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Electronic Fluctuations in Nanotube Circuits and Their Sensitivity to Gases and Liquids

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ABSTRACT

The temperature-dependent noise of individual, single-walled carbon nanotubes is measured here in a variety of different gases and liquids. The ambient environment is found to have only a weak relationship with device noise, even in cases where adsorption significantly changes the dc resistance. Correspondingly, a 450 K degassing procedure typically reduces the device noise by only 1 order of magnitude. An important exception to this finding is a pronounced, 100-fold increase in noise observed near gas–liquid phase transitions of the ambient. Wide-range temperature scans clearly identify the condensation of N₂, H₂, and CH₄ onto metallic nanotubes, but not the sublimation of CO₂. The observations suggest that nanotube devices can directly transduce ambient density fluctuations, though without an inherent gas specificity. Even so, the method is a particularly sensitive characterization of nanotube chemical interactions, one which is successful even for the extreme case of inert gases adsorbed on metallic nanotubes.

Field-effect transistors, chemical sensors, and field emission sources and displays¹ are three carbon nanotube (CNT) research areas seeing preliminary commercialization efforts. In all three applications, and particularly in the first two, high levels of electronic noise threaten commercial viability. The noise levels of CNT devices are substantially higher than those in macroscopic films or materials of comparable resistance,² so controlling noise may be critical to the success of these applications. Despite this potential hurdle, noise sources in CNTs have remained relatively poorly characterized, particularly in comparison to the low temperature, quantum properties of these circuits.

While the exact mechanisms have not yet been identified, the observed noise magnitude of CNTs^{2–6} is compatible with the empirical Hooge observation⁷ that $1/f$ noise scales inversely to the number of carriers in a system. Large amplitude noise is common in nanoscale circuits,^{8,9} and a typical single-walled nanotube (SWNT) conductor 100 nm long incorporates less than 10 000 atoms and even fewer free carriers. The Hooge law predicts a $1/f$ noise singularity in very small circuits which is of interest from both fundamental and applied points of view, and SWNT circuits represent an ideal model system to further examine this issue.⁹

However, to do so one must distinguish between noise sources extrinsic and intrinsic to the SWNT conductor. Because a SWNT's charge carriers wholly reside on the outer

surface of the hollow tube, one might expect noise to depend strongly on the chemical environment surrounding the SWNT. In this paper, we investigate the role of adsorbates on noise properties of SWNT devices using various ambient environments—liquids, gases, and vacuum—in an attempt to determine the extrinsic noise contributions of the surroundings. Simple devices incorporating individual, isolated, single-walled carbon nanotubes were characterized as a function of temperature and ambient environment. The primary result is that SWNT noise, despite its large amplitude, is not particularly sensitive to either temperature or environment except for the special case of adsorbates undergoing a phase transition.

Experimental Methods. SWNT circuits were fabricated using standard lithographic and chemical vapor deposition techniques.¹⁰ SWNTs with diameters between 1.0 and 2.0 nm were grown at 900 °C from the decomposition of methane at catalytic islands. They were subsequently contacted by multiple interdigitated electrodes using optical lithography at pitches of 0.7–1.5 μm . The devices were fabricated using either Au/Ti or pure Ti electrodes on heavily doped Si wafers with 200 nm thermal oxides. Each device was imaged by atomic force microscopy and electrically categorized as being primarily metallic or semiconducting based on the response of the dc conductance to electrostatic gating. Typical devices included a single SWNT directly connecting the source and drain electrodes. This geometry is substantially different from the large area, random

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Table 1. Effects of Liquids and Gases on the Room Temperature Noise of Metallic (met-) and Semiconducting (sm-) SWNT Devices

sample	test environment	ΔR_{dc} (%)	ΔA (%)	$\Delta\alpha$	initial $A/R \times 10^{11}$	test $A/R \times 10^{11}$	$\Delta A/R$ (%)
met-A	N ₂	+1	+56	0.04	1.3	2.1	+55
met-B	N ₂	+3	-9	0.03	4.4	3.9	-12
met-A	He	+1	+9	0.00	1.7	1.8	+8
met-B	He	-1	+21	-0.01	6.8	8.2	+22
met-A	Ar	+3	-11	0.02	1.8	1.5	-14
met-B	Ar	+5	+22	0.02	4.2	4.9	+16
met-C	benzene	+3	-8	0.04	5.2	4.6	-10
met-D	ethanol	+5	-15	0.01	3.3	2.7	-20
met-E	2-propanol	-34	-29	0.10	2.3	2.5	+8
met-F	water	-97	-97	0.94	4.7	3.9	-17
sm-A	N ₂	-0	+20	0.16	0.8	0.9	+20
sm-B	N ₂	-19	-19	0.04	1.0	1.0	+0
sm-A	He	-4	+5	0.26	0.6	0.7	+9
sm-B	He	-1	-52	0.01	1.7	0.8	-52
sm-A	Ar	-0	+159	-0.01	0.7	1.8	+159
sm-B	Ar	-7	-22	-0.04	1.1	1.0	-15
sm-C	benzene	+34	+572	0.32	1.2	6.0	+400
sm-D	ethanol	-100	-82	0.06	0.9	62.9	+6661
sm-E	2-propanol	-18	+51	0.25	2.3	4.3	+83
sm-F	water	-97	-60	0.00	0.6	9.1	+1301

networks used for certain SWNT applications,^{11–13} but the primary conclusions may apply equally well.

Electrical measurements were performed using a low noise voltage calibrator (EDC 501J) biased at or below 100 mV. CNT currents on the order of 0.01–1 μ A were monitored using a relatively low gain but high bandwidth commercial preamplifier (Keithley 428). The preamplifier output was digitized at 50 kHz and monitored and analyzed continuously as the temperature and chemical environment of the circuit changed under computer control. The acquisition time for a noise power spectrum was 2.5 s, and most noise parameters were determined from an average of 25 spectra.

In the first series of experiments, one metallic SWNT device and one semiconducting SWNT device were each characterized in air and then again surrounded by a liquid or gas environment. To avoid any artifacts from irreversible chemisorption, a different pair of samples was used for each new test chemical. Semiconducting SWNTs, which remained predominantly p-type, were biased at a large negative gate voltage, $V_g = -10$ V, to saturate the conductance. This procedure allowed us to distinguish changes in the noise which were separate from the shifting threshold voltage associated with dc chemical sensing.¹⁴

In the second series of experiments, additional noise characterization was performed on metallic SWNTs inside a high-vacuum cryostat over a temperature range of 4–450 K. The enclosure allowed devices to be outgassed using moderate temperatures and then kept in a vacuum. To clearly identify the effects of adsorbates, noise spectra were measured at different temperatures both before and immediately after outgassing. In addition, various test gases could be vented into the evacuated chamber at the conclusion of outgassing. Then the sample was cooled while noise was measured.

Results and Discussion. Different environments had significant effects on the measured electrical properties of

the devices at room temperature. Representative measurements are summarized for both metallic and semiconducting devices in Table 1. In this table, the noise power spectrum is represented in its simplest form by two parameters, A and α , which quantify the magnitude and the frequency dependence of the noise power according to the equation $S(f) = \langle \delta I^2 \rangle = A f^\alpha$.

In the metallic SWNT devices, the low bias, dc resistance R_{dc} was only weakly dependent on changes in the environment. Almost all of the R_{dc} values increased by a few percent when moved from air to the test environment, and the noise power spectrum in both cases was 1/ f -like with α values close to 1.0. The noise magnitude A , on the other hand, changed measurably. The tendency of liquid environments was to reduce the noise by 10% or more. Even inert gases showed effects on the measured noise, but as Table 1 shows, the absolute change exhibited large sample-to-sample variability. Because the same gas increases the noise of one device and decreases the noise of another, it is unlikely that these effects are directly related to the physical or chemical properties of the particular gas. Furthermore, the changes are generally small considering the total noise amplitude, with changes no more than a factor of 2 between air and test environment. Similar results were reproduced by venting from vacuum to test environment. Therefore, mere physical contact with different environments is not sufficient to account for the large noise observed in CNT devices generally.

Among the batch of environments tested, water and 2-propanol gave outlier results on the metallic SWNTs. The high conductivity of water causes the observed drop in both R_{dc} and A , since the device microelectrodes were not specially protected with passivating coatings. 2-Propanol, on the other hand, is a highly insulating liquid and may truly interact with the SWNTs more strongly.

Semiconducting SWNT devices are much more sensitive to their local chemical environment, a well-established

Figure 1. Amplitude of the $1/f$ noise in a metallic SWNT device measured in dynamic high vacuum. Following air exposure, the SWNT remains in a high noise state until heated above 350 K. Following a 15 min soak at 450 K, a stable equilibrium state is obtained having a noise which is 80% lower over the temperature range 77–350 K.

result^{14,15} which has prompted investigation into chemoresistive sensor applications. Consequently, larger changes are observed in both the R_{dc} and A for these devices. In the three test gases used, R_{dc} always exhibited nominal decreases with no clear correlation to the noise spectra changes. For example, the noise of sample sm-A increased when moved from air to any of the three test gases, whereas the noise of sample sm-B decreased under the same conditions. These measurements, in which air was replaced by a dry, inert gas, may implicate a role for oxygen¹⁵ or water¹⁶ in the noise generation. In the four test liquids, dramatic increases and decreases were both observed. Benzene and ethanol changed A by a factor of 5, but in opposite directions and despite having little effect on metallic SWNT devices. Finally, we note that some of the measurements had increased α values, indicating an increase in the noise at the lowest measurement frequencies and a deviation from simple $1/f$ behavior. In these cases, the simple two-parameter fit may not be representative of the noise spectrum and, as will be described below, additional mechanisms include two-level switching.

For both metallic and semiconducting devices, no correlation or pattern was found between the change in device noise and any other measured parameters. Minimal changes in R_{dc} are observed in the metallic SWNTs, which is consistent with the literature, but no similar generalizations can be stated for the noise sensitivity. In particular, we considered relationships between the device resistance R_{dc} and the noise magnitude A such as the ratio A/R_{dc} , which has been found in previous work to be a good noise estimator for CNT devices.^{2,5} Although Table 1 lacks a clear identification of noise-causing mechanisms, this preliminary set of measurements does indicate a weak but nonzero role for ambient environment in SWNT device noise.

In the second set of experiments, devices were heat-treated in a vacuum in an attempt to remove surface adsorbates and replace them with known species. For these experiments, metallic SWNTs were exclusively used because such heat treatments are known to substantially change the Fermi level pinning and Schottky barriers of semiconducting devices.^{17,18} Figure 1 shows the noise amplitude A of a metallic SWNT measured in high vacuum as it was heated from 77 to 450 K, outgassed for 15 min, and then cooled back to 77 K. The

heat treatment decreased A uniformly by 70–80% over most of the temperature range, with most of the change occurring as the sample is heated from 350 to 425 K. This temperature range indicates that weakly physisorbed species including water contribute to the observed effect; it is far too low to initiate annealing or modification of the carbon network in the SWNT sidewall. To test whether the observed decrease was real and stable, the device was left under vacuum and thermally cycled three more times over a 2-week period. Each measurement reproduced the lower curve in Figure 1, with the device returning to its higher noise state only after re-exposure to ambient air.

This result more clearly implicates surface adsorbates in the electronic noise of SWNT devices. Nevertheless, the effect observed accounts for only a small fraction of the total $1/f$ noise. Furthermore, this experiment is unable to distinguish between noise generation on the SWNT body and at the electrical contact to the connective electrodes, and even though metallic SWNTs were used in this experiment, substantial contact resistances contribute to R_{dc} . Our attempts to passivate the SWNT contacts and distinguish their contribution to the noise have instead led to substantial noise increases, perhaps due to the quality of the passivating oxides or else damage induced by electron-beam lithography.¹⁹

As a SWNT device is cooled further below 77 K, the current and its noise power spectrum deviate from a simple $1/f$ behavior. The current jumps stochastically between two bistable levels such as a “random telegraph signal” (RTS), a very common type of noise in low temperature, nanoscopic electronics.^{8,20} We have developed a real-time data analysis algorithm²¹ which identifies and removes the discrete RTS jumps so that the remaining $1/f$ portion of the noise spectrum can be accurately characterized. This technique allows the temperature evolution of the RTS and $1/f$ noise components to be independently characterized.

Figure 2 shows this effect for a metallic SWNT device maintained in a vacuum following outgassing. Peaking near 60 K, the total measured noise jumps 100-fold due to RTS fluctuations. Following removal of the RTS events, the residual power spectrum has a clean $1/f$ dependence and its amplitude exhibits a significant drop, not an increase, in the same temperature region. While different samples have somewhat different noise profiles at high temperatures, the noise peaks observed in Figure 2 are common to all SWNT devices measured.

The interpretation of Figure 2 is relatively straightforward using the Dutta–Horn model of $1/f$ noise.²² In this model, some number of independent RTS fluctuators have a range of characteristic time constants and jointly produce a power spectrum with $1/f$ frequency dependence. Apparently, one of these fluctuators becomes so enhanced that its effects on the current can be individually resolved in the 50–70 K temperature range.²³ As its individual contribution to the total noise is identified and removed, the $1/f$ noise from the remaining ensemble of fluctuators decreases. A similar effect occurs for another fluctuator, peaking near 10 K.

Although the sample has been prepared using the outgassing protocol described above, the measurement system has

Figure 2. Low-temperature noise amplitude in a metallic SWNT before (dashed line) and after (solid line) data processing to remove distinguishable RTS events. A single, thermally activated fluctuator is easily identified and isolated in the temperature range $50 < T < 70$ K. At higher temperatures, the fluctuator generates noise too rapidly to be individually detected, but adds its weight to the $1/f$ spectrum. The inset clearly shows the temperature range of interest and a second noise peak at 10 K due to an independent fluctuator. The temperatures of the two noise peaks correspond to the phase transition temperatures of the primary residual gases in the system, namely, N_2 and H_2 .

a typical base pressure of 10^{-6} Torr. This pressure is insufficient to keep the sample surface clean of molecular adsorbates, and a mass spectrum of the residual gases indicates H_2O , N_2 , and H_2 in substantial quantities. At these pressures, bulk N_2 and H_2 sublime from the solid to gas phase at bulk transition temperatures near 60 and 10 K, respectively.²⁴ The agreement between these temperatures and the two peaks in Figure 2 strongly suggests that the SWNT is electronically sensitive to a phase transition in the surrounding environment. This preliminary agreement risks overinterpretation of the data, which have been temperature smoothed, but the potential exists to study the effect with much higher resolution. Presumably, the SWNT is most

sensitive to only the first few monolayers of adsorption and crystallization, the thermodynamics of which is dominated by capillary condensation at temperatures near the bulk phase transitions.²⁵

To test the hypothesis that the noise peak might arise from an environmental phase transition, additional measurements have been performed using 0.1 atm of high-purity CO_2 and CH_4 in an attempt to displace the trace quantities of adsorbed N_2 and H_2 . Both gases are only weakly chemically active and experimentally have little effect on SWNT electronic properties.^{26–28}

Figure 3 depicts $A(T)$ for a SWNT device sequentially measured in high vacuum, CO_2 , and CH_4 , with an outgassing cycle before each measurement. The measurement in a vacuum shows characteristic noise peaks near 10 and 60 K which are absent when the same sample is measured in CO_2 or CH_4 . The measurement in CH_4 has a new noise peak at 130 K, and measurement in CO_2 is relatively featureless. The removal of the 10 and 60 K peaks when residual N_2 and H_2 gas is absent confirms their assignment. Furthermore, the absence of any noise peaks in CO_2 , which does not form any liquid phase even with the help of capillary condensation,²⁵ suggests that the environment-dependent peak is exclusively due to liquid condensation. We note that the temperature of the CH_4 noise peak is in poor agreement with its expected boiling point at 0.1 atm (130 K vs 90 K), but it does agree with neutron scattering measurements which observe liquidlike CH_4 binding to SWNTs for $T < 120$ K.²⁹

The peaks in the electronic noise may result indirectly from the formation of a condensate phase, the density of which exhibits RTS-like number fluctuations near a phase transition.³⁰ If so, this transduction mechanism would indicate a new technique for studying nanoscale adsorption, complementary to traditional adsorption isotherms and calorimetry. While such a sensitivity seemingly contradicts the results of Table 1, in which different species played little discernible role in the noise, it is consistent with the large, room temperature $1/f$ noise observed in SWNT circuits. In fact, Figure 3 agrees with Table 1 in the sense that all of the

Figure 3. SWNT noise amplitude exhibits dramatic peaks which depend on the surrounding environment. In a vacuum (●) peaks at 10 and 60 K suggest the capillary condensation of the residual gases H_2 and N_2 . These residual gases may be displaced by CH_4 (■), which shows its own condensation noise peak at 130 K, or by CO_2 (▲), which does not exhibit any peak at all. CO_2 is the only gas which does not condense to a liquid phase, suggesting that the observed noise enhancement is specifically linked to only the liquid phases of the condensates.

different test gases will be indistinguishable at or above room temperature.

Finally, Figure 3 demonstrates a dramatic difference from the chemical sensor literature, in which metallic SWNTs have shown virtually no electronic responses to changes in environment. Except for changes to the thermopower,²⁸ the relatively inert gases discussed here also fail to affect SWNT devices of any type—metallic or semiconducting. Thus, the discrimination of a significant interaction between N₂ and metallic SWNTs appears unique to the noise characterization method, and it indicates a potentially fruitful research direction for future work.

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