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, which is induced by adsorbed NH$_3$ molecules working as charge traps. Both the doping-dependent response and the gate-screening effect will be especially valuable and helpful for understanding the detailed sensing mechanism of semiconducting metal oxide materials. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1604194]

Indium oxide is known to be an n-type semiconductor in its nonstoichiometric form due to oxygen vacancy doping.[1] Its low-dimensional structures, such as In$_2$O$_3$ thin films and nanowires, have been extensively studied as chemical sensing devices for a long time.[2–6] The conductance modulation of In$_2$O$_3$ is usually attributed to electron transfer between the sensing material and the gas molecules to be detected, as oxidizing (reducing) species can serve as electron withdrawing (donating) groups and thus alter the carrier concentration of semiconducting In$_2$O$_3$.[7] NH$_3$, as a typical target chemical, is usually believed to be a reducing agent, as confirmed by the suppressed conductance observed with p-type carbon nanotube chemical sensors,[8] and hence an enhanced conductance upon NH$_3$ exposure is expected for n-type In$_2$O$_3$ sensing systems. This established model successfully interpreted most published experimental data until some discordance was heard recently: suppressed conductance was observed in the NH$_3$ sensing measurements performed with In$_2$O$_3$ nanowires pretreated with ultraviolet (UV) light illumination.[9] It therefore becomes extremely necessary and crucial to gain a better understanding of the detailed interaction between In$_2$O$_3$ nanowires and NH$_3$, and that is where our work started. In this letter, we have investigated the correlation between the NH$_3$ sensing behavior of In$_2$O$_3$ nanowires and their oxygen vacancy doping concentrations. This doping-dependent sensing mechanism was thoroughly studied and can explain the inconsistency in the reported results. In addition, we have also observed and studied a gate-screening effect caused by adsorbed NH$_3$ molecules working as charge traps, which has been rarely examined attentively before.

The schematic structure of In$_2$O$_3$ nanowire sensors is depicted in Fig. 1. A high-resolution transmission electron microscopy (HRTEM) image was also displayed in the figure, which indicates the single-crystalline structure of our In$_2$O$_3$ nanowires. Details of the growth and device fabrication can be found elsewhere.[10] Results presented in this letter were obtained with two sensor devices similar in appearance. The upper-left inset in Fig. 1 shows a scanning electron mi-

croscopy (SEM) image of one of them, where an In$_2$O$_3$ nanowire bridging two Ti/Au electrodes with a separation of 2 μm can be clearly seen. During NH$_3$ sensing measurements, the devices were mounted in a sealed chamber with electrical feedthroughs and gas flow channels.

Before exposing the devices to diluted NH$_3$ gas, we evacuated the chamber using a turbo pump while illuminating the samples with UV light for 10–20 min. The nanowire conductance increased rapidly upon UV illumination and stabilized at a higher level after the UV lamp was turned off (not shown). The mechanism in the photoconductive In$_2$O$_3$ nanowires was explained in our previous publication.[11] 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, and thus lead 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 nA at $V_g = 0$ V 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.[12] 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 505 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 $C\Delta V_{th} \sim 9.5 \times 10^7$ cm^{-1}, where C is the capacitance between the nanowire and the gate electrode, and ΔV_{th} is the shift in the threshold gate voltage.[12] Figure 2(b) compares two I–V_d curves taken at $V_g = -50$ V before and after NH$_3$ flowing, where the con-

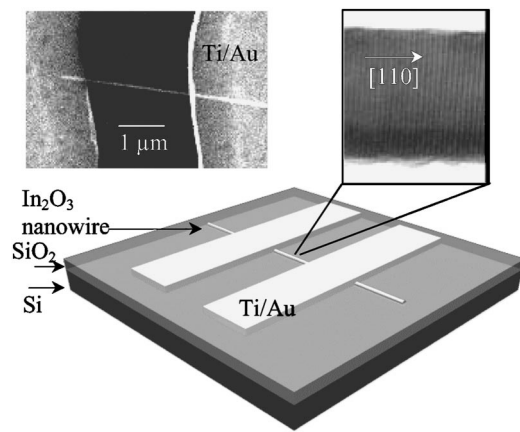[a)]Author to whom correspondence should be addressed; electronic mail: chongwuz@usc.edu

FIG. 1. Schematic diagram of an In_2O_3 nanowire sensor and a HRTEM image of an In_2O_3 nanowire indicating the single-crystalline nature. The upper-left inset shows a SEM image of a nanowire sensor device.

FIG. 2. (a) $I-V_g$ characteristics and (b) $I-V_d$ curves of sample 1 before and after exposure to 1% NH_3. Inset in (b): energy band diagrams of heavily doped In_2O_3 and NH_3 molecules.

ductance drop of the In_2O_3 nanowire is clearly illustrated.

Identical measurements were performed on sample 2 and the data were plotted in Fig. 3(a). This device can be easily depleted with a gate voltage of -3.5 V, as compared to a threshold gate voltage of -80 V for sample 1. What surprised us is the opposite response to NH_3 gas exhibited by those two samples. Instead of a reduction in the conductance, sample 2 showed an increase in conductance with the introduction of 1% NH_3: the current at $V_g=0$ 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 $I-V_d$ curves taken before and after NH_3 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 $CV_{th} \sim 2.2 \times 10^8$ and 9.8×10^6 cm^{-1} 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 In_2O_3 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 E_c, E_v and E_F correspond to the conduction band, the valence band and the Fermi level of the In_2O_3 nanowires. To simplify our discussion, an energy level (denoted E_{NH_3}) is drawn for NH_3 to represent the chemical potential of the electrons that can participate in the electron transfer process. Once NH_3 molecules adsorb onto the In_2O_3 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 E_F is fairly close to the conduction band and located above E_{NH_3} [Fig. 2(b) inset]. Therefore electrons should migrate from the nanowire to the adsorbed NH_3 species and result in a reduction in the nanowire carrier concentration. This effectively leads to the observed suppressed
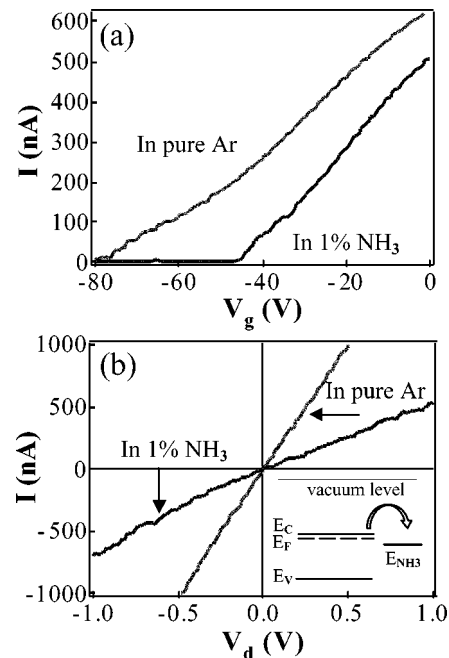
conductance for sample 1. In contrast, a relatively low doping concentration was found for sample 2, suggesting E_F is way below the conduction band, presumably even below E_{NH_3}. As a result, electrons transfer from the adsorbed NH_3 molecules into the In_2O_3 nanowire and hence enhanced conduction was observed after the exposure. This hypothesis is backed by our calculation on the difference between $E_c - E_F$ values for samples 1 and 2, which is estimated to be $(E_c - E_F)_{sample1} - (E_c - E_F)_{sample2} = kT \ln(n_2/n_1) = 81.1$ meV, where n_1 and n_2 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 ($V_{th} > -10$ V) and eight highly doped ($V_{th} < -40$ V) In_2O_3 samples, the doping-dependent NH_3 sensing behavior, i.e., suppressed conduction for heavily doped nanowires and enhanced conduction for lightly doped nanowires, has been consistently observed.

In addition to the doping-dependent response to NH_3 gas, another interesting behavior exhibited by our In_2O_3 nanowire sensors was also observed and studied. We found that when the nanowire transistor sensors were exposed to high concentration NH_3, their gate effect, namely, the efficiency of gate bias to modify the channel conductance, can be substantially weakened by the adsorbed NH_3 species. The thin curve in Fig. 4(a) is a double-sweep $I-V_g$ curve we took with sample 1 in 10% NH_3. The drain-source bias was fixed at $V_d=50$ mV while the gate was swept at a rate of 0.36 V/s. By comparing this $I-V_g$ curve with those two recorded in pure Ar and 1% NH_3 [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
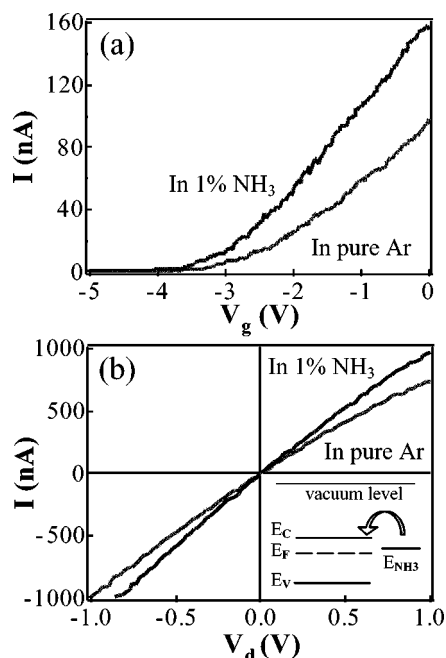
FIG. 3. (a) $I-V_g$ characteristics and (b) $I-V_d$ curves of sample 2 before and after exposure to 1% NH_3. Inset in (b): energy band diagrams of lightly doped In_2O_3 and NH_3 molecules.
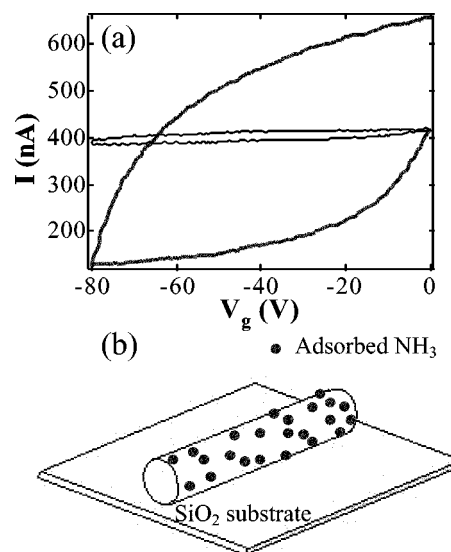

FIG. 4. (a) Two double-sweep $I-V_g$ curves recorded on sample 1 using slow (thin curve) and fast (thick curve) sweeping rate, respectively. (b) Schematic drawing depicting adsorbed NH_3 molecules working as charge traps.

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 ~ 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.[13] 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 $\rightarrow$ -80 V $\rightarrow 0$ 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_2O_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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