Doping dependent NH$_3$ sensing of indium oxide nanowires

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NH$_3$ gas sensing properties of In$_2$O$_3$ nanowires were carefully studied. Change of conductance in opposite directions was observed with different nanowire sensors. We suggest that this differential response is caused by various doping concentrations in the semiconducting In$_2$O$_3$ nanowires. In addition, we have also investigated a gate-screening effect exhibited in our nanowire chemical sensors at high NH$_3$ concentrations. This mechanism in the photoconductive In$_2$O$_3$ nanowires was explained in our previous publication. It is believed that photogenerated holes in In$_2$O$_3$ nanowires can recombine with OH$^-$ groups and oxygen ions (O$_2^-$) adsorbed on the nanowire surface, thus leading to the desorption of such species. Through the above process, electrons originally withdrawn from the nanowire by adsorbed oxygen or OH$^-$ species were released back to the nanowire and the device was brought to the original electron-rich state. We take the conductance of such UV-cleaned In$_2$O$_3$ nanowires as the reference of our sensing measurements. Therefore, the interference of adsorbed O$_2^-$ and OH$^-$ species was effectively excluded from the interaction between the nanowire and NH$_3$ molecules.

The current versus gate bias ($I$–$V_g$) curve obtained with sample 1 in pure Ar flow is shown in Fig. 2(a) (the left curve). We kept the drain-source bias at 50 mV while sweeping the gate voltage from 0 to $-80$ V. Negative gate voltages progressively reduced the current through the nanowire from 620 to 3 nA at $V_g = -80$ V. This typical n-type transistor characteristic of the metal/In$_2$O$_3$ nanowire/metal system has been observed and discussed before. The right curve in Fig. 2(a) was taken after the pure Ar flow was replaced by 1% NH$_3$ in Ar. It is found that the current at $V_g = 0$ V dropped gradually from 620 to 3 nA upon NH$_3$ exposure, accompanied with a shift of the threshold gate voltage ($V_{th}$) from $-80$ to $-46$ V. The change of the carrier concentration was estimated to be $C A V_{th} \approx 9.5 \times 10^7$ cm$^{-2}$, where $C$ is the capacitance between the nanowire and the gate electrode, and $\Delta V_{th}$ is the shift in the threshold gate voltage. Figure 2(b) compares two $I$–$V_g$ curves taken at $V_g = -50$ V before and after NH$_3$ flow, where the con-
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carrier concentration. A further reduction in the nanowire carrier concentration of 1% NH3 : the current at Vg = 0 V rose to ≈160 nA and a higher negative gate bias of −4.2 V was needed to fully deplete the nanowire, as demonstrated by the left curve in Fig. 3(a). Again, in Fig. 3(b), we displayed two I–Vd curves taken before and after NH3 exposure to reveal the conductance difference between the two states.

From the threshold gate voltages for those two devices measured in pure Ar, the carrier concentrations were estimated to be CVg=2.2×1011 cm−2 and 9.8×1010 cm−2 for samples 1 and 2, respectively. This discrepancy in doping was caused by different oxygen partial pressures used during the laser ablation process, as a lower oxygen concentration can lead to more oxygen vacancies and consequently higher doping in the synthesized In2O3 nanowires. Details of this doping-control synthesis process will be published elsewhere. We believe this doping concentration discrepancy lies in the heart of the opposite sensing response we observed, as described below.

Two energy band diagrams were drawn in the inset of Figs. 2(b) and 3(b) for samples 1 and 2, respectively, where Ec, Ev, and EF correspond to the conduction band, the valence band and the Fermi level of the In2O3 nanowires. To simplify our discussion, an energy level (denoted EnH3) is drawn for NH3 to represent the chemical potential of the electrons that can participate in the electron transfer process. Once NH3 molecules adsorb onto the In2O3 nanowire surface, electron transfer from the material with higher chemical potential to the material with lower chemical potential proceeds until the system reaches equilibrium. Our hypothesis is that for sample 1, the heavily doped device, the nanowire Fermi level EF is fairly close to the conduction band and located above EnH3 [Fig. 2(b) inset]. Therefore electrons should migrate from the nanowire to the adsorbed NH3 species and result in a reduction in the nanowire carrier concentration. This effectively leads to the observed suppressed conductance for sample 1. In contrast, a relatively low doping concentration was found for sample 2, suggesting Ef is way below the conduction band, presumably even below Ec. As a result, electrons transfer from the adsorbed NH3 molecules into the In2O3 nanowire and hence enhanced conductance was observed after the exposure. This hypothesis is backed by our calculation on the difference between Ec−EF values for samples 1 and 2, which is estimated to be (Ec−EF)sample1−(Ec−EF)sample2= kT ln (n2/n1)=81.1 meV, where n1 and n2 are the electron concentration for samples 1 and 2, respectively. This value is significant even at room temperature and may very well cause the electron transfer in opposite directions for nanowires with different doping concentrations. Our work should stimulate in-depth theoretical studies that are required to gain a thorough understanding of this intriguing system and to corroborate our hypothesis. Finally we emphasize that similar studies have been carried with five lightly doped (Vib>−10 V) and eight highly doped (Vib<−40 V) In2O3 samples, the doping-dependent NH3 sensing behavior, i.e., suppressed conduction for heavily doped nanowires and enhanced conductance for lightly doped nanowires, has been consistently observed.

In addition to the doping-dependent response to NH3 gas, another interesting behavior exhibited by our In2O3 nanowire sensors was also observed and studied. We found that when the nanowire transistor sensors were exposed to high concentration NH3, their gate effect, namely, the efficiency of gate bias to modify the channel conductance, can be substantially weakened by the adsorbed NH3 species. The thin curve in Fig. 4(a) is a double-sweep I–Vg curve we took with sample 1 in 10% NH3. The drain-source bias was fixed at Vd=50 mV while the gate was swept at a rate of 0.36 V/s. By comparing this I–Vg curve with those two recorded in pure Ar and 1% NH3 [shown in Fig. 2(a)], we can see that the current at zero gate bias dropped to 400 nA, indicating a further reduction in the nanowire conductance when exposed...
to higher concentration NH$_3$. However, the measured gate dependence was not expected: the conductance kept a nearly constant level while the gate voltage was double swept between 0 and $-80$ V, indicating a substantially weakened gate effect.

We attribute this gate screening effect to the adsorbed NH$_3$ species working as charge traps. By assuming the surface concentration is proportional to the partial pressure in the gas phase, the concentration of the surface-adsorbed NH$_3$ species in 10% NH$_3$ is estimated to be $\sim 10$ times greater than that in 1% NH$_3$. This many NH$_3$ molecules residing on the nanowire surface can be charged and discharged by sweeping the gate bias and hence effectively work as charge traps screening the electric field induced by the gate bias, as schematically shown in Fig. 4(b). A similar screening effect induced by adsorbed OH$^-$ groups on carbon nanotube devices has been observed before. Since the charging of the adsorbed NH$_3$ species requires electron transfer from the nanowire, which can be a slow process, it is expected that gating effect can be restored if a fast $V_g$ sweep is used. The hypothesis is proved by the $I$--$V_g$ measurement we performed with a sweeping rate of 16 V/s, which is 44 times faster than that for the thin curve in Fig. 4(a). The current followed a clockwise loop as $V_g$ was swept from 0 V to $-80$ V, as shown in the thick curve in Fig. 4(a). A significant hysteresis was observed, as a fingerprint of slow charge traps. We also exposed sample 2 to 10% NH$_3$, and similar behavior was observed, indicating that this charge trapping effect is insensitive to the doping concentration.

In summary, the NH$_3$ sensing behavior of semiconducting In$_2$O$_3$ nanowires with different doping concentrations was investigated. We conclude that the density of oxygen vacancies along the nanowire sensors can determine the sign, as well as the amplitude, of their response. In addition, it is observed that chemisorbed NH$_3$ molecules can screen the gate electric field by working as charge traps. We believe our work will be very instructive and beneficial for future gas-sensing studies, especially for semiconducting metal oxide gas sensors.

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