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Tunable threshold voltage in solution-processed single-walled carbon nanotube thin-film transistors

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ABSTRACT

We have investigated tunable threshold voltage in solution-processed single-walled carbon nanotube thin-film transistors (SWCNT TFTs) employing a simple and reproducible method of chemical encapsulation. Compared to a pristine one, SWCNT TFTs encapsulated with ammonium hydroxide (NH_4OH) and nitric acid (HNO_3) exhibit a negative shift and a positive shift in threshold voltage, respectively. Such results can be explained by the modification of the energy band at the interface between the source metal electrode and the SWCNT network. By using the Y-function method, we also characterized electrical properties such as field-effect mobility, threshold voltage, and contact resistance for TFTs treated with NH_4OH or HNO_3. The technique to favorably tune threshold voltage in solution-processed SWCNTs is significant for constituting CNT-based nanoelectronics.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) have great potential for various nanoelectronics from simple logic circuits to CNT-based computer thanks to excellent mechanical and electrical properties [1–8]. Significantly, random networks of SWCNTs by solution-process at low deposition temperature can enable us to realize large-area flexible electronics. Since the coexistence of metallic and semiconducting SWCNTs leads to low on/off current ratio and poor reliability in thin-film transistors (TFTs), various methods for separation of metallic and semiconducting SWCNTs have been investigated [9–12]. By using density gradient ultracentrifugation method well-known for sorting mixtures of SWCNTs, solution-processed SWCNT TFTs possess a large on/off current ratio (~10^5) with a high field-effect mobility (~30 cm^2/V s) in the linear region [13,14]. However, large positive threshold voltage (V_T) resulting in a depletion mode of operation, normally observed in solution-processed SWCNT TFTs, can be still a big challenge to realize high performance CNT-based nanoelectronics [15,16]. Furthermore, it is a critical factor to develop molecular-scaled devices requiring low power consumption.

In this work, we demonstrate a simple and reproducible technology to favorably tune V_T in solution-processed SWCNT TFTs employing chemical encapsulation with ammonium hydroxide (NH_4OH) and nitric acid (HNO_3). We believe that this work presents an important approach toward further control of electrical characteristics in SWCNT TFTs which are adaptable to all-solution process.

2. Experimental details

2.1. Fabrication process for solution-processed SWCNT TFTs

The overall device configuration of a solution-processed SWCNT TFT is shown in Fig. 1. Bottom gate and top contact structure were adopted. A heavily doped p-type Si wafer and a 200 nm thick thermally grown SiO_2 layer were used as a gate electrode and gate dielectric, respectively. The substrates were cleaned with acetone and isopropyl alcohol in ultrasonic bath, dried with nitrogen gas, and baked in an oven at 100 °C for 1 h in order to remove organic contaminants from the surface. After cleaning processes, the substrates were exposed by an ultraviolet lamp in the ozone chamber for 3 min by drop-casting of poly-L-lysine (Sigma–Aldrich; 0.1% (w/v) in H_2O) solution onto the surface of the SiO_2 for 5 min, and a rinse with deionized (DI) water. An as-supplied 95% semiconducting single-walled CNT suspension (NanoIntegris Inc.) was drop-casted

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for 2 min, and the samples were rinsed with DI water. This surface functionalization promotes the attachment of semiconducting species of SWCNTs with dense and uniform assembly of nanotube random networks on the SiO_2 surface [17–20]. A 100 nm thick gold (Au) as source/drain (S/D) electrodes was deposited by thermally evaporation under a vacuum of ~10^{-6} Torr. The dimension of fabricated SWCNT TFTs possesses a channel width of 1000 μm and a channel length of 150 μm, respectively.

2.2. Post-treatments for tunable threshold voltage in solution-processed SWCNT TFTs

NH_4OH and HNO_3 were purchased from Sigma–Aldrich, and molar concentration used in this work was 1 M. The acid/base solutions were drop-casted onto SWCNT TFT samples for 30 s, followed by removing the solution by nitrogen gas. The samples were baked on a 70 °C hot plate for 5 min to minimize residual solvent.

Electrical characteristics for all samples were measured with a Hewlett–Packard (HP) 4145B analyzer in ambient air. The applied voltages of the drain and source electrodes were −50 mV and 0 V, respectively, resulting in the linear mode of the transfer characteristics.

3. Results and discussion

Fig. 2(a) shows transfer characteristics of solution-processed SWCNT TFTs with and without post-treatments by NH_4OH and HNO_3. The measurements of transfer curves were performed by sweeping the gate voltage from +5 to −5 V. As-deposited sample exhibits clearly p-type carrier transport characteristics, and a large positive turn-on voltage and V_T of about +2 V as previously reported papers of solution-processed SWCNT TFTs [5,21,22]. On the other hands, after post-treatments with NH_4OH, on-current decreased compared to the pristine sample but the turn-on voltage and V_T were shifted toward 0 V for the same gate voltage sweep range. Also in the case of post-treatment with HNO_3, the turn-on voltage and V_T were shifted in the positive direction with the magnitude of over 1 V Fig. 2(c), (d), and Table 1 summarize the mobility, V_T and on/off current ratio of the samples. By measuring 25 different TFTs for each experiment with NH_4OH or HNO_3, the statistic data and standard deviations were obtained.

The Y-function method was used in this work, which is useful for extracting the mobility, V_T, and contact resistance between the S/D electrodes and the active layer, discussed in this paper, the SWCNT network [23–26]. Compared to the field effect mobility (μ_{FE}) resulted from the maximum transconductance ($g_m = \mu_{FE} C_{ox} V_D W/L$), the extracted mobility from the Y-function method is called the low field mobility which is less affected by the contact resistance and/or gate voltage. The Y-function is defined as [23].

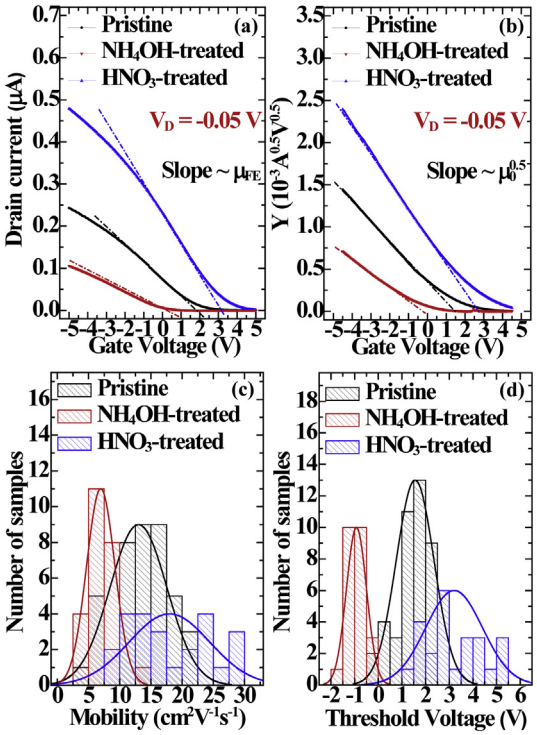

Fig. 2. (a) and (b) Transfer curves and calculated Y-function of NH_4OH- and HNO_3-treated samples, respectively. (c) and (d) Distribution charts of the low field mobility and V_T for each group.

$$Y = \frac{I_D}{\sqrt{g_m}}, \tag{1}$$

where g_m is the transconductance defined as dI_D/dV_G. Considering the contact resistance at the S/D electrodes and assuming that the drain voltage is much smaller than $V_G - V_T$, the drain current equation can be expressed as [24].

$$I_D \cong \mu_0 C_{ox} \frac{W}{L} (V_G - V_T)(V_D - I_D R_C), \tag{2}$$

where W and L are the channel width and length, C_{ox} is the gate oxide capacitance per unit area, μ_0 is the low field mobility, V_G and V_D are the gate and drain voltage, and R_C is the contact resistance at the S/D electrodes. Combining the Equations (1) and (2), the Y-function can be simplified as

$$Y = \sqrt{\mu_0 C_{ox} V_D \frac{W}{L}} (V_G - V_T), \tag{3}$$

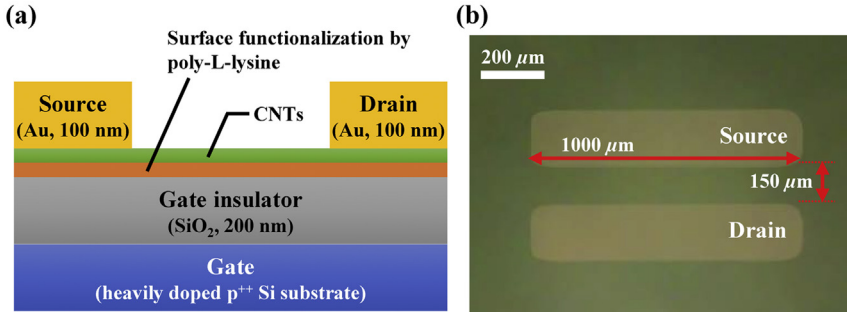

Fig. 1. (a) The schematic cross-section of a solution-processed SWCNT TFT and (b) an optical image of a SWCNT TFT with thermally evaporated gold as S/D electrodes.