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High Density Horizontal-aligned Carbon Nanotube Thin Film with Oxygen Plasma Treatment as pH Sensing Membrane of Extended-Gate Field-Effect Transistor

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Abstract

High-performance pH sening membranes of extended-gate field-effect transistors (EGFETs) composed of high density horizontal-aligned carbon nanotube thin films (HACNTFs) with oxygen plasma treatment are demonstrated. Amount of oxygen-containing functional groups are decorated on the carbon nanotubes (CNTs) after the oxygen plasma treatment. These functional groups act as the sensing sites and respond to the H^+ or OH^- ions in different pH solution. Therefore, these functionalized CNTFs as the pH-EGFET sensing membranes can achieve a high current sensitivity of 0.78 $uA^{1/2}$/pH, a large current linearity of 0.998, and a wide sensing range from pH 1 to 13.

1. Introduction

Ion-sensitive field-effect transistors (ISFETs) is composed of an ion-selective electrode and a field-effect transistor (FET), which possess low power consumption and rapid initial pH response. However, there are several disadvantages with ISFETs such as low current sensitivity and device instability. Unlike the integration in ISFETs, extended-gate field-effect transistors (EGFETs) [1] have a structure that isolates the FET from its chemical environment, in which a sensing head extends from the gate electrode through a signal wire. Therefore, EGFETs are an alternative to conventional ISFETs with lower cost, less sensitivity to the environment, simpler packaging, and better long-term stability [2]. Recently, carbon nanotube thin films (CNTFs) have been proposed as a promising pH-sensing membrane for EGFETs [3] because they possess high mechanical strength, high surface-to-volume ratio, good electrical conductivity, and high chemical inertness. However, to date, CNTFs have been mingled with polymer [4] or metal [5] to improve the pH sensing characteristics of pristine CNTFs. Nevertheless, the complicated processes and contamination issues restrict their applications.

According to the site binding model [6], the sensing films require sufficient sensing sites such as functional groups to respond to the ions of interest in a buffer solution. However, it is hard to create efficient functional groups which act as sensing sites for different pH levels on the carbon nanotubes (CNTs) because of the perfect nature of the sp^2 graphitic structure of the CNTs. In this study, we utilize oxygen plasma to effectively create a sufficient number of oxygen-containing groups on the high density HACNTFs, and these functionalized HACNTFs with high conductance and high-performance sensing characteristics of pH-EGFET sensors are demonstrated.

2. General Instructions

Device structure and fabrications

The detail processes of grown the multi-walled carbon nanotubes (MWCNTs) is described in our earlier study [7]. After grown of MWCNTs, the strip-patterned MWCNTs was mechanically pulled down and densified by alcohol, which step formed the high density HACNTFs. Subsequently, the high density HACNTFs were treated with the oxygen plasma generated in a high-density-plasma (HDP) reactive ion etching system at 10^{-2} Torr with the oxygen flow rate of 20 sccm under the inductively coupled plasma power of 300 W and bias power of 100 W for 60 s. Finally, both the as-sprayed CNTFs and oxygen-plasma-treated ones with a sensing window defined as 2 mm × 2 mm were bonded to the metal wires with the silver paste, packaged with epoxy resin, and baked at 120 ^oC for 30 minutes to form the sensing heads of EGFETs. A Keithley 236 semiconductor parameter analyzer was utilized to measure the output characteristics of the pH-EGFET sensors, connected to the gate of a commercial standard MOSFET device (CD4007UB), in the pH=1, 3, 5, 7, 9, 11, and 13 phosphate buffer solutions (PBSs).

Results and discussion

Fig. 1(a) is the cross-section of high density HACNTFs. The original CNT strips were 10 um in thickness, after the mechanically pulled down and densified by alcohol, the film thickness decrease to 5 um and horizontal aligned with the substrate. Fig. 1(b) is the top view, which shows the perfect periodic structure of HACNTFs with strip-patterned MWCNTs. The as-grown CNTs on a Si substrate are aligned with smooth surface, as shown in Fig. 1(c). After the oxygen plasma treatment, the morphology of the CNTs significantly changes from smooth to a rougher surface, as exhibited in Fig. 1(d). Which means the plasma treatment create some functional groups or defect on the surface of CNTs.

The output characteristics (drain current versus drain voltage, I_{DS}-V_{DS}) in the saturation region for the pH-EGFET sensors with oxygen-plasma-treated CNTFs are shown in Fig. 2(a) for V_{DS} varied from 0 to 6 V with V_{REF} fixed at 3 V. The I_{DS}-V_{DS} curves exhibit the saturation current decrease with increasing hydroxide ion concentrations in the range of pH 1-13. The sensitivity of as-grown high density HACNTFs is not stable because of the prime CNTs are hydrophobic and the H^+ or OH^- ions in solution cannot attaché to the CNTs. After the oxygen plasma treatment, the current sensitivity and the extracted pH current linearity are significantly improved to 0.78 $uA^{1/2}$/pH and 0.998, respectively.

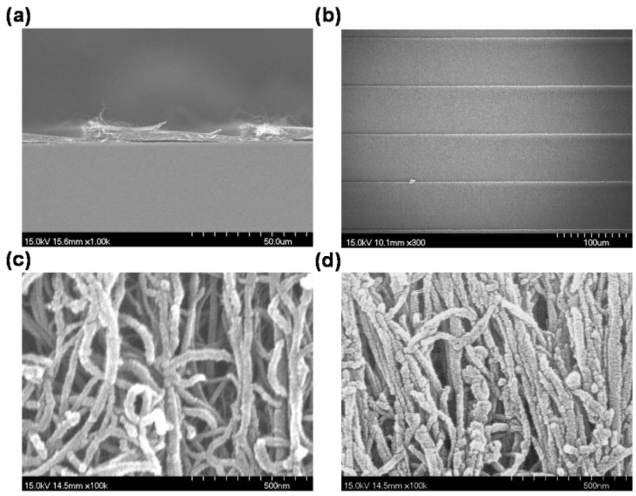

Fig. 1 FE-SEM images of (a) cross-section and (b) top view of HACNTFs. (c) as-grown and (d) oxygen-plasma-treated HACNTFs.

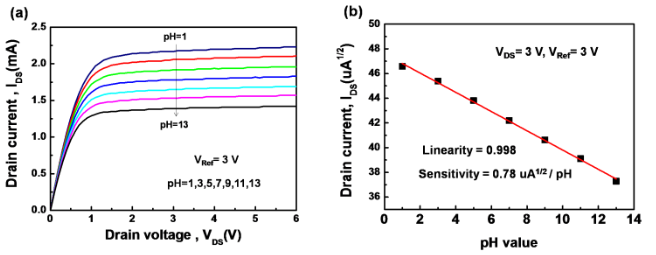

Fig. 2 (a)The output characteristics, the saturation region for oxygen-plasma-treated ones.(b)The extracted pH current sensitivity and linearity for the oxygen-plasma-treated HACNTFs

3. Conclusions

In summary, the current sensitivity and the extracted pH current linearity of oxygen-plasma-treated high density HACNTFs can be significantly improved to 0.78 $uA^{1/2}$/pH and 0.998, respectively. These superior pH sensing characteristics of oxygen-plasma-treated HACNTFs indicate that oxygen-plasma functionalization is an efficient way to decorate sufficient sensing sites on the surfaces of CNTs.

Acknowledgements

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