

POLYMER COATINGS OF CARBON NANOTUBE SENSORS

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Introduction

Single-walled carbon nanotubes (SWNTs) have attracted recent attention for a variety of potential applications.¹ Furthermore, polymer-SWNT systems have also received much attention for solubilizing carbon nanotubes.² In addition, polymer coatings have been shown to modify the characteristics of field-effect transistors (FETs) made of semiconducting SWNTs.³ In particular, polyethylene imine (PEI) polymer was found to shift the FET device characteristics from p to n-type, presumably due to the electron-donating ability of amine groups in the polymer. Here we examine protonation of PEI polymer with HCl and the resulting effect on the FET device properties.

Experimental

Materials. All reagents were used without further purification. Poly(ethylene imine) (PEI, average molecular weight ~25,000) was purchased from the Aldrich Chemical Co.

Carbon Nanotube Devices. SWNT FETs 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 μm between source and drain. The system configuration has been described previously.⁴

PEI Polymer Protonation. To a 40 mL solution of 1% PEI by weight in water a 1 M solution of HCl was added dropwise from burette. A pH meter (VWR) with a glass electrode probe was used to record the pH of the PEI solution as a small measured amount (0.1-0.2 mL) of HCl was added.

Functionalization of the Carbon Nanotube Devices. The devices were submerged in aqueous solutions of poly(ethylene imine) at different pH levels. After soaking overnight, they were removed, rinsed with water and blown dry in nitrogen flow.

Results and Discussion

Figure 1A depicts the schematic layout of the SWNT FET device architecture. SWNTs on silicon substrates contacted with metal (Ti / Au) contacts, together with a doped Si back gate, form the basic elements of the SWNT FET. In the devices examined, multiple nanotubes are connecting the source and drain electrodes. We have monitored the change of the source-drain current (I_{sd}) as a function of the gate voltage (V_g) both with increasing and decreasing gate voltages. In devices that have a multitude of nanotubes, both metallic and semiconducting nanotubes contribute to the source-drain current. Here we report experiments on devices with only semiconducting nanotubes, therefore the devices have near- zero conductivity for positive V_g values. A typical device characteristic for these devices in air is shown in Figure 1B (curve a). The devices display p-type behavior, known to be related to atmospheric oxygen on the device,⁵ and they also exhibit a small hysteresis which may be related to a hydration layer.⁶

Deposition of PEI on the SWNT FET device results in the change of the device characteristic (Figure 1B (curve b)). The I_{sd} - V_g curve shifts toward more negative gate voltages. The gate voltage shift is the result of charge transfer between the SWNT FET device and the amino groups in PEI polymer adsorbed onto the carbon nanotube conducting channel. The gate voltage shift (ΔV_g) between the device characteristics for different devices is defined as the change in the midpoints of the hysteresis. We find that the charge transfer between the polymer and nanotube is dependent on the number of amino groups in the polymer and their basicity. This has been confirmed by deposition PEI polymer from different aqueous solutions with different pH values.

Commercial polyethyleneimine (PEI) polymer is highly branched, has a molecular weight of about 25,000, and contains about 500 monomer residues. About 25% of the amino groups of PEI are primary with about 50%

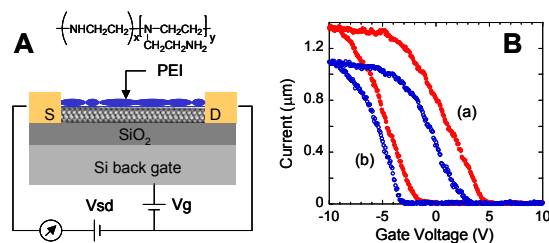


Figure 1. (A) Schematic view of a field-effect transistor device with a SWNT transducer contacted by two Ti/Au electrodes (source and drain) and a silicon back gate. SWNT conducting channel is exposed to poly(ethylene imine) (PEI) polymer. (B) The source-drain current – gate voltage dependence (I_{sd} - V_g) of a bare SWNT FET device in air (curve a) and after functionalization with PEI at pH = 5 (curve b).

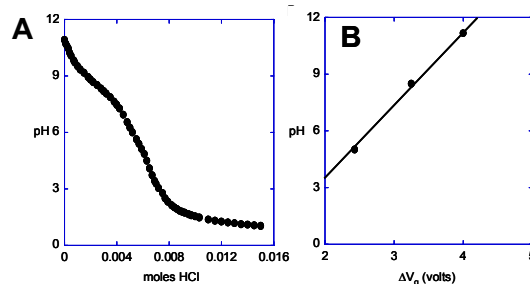


Figure 2. (A) The effect of adding HCl to a basic 1% wt. PEI solution in water. Discontinuities in the plot reflect complete protonation of various amine groups within the PEI polymer. (B) Correlation between the gate voltage shift (ΔV_g) of SWNT FET device and pH of the PEI solution used for the deposition

secondary, and 25% tertiary. Since each type of amine has a different basicity, different amino groups can be protonated at different pH levels. This fact was evident from the titration curve of a PEI polymer aqueous solution with HCl (Figure 2A). PEI solutions with three pH values were used for SWNT FET device functionalization. The gate voltage shift (ΔV_g) value is progressively increasing with increasing pH value (Figure 2B).

Conclusions

PEI polymer protonation results in a decrease of charge-transfer between polymer amine groups into SWNT, as evident from SWNT FET device characteristic changes.

Acknowledgements. We thank the Nanomix technical staff for their assistance with device fabrication and measurements.

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