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Influence of Mobile Ions on Nanotube Based FET Devices

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ABSTRACT

Carbon nanotube field-effect transistors often exhibit a hysteresis effect in the gate-voltage dependence. We report devices fabricated with small hysteresis, and demonstrate a method to introduce this effect controllably by coating nanotube devices with charged polymers. In addition, the hysteresis is sensitive to humidity on sub-second time scales, showing promise as a humidity sensor. The polymer charge is related to the threshold shift observed, proving that the induced hysteresis results from ionic motion.

Carbon nanotube-based field-effect transistors[1,2] offer advantages over traditional FETs, including high carrier mobilities[3] and chemical sensitivity.[4] To make progress in improving device performance, attention has been focused on understanding the fundamentals of device operation.[6,7] Only recently has hysteresis, an important attribute, been investigated,[3,5,8] though it has not yet been controlled or eliminated. We report here nanotube FETs with little hysteresis. We have examined the source of the hysteresis by subsequently inducing the hysteresis in these devices by adding a charged polymer layer.

We have directly tested the possibility that cation diffusion causes nanotube hysteresis. First, devices which exhibit very small hysteresis are fabricated. Subsequently, we modify the devices by the addition of an electrolytic coating that results in mobile ions on the surface of the device. We observe the appearance of advanced hysteresis similar to the previous observations; the hysteresis was asymmetric, exhibiting larger shifts during right-moving sweeps than during left-moving sweeps. To explore possible mechanisms for cation-induced hysteresis, we performed additional measurements, varying the humidity that changes the hydration layer around the nanotubes, and thus leads to the increase of the ionic mobility. We found that humidity affects the hysteresis significantly, with hysteresis increasing with higher humidity. Taken together, these observations imply that ionic motion is the cause of the hysteresis.

Devices were prepared using rigorously clean 100 mm lithography techniques, paying particular attention to sources of ionic contamination. All processing was performed on 100 mm wafers. Figure 1a shows a schematic of the nanotube devices. The nanotube devices were fabricated using nanotubes grown on 200 nm of silicon dioxide on doped silicon by chemical vapor deposition (CVD) from iron nanoparticles with methane/hydrogen gas mixture at 900 °C; electrical leads were patterned from titanium films 35 nm thick capped with gold layers 5 nm thick, with a gap of 0.75 um between source and drain. The AFM image in Figure 1b illustrates a device. Note that along the length of the contacts, devices typically include three to five nanotubes. Most devices include a metallic nanotube, which is reflected in nonzero conductance at high positive gate voltages. After initial electrical measurements, the substrates were then submerged in a solution of poly(sodium 4-styrenesulfonate) (Figure 1a) (NaPSS, average molecular weight ~70 000, Aldrich) at 10 wt % in water. After soaking overnight, they were removed, rinsed with deionized water and blown dry in nitrogen flow. A thin, uneven layer (<10 nm) of NaPSS was observed to coat the devices by AFM.

We explored the effect of the coating on the hysteresis by several means. First, the transfer characteristics of the devices before and after coating were compared at several different frequencies. Second, we tested the effect of humidity on the coated devices. Finally, since the hysteresis was found to respond significantly to changes in humidity, we measured the speed of the response.

Figure 2 shows the transfer characteristic of the nanotube device before and after coating with the NaPSS polymer. The nanotube shows a dominant p-type behavior, known to be related to the role of atmospheric oxygen on the device.[4,9] To observe the hysteresis, the gate voltage was swept as a sine wave with a frequency of 12 Hz. The hysteresis is significantly smaller than has previously been reported[3,4,8] for measurements at this frequency. We believe the reduction

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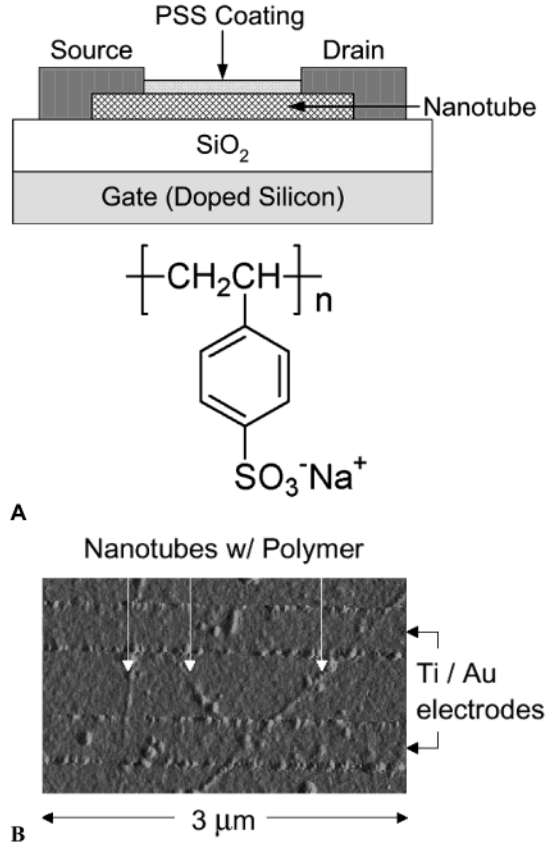

Figure 1. Nanotube device structure. (A) Geometry of the polymer-coated nanotube FET device and chemical structure of poly(sodium 4-styrenesulfonate) (NaPSS) polymer. (B) Atomic force microscopy image of typical polymer coated NTFET device. The device has multiple nanotubes crossing the source and drain electrodes. A segment of the device containing three nanotubes is presented here. Polymer material is observed to coat nanotubes with an amorphous layer.

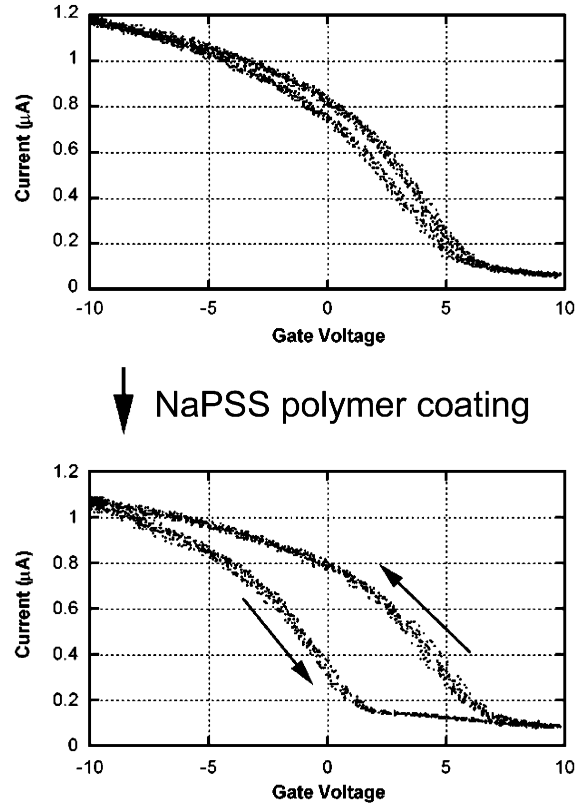

Figure 2. Nanotube FET transfer characteristics. (A) As fabricated, in air. 20 mV bias voltage. (B) After applying the NaPSS coating, in air. 30 mV bias voltage. Arrows indicate the direction of the hysteresis loop.

of hysteresis is due to the rigorously clean fabrication process which leaves few ionic species on the as-fabricated device. This observation by itself is suggestive to the fact that ionic species are responsible for the hysteresis observed by others. After coating with the NaPSS polymer, the nanotube device exhibits a significantly larger hysteresis effect in the conductance−gate voltage curves. The hysteresis is advanced in character, as indicated by the arrows. In addition, in Figure 2 only one side of the hysteresis exhibits a change in threshold voltage. For a 12 Hz gate voltage frequency, only the right-moving sweep (the left curve) is shifted; the left-moving sweep (the right curve) nearly overlaps the uncoated device characteristic.

To further explore the influence of ionic species, we examined the effect of gate voltage frequency and humidity. For the frequency tests, the gate voltage was driven with a triangle-shaped waveform of ± 10 V amplitude. We find that the hysteresis increases when the gate voltage was cycled at lower frequencies, indicating slowly moving species are responsible for the hysteretic behavior. For the humidity tests, humid air was generated by bubbling compressed air through hot water ($\sim$50 °C) and flowing it over the device, while sweeping the gate voltage at 12 Hz. The effect of the humidity on device operation is shown in Figure 3. Upon

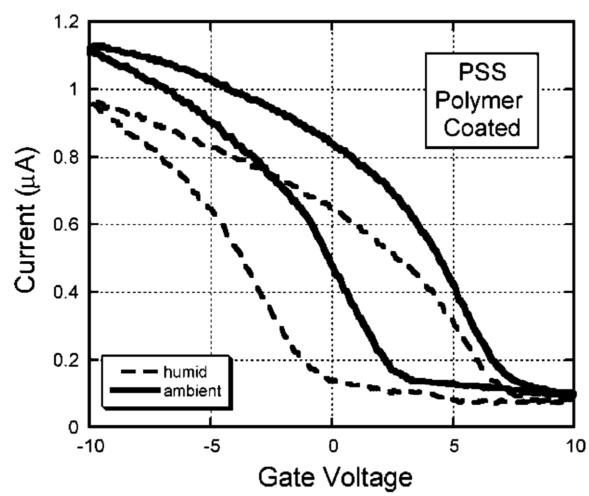

Figure 3. Observation of the shift in the FET characteristic of the NaPSS-coated nanotube device upon exposure to humid air. 30 mV bias voltage.

water exposure, the amount of hysteresis noticeably increases. In particular, only the right-moving sweep exhibited a threshold shift, of negative three volts. In addition to full humidity, the devices were measured in vacuum. Devices were exposed to vacuum of 10^{-6} Torr for 1 h and then measured. Under this condition, no hysteresis was found. The process was carried out on several nanotube devices and all the devices examined showed qualitatively the same hysteresis and humidity effects.

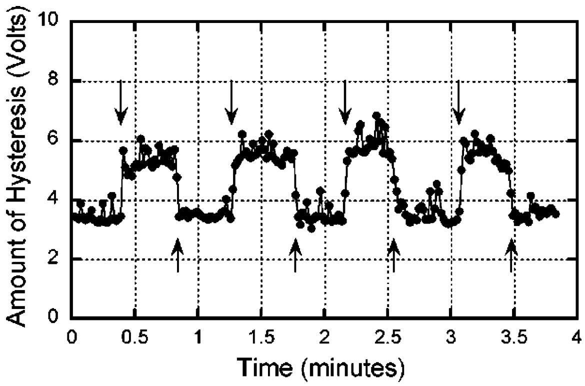

Figure 4. Operation of the NaPSS-coated nanotube device as a humidity sensor. Down arrows indicate the exposure to humid air, and up arrows indicate the removal of the humid air.

Since the devices were found to be sensitive to humidity on a 1-h time scale, we attempted to measure the speed of their response. We found an upper limit of 0.5 s for the response time. Fully humidified air was generated as described above. Devices were exposed to an alternating flow of humidified air and ambient air at 30% relative humidity. During the exposure the gate voltage was swept continuously between +10 V and −10 V at a frequency of 2 Hz. The switching voltage was analyzed for each sweep; switching voltage was defined as the gate voltage at which the current reached its midpoint. Positive and negative sweeps were separated into pairs. For each pair, the switching voltages of the two sweeps were subtracted from each other. This difference voltage is defined as the width of the hysteresis for a full cycle of gate voltage. In Figure 4, the difference voltage is plotted as a function of time for the length of the exposure. In humidified air, the hysteresis was broad, as the dotted line in Figure 3; in ambient air, the hysteresis was narrower, as the solid line in Figure 3. Arrows indicate the times at which the flow was switched between humidified air and ambient air. When the humidified air was introduced, the hysteresis attained its full width rapidly; when the ambient air was restored, the hysteresis narrowed just as rapidly. For each switching of the flow, the response was complete within one or two gate voltage cycles. This response time may have been limited by the flow dynamics of the test setup. However, we can conclude that the hysteresis responds within one second of a humidity change. Such a rapid response is competitive with commercial humidity sensors.[10,11]

To summarize the observations, our unmodified devices exhibit very small hysteresis, while the devices with deposited NaPSS exhibit a broad hysteresis. The hysteresis is advanced, as also observed by others.[3,8] The magnitude of the effect changes within a single gate sweep as the humidity is adjusted. Taken together, these observations clearly demonstrate that mobile ions contribute significantly to the advanced hysteresis. This is different from the case in traditional MOSFETs, in which mobile ions cause retarded hysteresis.[19] The mechanism by which mobile ions cause advanced hysteresis in nanodevices remains to be elucidated.

Note: Since this paper was submitted, Kim et al.[20] have reported that vacuum baking eliminates hysteresis in as-fabricated nanotube devices.

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