Charge Transfer from Ammonia Physisorbed on Nanotubes

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We report the use of nanotube field-effect transistor devices for chemical sensing in a conducting liquid environment. Detection of ammonia occurs through the shift of the gate voltage dependence of the source-drain current. We attribute this shift to charge transfer from adsorbed ammonia molecules, with the amount of charge estimated to be as small as 40 electrons for the smallest shift detected. Using the concentration dependence of the response as an adsorption isotherm, we are able to measure the amount of charge transfer to be 0.04 electron per ammonia molecule.

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Since nanotube field-effect transistors (NT-FETs) were first measured in 1998 [1,2], great progress has been made in understanding their operation [3]. However, the observation of chemical sensitivity in nanotubes [4–6] remains unexplained, despite continued advances in the development of NT-FET sensors for chemical and biological applications [7]. Possible mechanisms include charge transfer from adsorbed species, modifications of contact work functions, substrate interactions, and carrier scattering by adsorbed species. Ammonia sensitivity has been attributed to nanotube doping [8], despite calculations that predict a weak interaction [9]. In this Letter we examine the case of ammonia, using a liquid environment to control the ammonia exposure. We successfully reconcile our experiments with the theoretical prediction by directly measuring the amount of charge transfer.

Ammonia represents the difficulties involved in understanding the chemical sensitivity of carbon nanotubes. NT-FETs in air have been reported to be sensitive to 1% NH_3 gas [6], as shown in Fig. 1. At the same time, theoretical calculations have predicted that ammonia molecules adsorbed to nanotubes donate 0.04 electron per molecule [9]. It is difficult to understand how such a weak charge transfer can produce the large threshold voltage shift shown in Fig. 1. Moreover, we have found that NT-FETs which have been heated in vacuum are not sensitive to ammonia, as shown in Fig. 1. Several differences between ambient and degassed conditions may contribute to this effect. For example, oxygen molecules, which are known to affect device properties [4,5], are largely absent from the degassed devices. The interaction of ammonia with NT-FETs may require the presence of oxygen. At the same time, a thin layer of adsorbed water, which must be present in ambient conditions, is also absent from degassed devices. We have measured the response to ammonia of NT-FETs immersed in liquids and studied its dependence on concentration. We will use the resulting threshold voltage-concentration isotherms to demonstrate that nanotube sensors adsorb ammonia that is dissolved in the water layer.

NT-FETs were fabricated [10–12] using SWNTs grown by chemical vapor deposition (CVD) on silicon substrates coated with 200 nm silicon dioxide films. Iron nanoparticles were exposed to flowing methane and hydrogen at 900 °C to grow nanotubes between 1 and 3 nm in diameter. After growth, optical lithography was used to pattern electrical leads (35 nm titanium capped with 5 nm gold) on top of the nanotubes. Source and drain electrodes were separated by 0.75 μm. We measured the transfer characteristics (conductance versus gate voltage curves) of devices in air (with the gate voltage applied to the substrate) and immersed in water (with the gate voltage applied to the water) by cycling the gate voltage with triangle waves at 1 Hz.

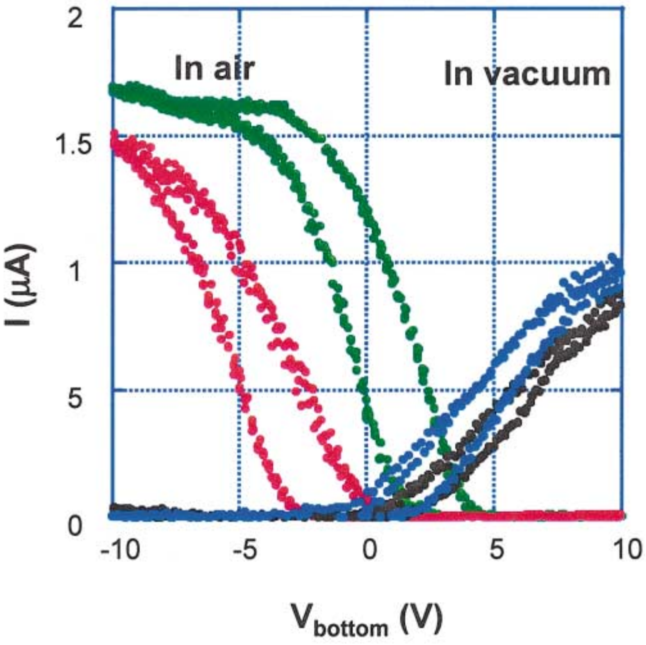

FIG. 1 (color). NT-FET transfer characteristic using the bottom gate, in air (green) and in 1% ammonia in air (red); in vacuum after heat treatment (black) and in 10 Torr ammonia after heat treatment (blue).

Figure 2 shows the transfer characteristics of a NT-FET measured in air, using the silicon as the gate electrode, and in water (1.2 mM NH_3 solution), using the water as the gate electrode. In agreement with previous work [13], we find that water is more effective as a gate electrode than the bottom gate. Because of the intimate contact of the water with the nanotubes, the capacitance between the nanotubes and the water is the typical electrochemical double-layer capacitance [14]. Since the potential between the conducting liquid and the nanotube electrode decays over a distance of approximately 10–60 Å in water (with dielectric constant $k = 80$) [14], the capacitance per area of contact is of order of magnitude 10–70 $\mu F/cm^2$. For each nanotube of diameter 2 nm and length 0.75 mm, this yields a liquid-gate capacitance between 300 and 2000 aF for each nanotube. By comparison, the capacitance between the nanotubes and the bottom gate can be estimated [2] from electrostatics to be 15 aF for each nanotube. Thus, the capacitance from the nanotube to the water is an order of magnitude greater than to the bottom gate. This difference is reflected in the transfer characteristics, which swing between on and off over 10 V for bottom gating and over 0.5 V for water gating. The scaling factor of 20 between the two measurements agrees with our minimum estimate of the liquid-gate capacitance, 300 aF as compared with the bottom-gate capacitance of 15 aF.

Using the liquid gate, we are able to make a clear measurement of the NT-FET response to chemicals dissolved in water. Figure 3(a) shows the result of adding ammonia to water while the water is used as the gate. The effect of increasing ammonia concentration is a rigid shift of the transfer characteristic, with no change in the transconductance. The threshold voltage shift in 1.2 M ammonia (pH = 11.5) corresponds to a complete traversal of the Fermi level across the nanotube band gap of 0.4 V. Various stages in the traversal can be observed, including the condition in 0.3 M solution when the device is nearly compensated, with equal p-type and n-type thresholds. In this range of concentrations, when both thresholds are observable, they shift simultaneously, maintaining a gap of 0.4 V. With 0.4 V subtracted from the n-type thresholds, the threshold shift can be plotted over the whole range of concentrations, as in Fig. 3(b). There is no jump corresponding to the transition between primarily p-type and primarily n-type.

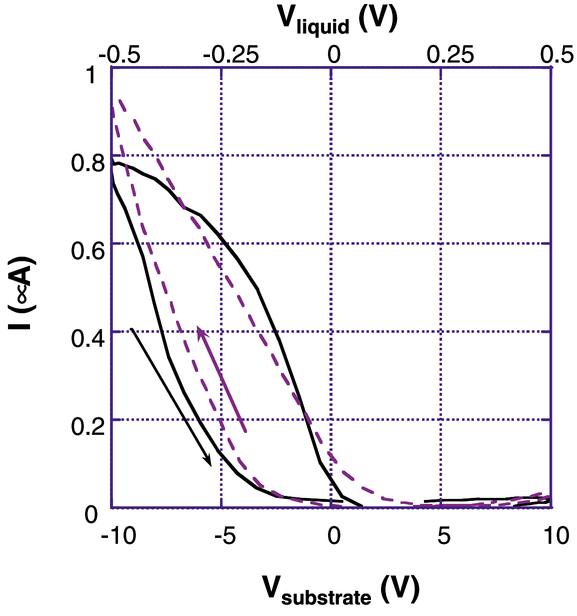

FIG. 2 (color online). NT-FET transfer characteristics in air (solid line), using the bottom gate, and in water (dotted line), using the liquid gate. Arrows indicate the direction of the hysteresis. Note the different x scales for the bottom gate and liquid gate.

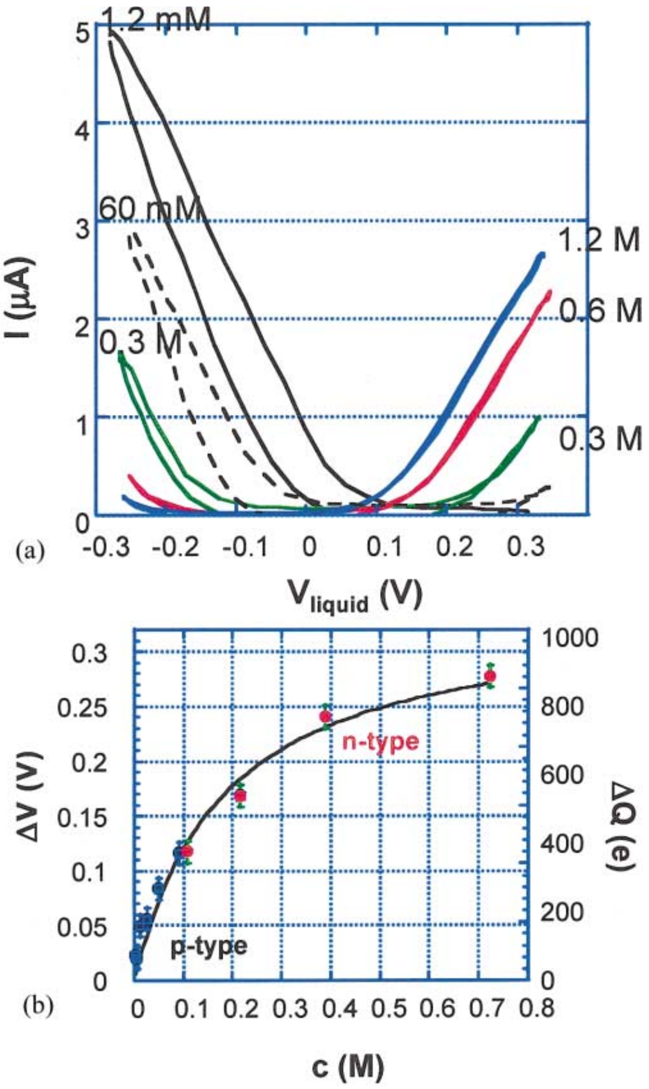

FIG. 3 (color). (a) NT-FET transfer characteristics in water (1.2 mM ammonia) and in various concentrations of ammonia. (b) Concentration dependence of the threshold shift. Left scale in volts, right scale in electron charges, assuming a capacitance of 500 aF. The full line is a guide for the eye.

These results can be analyzed in either of two frameworks, depending on the estimated liquid-gate capacitance. In both cases, the shift in threshold voltage can be regarded as the result of effective gating, in which adsorbed ammonia charges the nanotube. First, with the low capacitance estimate of 300 aF, the threshold voltage shift can be converted directly into the quantity of induced charge, using the formula $\Delta Q = C\Delta V$, as indicated in Fig. 3(b). The smallest threshold shifts observed here correspond to an induced charge of 6 aC, or 40 electrons.

Second, with the high estimate of 2000 aF, it is more appropriate to estimate the charge in terms of the quantum capacitance. As Rosenblatt *et al.* [13] have pointed out, adding or removing charge to a nanotube through gating requires a change in electrostatic potential at least as large as the change in electrochemical potential (Fermi level). This effect can be modeled by means of a "quantum capacitance," C_Q, which is the ratio between the charge on the nanotube and the change in the Fermi level. For a complete traversal of the band gap, the quantum capacitance C_Q is approximately $C_Q = (\sqrt{3}/\pi^2 V_0)\frac{a}{R}eN \approx 650$ aF [15] for a nanotube of length 0.75 μm. (Here $a = 0.14$ nm is the bond length, $V_0 = 2.5$ eV is the π-band tight-binding parameter, N is the number of carbon atoms, and R is the radius.) We use this average quantum capacitance to approximate the energy-dependent differential quantum capacitance. Consequently, the charge required for intermediate shifts can be approximated by the average quantum capacitance calculated above. For a given amount of charge induced in the nanotube, energy must be stored both in the electrochemical potential and in the electrostatic capacitance of the liquid-gate. Thus the correct capacitance is the series combination of the quantum capacitance and the liquid-gate capacitance [13,16], $1/C_{\mathrm{eff}} = 1/C_Q + 1/C_{\mathrm{lg}}$. For our high estimate of the liquid-gate capacitance, this effective capacitance is 500 aF, so that the smallest shift observed corresponds to 70 electrons.

Thus, there is an uncertainty of a factor of 2 in the capacitance, and thus in the amount of charge provided by adsorbed ammonia molecules. We use the value 500 aF, the middle of the capacitance range. The curve in Fig. 3(b) is an adsorption isotherm, indicating the fractional coverage of adsorbed molecules as a function of bulk concentration. The threshold shift can be converted quantitatively to fractional coverage as follows. First, the number of water molecules in contact with the nanotube can be estimated. Since the area of a water molecule is approximately 0.1 nm^2, the number of molecules in the first monolayer around the nanotube (diameter ~ 2 nm, length 0.75 μm) is 30 000. At a concentration of 1.2 M, only 2% of these molecules, or 650 molecules, are NH_3 molecules. With a pH of 11.5, the solution also contains $NH_4{}^+$ ions at a concentration of 5×10^{-3} M, so that 0.008% of the molecules near the nanotube are $NH_4{}^+$ ions. Second, the number of NH_3 molecules actually in contact with the nanotube can be estimated, using the calculated charge transfer between ammonia and nanotubes of 0.04 electron per molecule [9]. This quantity can be combined with the charge required for the maximum threshold shift observed, 940 electrons, to yield 23 000 molecules. Finally, this scale of 23 000 molecules for -0.3 V shift is divided by the number of molecules in a monolayer to produce the fractional coverage, θ, a dimensionless quantity which ranges from 0 for no coverage to1 for a full monolayer to above 1 for a multilayer. In total, the coverage is related to the threshold shift through the formula

$$\theta = \Delta V \times 500\ \mathrm{aF} \times \frac{1\ \mathrm{electron}}{1.6 \times 10^{-19}\ \mathrm{C}} \frac{1\ \mathrm{NH_3}}{0.04\ \mathrm{electron}} \times \frac{1\ \mathrm{monolayer}}{30\,000\ \mathrm{NH_3}}.$$

Note that these parameters are *a priori* estimates that are not provided by fitting to an adsorption isotherm.

Many models are available for describing plots of coverage as a function of adsorbate concentration [14]. The simplest model, the Langmuir model, is appropriate for submonolayer adsorption on nonmicroporous adsorbents such as the sidewalls of nanotubes. This model relates the coverage θ to the concentration c by means of the free energy ΔG_S of adsorption: $\theta = [\beta c/(1 + \beta c)]$, where $\beta = \exp(-\Delta G_S/RT)$. To assess the quality of fit to this isotherm, data are plotted as $1/\theta$ versus $1/c$; such a plot should yield a straight line, as shown in Fig. 4. The intercept of the line, corresponding to infinite concentration, is 1, corresponding to 1 ML of coverage. Since θ expresses fractional coverage, observing an intercept of 1 requires a correct estimate of the quantity of adsorbate which constitutes one monolayer. In our case, shown in Fig. 4, the intercept of 1.3 is quite close to 1, indicating that the assumptions used to convert threshold shift to coverage are reasonable. Since quantities such as the density of the adsorbed layer and the capacitance of the device are reasonably certain, this fit confirms that ammonia donates 0.04 electron per molecule, within a factor of 2. The slope of the line should be $1/\theta$, or $\exp(\Delta G_S/RT)$, from which we conclude that the free energy of adsorption $\Delta G_S = 4.0 \pm 0.5$ kJ/mol.

Importantly, this is the heat of adsorption relative to water solution. The free energy of solution of ammonia in water is 10 ± 0.2 kJ/mol at room temperature [17]; however, it is not correct to conclude that the free energy of ammonia adsorption to nanotubes is 14 kJ/mol, because two reactions are involved in the process of doping nanotubes. First, gaseous ammonia is dissolved in water: $NH_3(g) + H_2O \leftrightarrow NH_3(aq)$. Second, hydrated ammonia molecules are adsorbed on nanotubes: $NH_3(aq) \leftrightarrow NH_3(aq) \cdot NT$. The solvent, which concentrates the gaseous ammonia, is a crucial element which breaks the adsorption reaction into two phases.

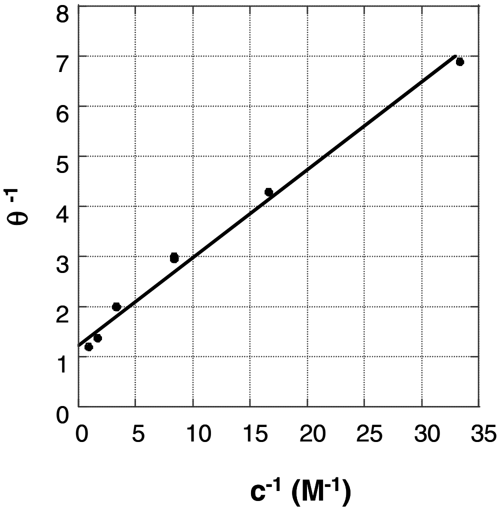

FIG. 4. Langmuir plot of the ammonia response. The x axis is the reciprocal of the concentration. The y axis is the reciprocal of the coverage, as defined in the text. The full line is a linear fit.

The reasonableness of this assertion can be demonstrated by comparing the two different types of ammonia sensitivity measurement. From the response of a different device to 1% ammonia in air in Fig. 1, a threshold shift (-4 V) can be determined. At the same time, the scaling between bottom-gate transfer characteristics and liquid-gate transfer characteristics can be used to convert this threshold shift to the equivalent threshold shift in ammonia solution, -0.2 V. Using the response curve to ammonia solution in Fig. 3(b), this threshold shift is equivalent to 0.45 M ammonia solution. Let us assume that the equivalence arises because of adsorbed water layers on the device in air. Since surfaces in air are covered with water, the device is not directly exposed to ammonia, but rather to a water layer which is exposed to ammonia. In this circumstance, the ammonia gas is dissolved in the water layer, and the resulting ammonia solution causes the device response. If these assumptions hold, then our data can be used to extract the Henry's law constant k for ammonia in water: $p = kc$. With 1% in air, a partial pressure of 0.01 bar, being equivalent to 0.45 M solution, we conclude that $k = 0.02$ bar/M. This number agrees remarkably well with the known value of 0.017 bar/M [17].

In the light of these results, we can understand the data in Fig. 1. Since ammonia does not affect the vacuum-degassed devices, we conclude that ammonia itself does not dope nanotubes directly. Instead, ammonia gas dissolves in the water layer adsorbed on NT-FETs in ambient conditions, and the concentrated ammonia in solution charges the NT-FETs. As a result, NT-FETs respond to ammonia gas only when they are in ambient (humid) conditions. When the NT-FETs have been degassed, the absence of a water layer makes them insensitive to ammonia gas.

In conclusion, by using the NT-FETs for sensing in liquids, we have elucidated the mechanism of nanotube ammonia sensing. We observe clear shifts in threshold voltage in response to ammonia solution, and these shifts can be correlated to the concentration. The shifts represent adsorption isotherms which saturate at monolayer coverage, confirming theoretical estimates of the charge transfer and positively demonstrating that the ammonia sensing involves adsorption of ammonia on nanotubes. However, the ammonia species adsorbed on nanotubes is solvated ammonia. Consequently, NT-FETs respond to ammonia in air, but not in vacuum.

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