Oxygen Plasma Functionalized Multiwalled Carbon Nanotube Thin Film as A pH Sensing Membrane of Extended-Gate Field-Effect Transistor

Wan-Lin Tsai, Bai-Tao Huang, Po-Yu Yang, Kuang-Yu Wang, Ching Hsiao, and Huang-Chung Cheng

Abstract—High-performance pH sening membranes of extended-gate field-effect transistors (EGFETs) composed only of oxygen-plasma-functionalized carbon nanotube thin films (CNTFs) are demonstrated. A large number of oxygen-containing functional groups are decorated on the sidewalls of carbon nanotubes (CNTs) after the oxygen plasma treatment. These functional groups act as the sensing sites and accurately respond to the ions of interest in different pH levels. Therefore, these functionalized CNTFs as the pH-EGFET sensing membranes can achieve a high voltage sensitivity of 56.8 mV/pH, a large voltage linearity of 0.9995, and a wide sensing range of pH 1–13. In addition, the oxygen-plasma-functionalized CNTFs also exhibit superior reliability with a small hysteresis voltage of 4.98 mV.

Index Terms—Carbon nanotube thin film (CNTF), extended-gate field-effect transistor (EGFET), sensor.

I. INTRODUCTION

ION-SENSITIVE field-effect transistors (ISFETs) integrate an ion-selective electrode and a field-effect transistor (FET), and they possess low power consumption and rapid initial pH response. In addition, the ISFETs have several disadvantages 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, simpler packaging, less sensitivity to the environment, and better long-term stability [2]. Recently, carbon nanotube thin films (CNTFs) have been proposed as a promising pH-sensing membrane for use in EGFETs [3] because they have high surface-to-volume ratio, good electrical conductivity, high mechanical strength, and high chemical inertness. Nevertheless, to date, CNTFs have been mixed with polymer [4] or metal [5] to improve the pH sensing characteristics of pristine CNTFs. The consequent complex processes and contamination issues, however, restrict their applications.

According to the well-known site binding model [6], the sensing films require sufficient sensing sites to respond to the ions of interest in a buffer solution. It is, however, quite difficult to introduce 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 CNT. In this letter, an oxygen plasma is used to effectively decorate a sufficient number of oxygen-containing groups on the CNTFs, and these functionalized CNTFs with high-performance sensing characteristics of pH-EGFET sensors are demonstrated. In addition, the mechanism by which these decorated functional groups can accurately respond to different pH values is also discussed.

II. DEVICE STRUCTURE AND FABRICATION

A homogeneous multiwalled carbon nanotube (MWCNT) solution was obtained after an acid treatment as described in [7]. Initially, the MWCNT solution was sprayed onto the glass substrates (Eagle 2000) at 200 °C to form CNTFs. Subsequently, the as-sprayed CNTFs were treated with the oxygen plasma generated in a high-density-plasma reactive ion etching system at 10^{-2} Torr with the oxygen flow rate of 20 sccm under the inductively coupled plasma power of 100 W and bias power of 60 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 °C for 30 min to form the sensing heads of EGFETs. A Keithley 236 semiconductor parameter analyzer was used to measure the transfer 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). In addition, the measurement system consisted of a digital multimeter (HP 34401A) and a commercial instrument amplifier (IC LT1167) was applied to analyze the hysteresis in the loop of pH = 7, 3, 7, 11, and 7 in sequence.

III. RESULTS AND DISCUSSION

Field-emission scanning electron microscopy (FE-SEM) images of the morphological variations of CNTFs before and after the plasma treatment are shown in Fig. 1(a) and (b). The as-sprayed CNTs on a glass substrate can be recognized individually and are distributed arbitrarily with smooth surface
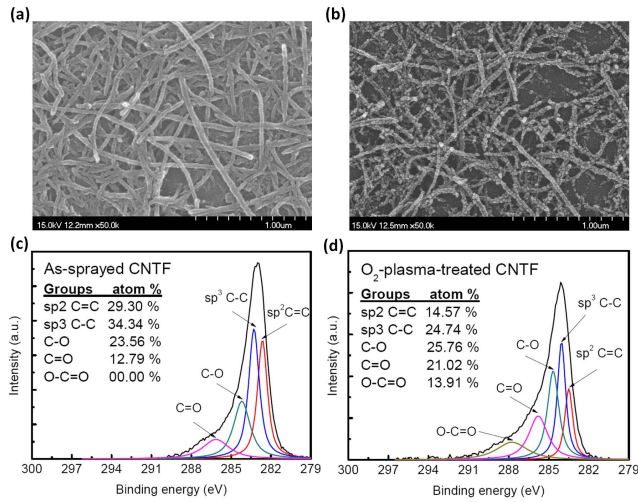
Fig. 1. FE-SEM images of (a) as-sprayed and (b) oxygen-plasma-treated CNTFs. XPS C 1 s spectra of (c) as-sprayed and (d) oxygen-plasma-treated CNTFs could be deconvolved into five Gaussian peaks: 284.1 ± 0.2, 285.1 ± 0.2, 286.2 ± 0.2, 287.2 ± 0.2, and 288.9 ± 0.2 eV in sequence.
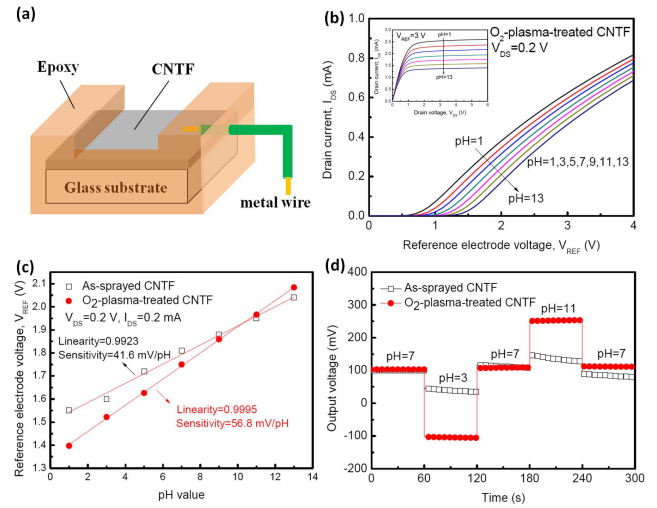

Fig. 2. (a) Schematic diagram of the sensing head structure. (b) Transfer characteristics, I_{DS}–V_{REF}, of the pH-EGFET sensors in the linear region for oxygen-plasma-treated ones. Corresponding curves in the saturation region with $V_{REF} = 3$ V are also shown in the inset of (b). (c) Extracted pH voltage sensitivity and linearity for the as-sprayed CNTFs and oxygen-plasma-treated ones. (d) Hysteresis characteristics of as-sprayed CNTFs and oxygen-plasma-treated ones.

as shown in Fig. 1(a). After the oxygen plasma treatment, the appearance of the CNTF significantly changes from smooth to a much rougher surface as shown in Fig. 1(b). X-ray photoelectron spectroscopy is further performed to examine the decorated functional groups on CNTs after the plasma treatment as shown in Fig. 1(c) and (d). XPS C 1 s spectra of examined CNTFs could be deconvolved into five Gaussian peaks [8]. The main peak at 284.1 ± 0.2 eV is attributed to the sp^2-hybridized graphite like carbon atoms (C=C). The peak at 285.1 ± 0.2 eV corresponds to the sp^3-hybridized carbon atoms (C-C). Other peaks at 286.2 ± 0.2 eV, 287.2 ± 0.2 eV, and 288.9 ± 0.2 eV are considered to originate from carbon atoms bound to one oxygen atom with a single bond, one oxygen atom with double bonds, and two oxygen atoms, respectively. As compared with the quantitative analysis between the as-sprayed and oxygen-plasma-treated CNTFs, it is obvious that the quantity of sp^2 C=C bonds decreases but those of the oxygen-containing groups, such as C-O, C=O, and O-C=O bonds, increase after plasma treatment. These consequences reveal that the oxygen plasma treatment is an efficient way to funtionalize the CNTs, which causes a large number of C=C bonds to be substituted by oxygen-containing groups.

For analyzing the sensing characteristics of these CNTFs, both as-sprayed CNTFs and oxygen-plasma-treated ones are packaged as shown in Fig. 2(a). The transfer characteristics (drain current versus reference electrode voltage, I_{DS}–V_{REF}) in the linear region for the pH-EGFET sensors with oxygen-plasma-treated CNTFs are shown in Fig. 2(b) for V_{DS} fixed at 0.2 V and V_{REF} varied from 0 to 4 V. The I_{DS}–V_{REF} curves exhibit a threshold voltages shift from left to right with decreasing hydrogen ion concentrations in the range of pH 1–13. The corresponding curves in the saturation region one with $V_{REF} = 3$ V is also shown in the inset. The voltage sensitivity for pH-EGFET sensors could be calculated from the slopes of the V_{REF} defined at the fixed I_{DS} of 0.2 mA and V_{DS} of 0.2 V as the functions of the pH values as shown in Fig. 2(c). Consequently, the voltage sensitivities of

the as-sprayed CNTFs and oxygen-plasma-treated ones are 41.6 and 56.8 mV/pH, respectively. Furthermore, the extracted pH voltage linearity for the oxygen-plasma-treated one is 0.9995 that is significantly > 0.9923 for the as-sprayed one. Fig. 2(d) shows the results of hysteresis measurements at intervals of 60 s for as-sprayed CNTFs and oxygen plasma treated ones, respectively. The output voltage is the difference of electrical potential between the reference electrode and CNTF. The hysteresis effect is defined as the voltage shift after a measurement loop because the characteristics of sensing films might be affected by prior measurements. The hysteresis measurement begun at pH = 7 and continued until the drift rate decreased 10^{-4} mV/s [9]. The hysteresis voltage shift is defined as the difference of the output voltage at initial pH = 7 and final pH = 7. Obviously, the oxygen-plasma-treated CNTFs exhibit a smaller hysteresis voltage shift of 4.98 mV as compared with the as-sprayed ones of 21.30 mV. The drift rates at pH = 7 are 1.24 and 6.63 mV/pH for oxygen-plasma-treated CNTFs and as-sprayed ones, respectively. Therefore, the oxygen-plasma-treated CNTFs are much more reliable and act as rapid-response pH-EGFET sensing membranes.

Although the site-binding model was initially proposed to explain the sensing mechanisms of ISFETs [6], the surface ion adsorption mechanisms for the pH-sensitive membranes in ISFETs and EGFETs are the same. Based on the model, the threshold voltage $V_{T(EGFET)}$ of pH-EGFET sensors could be expressed in the following equation [10], [11]

$$V_{T(EGFET)} = V_{T(MOSFET)} - \frac{\Phi_M}{q} + E_{REF} + \chi_{sol} - \phi \quad (1)$$

where $V_{T(MOSFET)}$ is the threshold voltage of the MOSFET, Φ_M is the work function of the metal gate (reference electrode, Ag/AgCl) relative to vacuum, E_{REF} is the potential of the reference electrode, χ_{sol} is the surface dipole potential of the
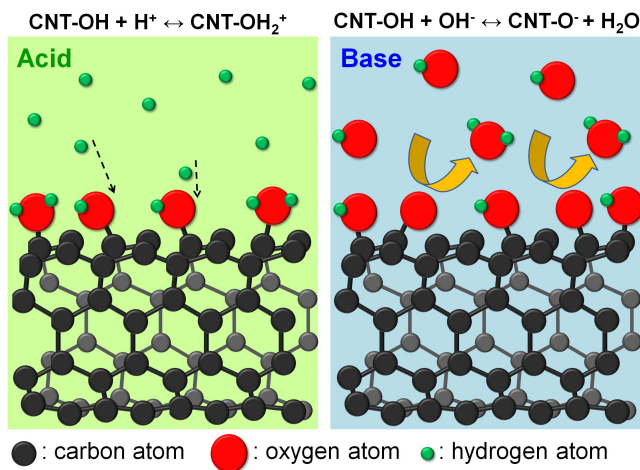
CNT-OH + H$^+$ ↔ CNT-OH$_2$$^+$ CNT-OH + OH$^-$ ↔ CNT-O$^-$ + H$_2$O

●: carbon atom   ●: oxygen atom   ●: hydrogen atom

Fig. 3.   Schematic diagram for sensing mechanism in acid (left) and base (right).

buffer solution, and φ is the surface potential at the interface of solution and CNTF.

After the oxygen plasma treatment, a large number of oxygen-containing groups are decorated on the surfaces of CNTs. Although the CNTFs immersed in the PBSs, these groups transfer to hydroxyl bonds, i.e. C-OH, and the interface between CNTF and solution would construct a layer of capacitance. Under the thermodynamic status, the reaction of H$^+$ combination in acid and dissociation in base could be shown in Fig. 3. In acid, H$^+$ ions combine with the hydroxyl bonds on the surface of CNTs as shown in Fig. 3 (left), resulting in a lower $V_{T(EGFET)}$ for the higher surface potential. Contrarily, surface potential is lower in the base because H atoms are dissociated from hydroxyl bonds by combining with OH$^-$ ions to form H$_2$O as shown in Fig. 3 (right), and then the threshold voltage $V_{T(EGFET)}$ will shift to the right with increasing pH. The charge density of CNT-O$^-$ is then changed with the variation of H$^+$ concentration in the PBSs. Therefore, oxygen-plasma-treated CNTFs are more accurate, have a rapid-response and are reliable pH-EGFET sensing membranes because of the sufficient sensing sites formed on the CNTs after oxygen plasma treatment.

IV. CONCLUSION

The voltage sensitivity and extracted pH voltage linearity of oxygen-plasma-treated CNTFs can be significantly improved to 56.8 mV/pH and 0.9995, respectively. In addition, the oxygen-plasma-treated CNTFs exhibit a small hysteresis voltage shift of 4.98 mV. These superior pH sensing characteristics of oxygen-plasma-treated CNTFs indicate that oxygen-plasma functionalization is an efficient way to decorate sufficient sensing sites on the surfaces of CNTs. Furthermore, the fully low-temperature processes of oxygen-plasma- functionalized CNTFs also reveal the potentials for flexible and disposable biosensors.

REFERENCES

[1] J. V. Spiegel, I. Lauks, P. Chan, *et al.*, "The extended gate chemically sensitive field effect transistor as multi-species microprobe," *Sensors and Actuators*, vol. 4, pp. 291–298, May 1983.
[2] T. Prodromakis, Y. Liu, and C. Toumazou, "A low-cost disposable chemical sensing platform based on discrete components," *IEEE Electron Device Lett.*, vol. 32, no. 3, pp. 417–419, Mar. 2011.
[3] Y. S. Chien, P. Y. Yang, W. L. Tsai, *et al.*, "The pH sensing characteristics of the extended-gate field-effect transistors of multi-walled carbon-nanotube thin film using low-temperature ultrasonic spray method," *J. Nanosci. Nanotechnol.*, vol. 12, pp. 5423–5428, Jul. 2012.
[4] N. F. Anglada, M. Kaempgen, and S. Roth, "Transparent and flexible carbon nanotube/polypyrrole and carbon nanotube/polyaniline pH sensors," *Phys. Status Solid B*, vol. 243, no. 13, pp. 3519–3523, Nov. 2006.
[5] B. R. Huang and T. C. Lin, "Leaf-like carbon nanotube/nickel composite membrane extended-gate field-effect transistors as *p*H sensor," *Appl. Phys. Lett.*, vol. 99, pp. 023108-1–023108-3, Jul. 2011.
[6] D. E. Yates, S. Levine, and T. W. Healey, "Site-binding model of the electrical double layer at the oxide/water interface," *J. Chem. Soc., Faraday Trans.*, vol. 70, pp. 1807–1818, Nov. 1974.
[7] Y. S. Chien, I. C. Lee, P. Y. Yang, *et al.*, "The mechanism of the surface morphology transformation for the carbon nanotube thin film irradiated via excimer laser," *Appl. Phys. Lett.*, vol. 102, pp. 183111-1–183111-4, May 2013.
[8] T. I. T. Okpalugo, P. Papakonstantinou, H. Murphy, *et al.*, "Oxidative functionalization of carbon nanotubes in atmospheric pressure filamentary dielectric barrier discharge," *Carbon*, vol. 43, pp. 2951–2959, Nov. 2005.
[9] L. Bousse and S. Mostarshed, "Comparison of the hysteresis of Ta$_2$O$_5$ and Si$_3$N$_4$ pH-sensing insulators," *Sens. Actuators B*, vol. 17, pp. 157–164, Jan. 1994.
[10] S. M. Sze, *Physics of Semiconductor Device*, 2nd ed. New York, NY, USA: Wiley, 1981.
[11] M. J. Schoning, A. Simonis, C. Ruge, *et al.*, "A bio-chemical field-effect sensor with macroporous si as substrate material and a SiO$_2$/LPCVD-Si$_3$N$_4$ double layer as pH transducer," *Sensors*, vol. 2, pp. 11–22, Jan. 2002.