently leading to reduced conduction for our n-type In_2O_3 nanowire. Similar behavior was observed when In_2O_3 nanowire transistors were exposed to NO_2 gas.[9]

Armed with our understanding about the chemical gating effects, we have further created intrananowire junctions by

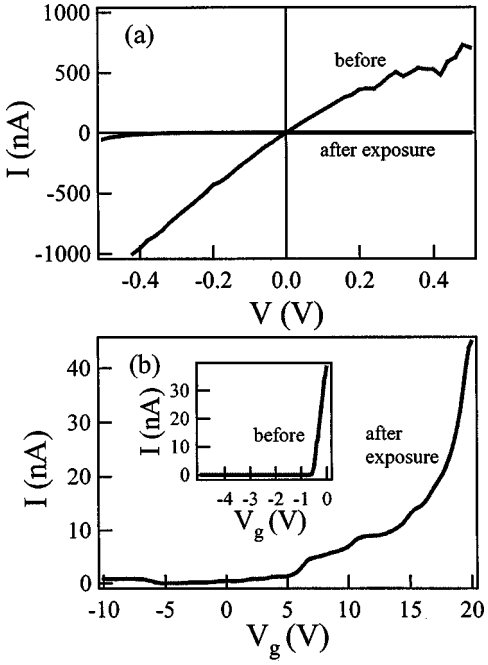

FIG. 2. (a) $I-V$ curves of an In_2O_3 device before and after exposure to butyl nitrite. (b) $I-V_g$ curve of the device after exposure. Inset: $I-V_g$ curve of the device before exposure. Here, $V=50$ mV.

exposing part of an In_2O_3 nanowire device to butyl nitrite. This was achieved by using photolithography to cover up the right half of a nanowire device with a thick layer of photoresist, while the left half remained exposed, as shown in the Fig. 3(b) inset. Electronic measurements were performed both before and after the molecule adsorption. To eliminate the asymmetry caused by the local gating effect, a ''symmetric'' bias scheme was used for data shown in Fig. 3, with $V/2$ applied to the drain and $-V/2$ applied to the source, thus giving a total bias of V. Fig. 3(a) shows a family of $I-V$ curves recorded with the device before the butyl nitrite ad-

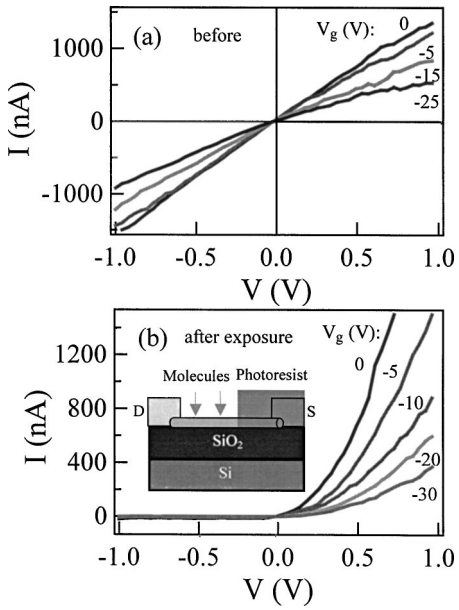

FIG. 3. (a) $I-V$ curves of the device before molecule absorption. Rather symmetrical $I-V$ curves were observed. (b) $I-V$ curves recorded after exposure to butyl nitrite molecules. Pronounced rectifying curves were observed with all gate biases. Inset: Scheme for molecular absorption on a device partially covered by photoresist.

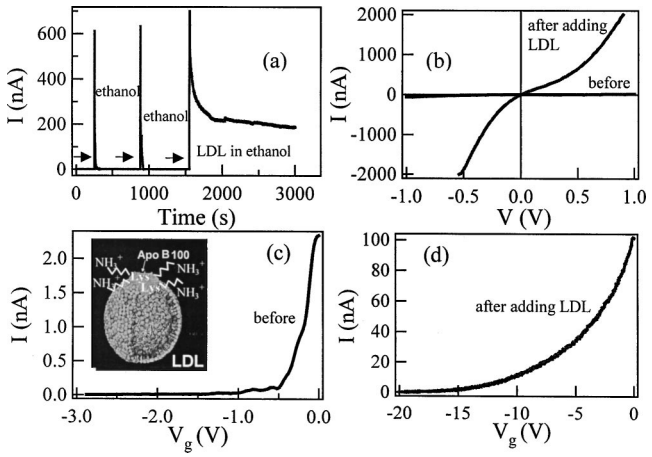

FIG. 4. (a) Time domain measurement for a device after exposure to pure ethanol twice and then LDL in ethanol. (b) $I-V$ curves of the device before and after exposure to LDL in ethanol. (c) and (d) $I-V_g$ characteristics of the device before and after the exposure, respectively. Here, $V=50$ mV. (c) inset: Schematic of an LDL particle (adapted from Ref. 11).

sorption, with $V_g=0$, -5, -15, and -25 V from the top curve to the bottom. All these curves are rather symmetrical, indicating the drain and the source contacts were about the same. However, the device exhibited a pronounced rectifying behavior after the butyl nitrite adsorption under all gate voltages used, as shown in Fig. 3(b). The rectification ratio, defined as the current at 0.7 V divided by the current at -0.7 V, is as high as 400 for $V_g=0$ V. We attributed this rectifying diode behavior to intrananowire junctions created by the partial adsorption of butyl nitrite molecules, as the nitro groups withdrew electrons from the nanowire, thus leading to a shift of Fermi level away from conduction band for the left half of the nanowire. This effectively rendered an intrananowire $n^{-}-n$ junction. By applying a forward bias, the potential barrier for electron flow was lowered, leading to a relatively large forward-bias current. On the other hand, reverse biases increased the barrier height and only the reverse-bias saturation current was allowed to go through, much like what happens for conventional $p-n$ junctions.

Based on the electron transfer process just discussed, In_2O_3 nanowires may also lend themselves to work as biosensors for bio species containing amino or nitro groups. We have chosen to work with LDL cholesterol, which is the major carrier of cholesterol in blood and the offending agent in coronary heart disease.[11] As shown in the Fig. 4(c) inset, an average LDL particle contains a hydrophobic core and a protein called apolipoprotein B-100 (apoB-100), which has positively charge amino groups (NH_3^+) at the outer surface.[11] Our sensing experiments started with making a suspension of 0.2 mg LDL powder (purchased from Sigma) in 2 ml 200% ethanol. Electronic measurements were performed before and after applying one drop of the LDL suspension onto our nanowire transistors, all under ambient conditions. As a control experiment, a drop of pure ethanol was first applied to our device with the current monitored over time under $V=0.1$ V and $V_g=0$ V, and the results are shown in Fig. 4(a). The current increased immediately after the ethanol drop was introduced, and then returned to the original state once the ethanol drop evaporated away within 1 min. This control experiment was performed one more time, and similar results were obtained [shown in Fig. 4(a)]. This was followed by applying one drop of the LDL suspension to the device. The current increased immediately; however, instead of returning to the original state, the device stabilized in a highly conductive state after a slight drop in current related to the ethanol evaporation. This enhanced conductance is also evident in Fig. 4(b), where the $I-V$ curve recorded after the LDL exposure shows a zero-bias resistance of 0.7 MΩ, as compared to a resistance of 118 MΩ before the exposure. Figures 4(c) and 4(d) depict the $I-V_g$ curves recorded before and after the LDL exposure, where a negative shift in the gate threshold voltage can be clearly seen, corresponding to an increase in the electron concentration. Two factors may account for the increased electron concentration in the nanowires. The first is that the amino groups carried by the ApoB-100 protein in LDL particles may function as reductive species and hence donate electrons to the nanowires. The second concomitant factor is due to positive charges carried by the amino groups, which can function as a positive gate bias to our nanowires, thus leading to the enhanced carrier concentration.

In conclusion, chemical gating effects of both organic molecules and bio species have been studied with In_2O_3 nanowire transistors. The amino groups in both butylamine and APTES were found to donate electrons to the n-type In_2O_3 nanowires and resulted in enhanced carrier concentrations and also conductance, whereas the nitro groups in butyl nitrite withdrew electrons from the nanowires, and led to reduced carrier concentration and conduction. Intrananowire junctions have been constructed by exposing part of a nanowire to butyl nitrite, leading to $n^{-}-n$ junctions and pronounced rectifying diode behavior with rectification ratios ~ 400. In_2O_3 nanowires were further demonstrated to work as LDL sensors via interaction with the amino groups carried by LDL particles. Our work clearly demonstrates the potential of using In_2O_3 nanowires as both chemical and biosensors.

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[1] X. Duan, Y. Huang, R. Agarwal, and C. M. Lieber, Nature (London) **421**, 241 (2003).
[2] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. Dai, Science **287**, 622 (2000).
[3] A. P. Alivisatos, Science **271**, 933 (1996).
[4] Y. Cui, Q. Wei, H. Park, and C. M. Lieber, Science **293**, 1289 (2001).
[5] M. Law, H. Kind, B. Messer, F. Kim, and P. Yang, Angew. Chem., Int. Ed. Engl. **41**, 2405 (2002).
[6] P. Qi, O. Vermesh, M. Grecu, A. Javey, Q. Wang, H. Dai, S. Peng, and K. J. Cho, Nano Lett. **3**, 347 (2003).
[7] J. Kong and H. Dail, J. Phys. Chem. B **105**, 2890 (2001).
[8] E. Comini, G. Faglia, G. Sberveglieri, Z. Pan, and Z. Wang, Appl. Phys. Lett. **81**, 1869 (2002).
[9] C. Li, D. Zhang, X. Liu, S. Han, T. Tang, J. Han, and C. Zhou, Appl. Phys. Lett. **82**, 1613 (2003).
[10] D. Zhang, C. Li, X. Liu, S. Han, T. Tang, and C. Zhou, Appl. Phys. Lett. **83**, 1845 (2003).
[11] A. Sevanian, L. Asatryan, and O. Ziouzenkova, Blood Purif **17**, 66 (1999).
[12] C. Li, D. Zhang, S. Han, X. Liu, T. Tang, and C. Zhou, Adv. Mater. (Weinheim, Ger.) **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).