

A Novel pH Sensor of Extended-Gate Field-Effect Transistors With Laser-Irradiated Carbon-Nanotube Network

Yun-Shan Chien, Wan-Lin Tsai, I-Che Lee, Jung-Chuan Chou, and Huang-Chung Cheng

Abstract—The extended-gate field-effect transistors (EGFETs) with only the carbon-nanotube (CNT) thin film as both the sensing membrane and the contact electrode have been demonstrated for the first time to exhibit superior pH sensing characteristics. The continuous-wave laser was necessary to improve the pH sensitivity to be 50.9 mV/pH and the linearity values to be 0.9978 for $pH = 3$ to $pH = 13$ wide sensing range, respectively. It implied that the laser energy would unzip the chemically modified multiwalled CNTs (MWCNTs) into numerous graphite slices, resulting in the elevated sensing sites and the improved electrical and sensing properties. Therefore, the laser-irradiated MWCNT network is promising for the applications in the flexible and transparent pH-EGFETs.

Index Terms—Carbon-nanotube (CNT) network, extended-gate field-effect transistor (EGFET), modified multiwalled carbon nanotube (MWCNT), pH sensor.

I. INTRODUCTION

THE ion-sensitive field-effect transistors fabricated by Bergveld [1] in 1970 possessed stable electrical properties and small device size, accelerating the developments in biomedical sensors. Subsequently, the EGFETs [2] which did not need the complicate fabrication process revealed many advantages, such as low cost, simple to package, insensitive to external environment, and flexible shape structures. High surface-to-volume ratio, excellent mechanical and electrical properties, and chemical stability of the carbon nanotubes (CNTs) have attracted many attentions on the sensing applications. CNTs grown by thermal chemical vapor deposition (CVD) had been used for the pH sensing [3]; however, the native hydrophobic property repelled the pH solution wetting and narrowed the pH sensing range. Moreover, the high-temperature process also confined the future applications. Lately, a 2-D network has been developed with low-temperature fabrication and hydrophilic properties. Nevertheless, the recently published papers applied

CNT network mainly focused on the CNT/polymer composites [4] or CNT with pH-responsive molecules [5] for pH sensors owing to the CNT network adhesion and low sensitivity issues. However, with an acid oxidation step [6], the CNTs would bond with oxygen-containing groups, which made CNTs dissolve easily in most solvent and favorable for the chemical sensing, serving as the ion sensing sites. The CNT network with averaging characteristics and modified chemical properties by functional groups possesses outstanding characteristics for replacing the conventional CNT forests or composites to be applied in future devices. In this letter, without any polymer or molecular residues, a simple and effective method was proposed to fabricate the ultrasonic-sprayed multiwalled CNT (MWCNT) network followed by continuous-wave (CW) laser irradiation. The sensing characteristics of laser-irradiated CNT network as both contact electrode and sensing membrane with enhanced electrical properties were systematically addressed for a wide pH sensing range from $pH = 3$ to 13.

II. DEVICE FABRICATION

For the oxidation step, the pristine MWCNTs grown by thermal CVD were modified with H_2SO_4/HNO_3 at 140 °C. Then, the oxidized CNTs were dissolved in the mixture of ethanol and deionized water and ultrasonically separated as well as centrifugally filtered. The obtained homogeneous CNT solution was ultrasonically sprayed on quartz substrate, forming a CNT continuous network. Subsequently, the CNT network was placed into a chamber pumped down to 2×10^{-4} torr, and the Nd:YVO₄ CW laser with 4-W power energy was utilized to enhance the electrical conductivity. The sprayed times of CNT network were controlled to 15 times. The area of the as-sprayed CNT network was fixed at 1×2 cm², and the thickness of CNT network was measured to be about 250 nm. Then, the samples were bound to the metal wires with silver paste, packaged with epoxy resin, and baked at 120 °C. Finally, the encapsulated sensing devices of EGFET pH sensors measured the current–voltage (I – V) characteristics in $pH = 3, 5, 7, 9, 11,$ and 13 phosphate buffer solutions (PBSs) by the Keithley 236 semiconductor parameter analyzer. The features of the as-sprayed and laser-irradiated MWCNT networks were acquired by the scanning electron microscopy (SEM, Hitachi S-4700I). The structural variations were inquired by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3000F). The chemical modified bonding was analyzed by

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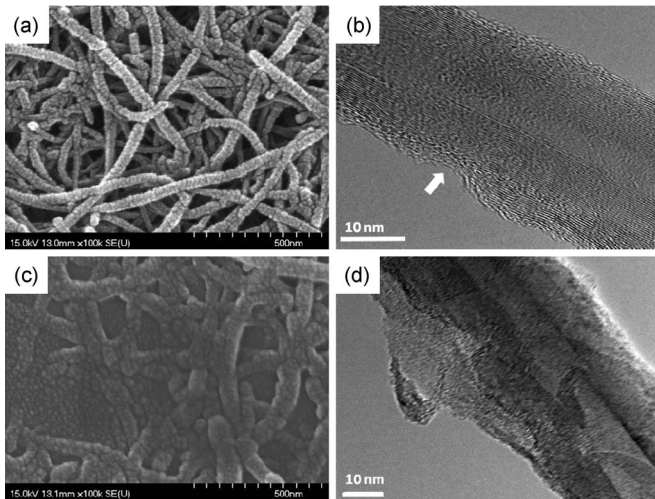


Fig. 1. (a) SEM image of the as-sprayed MWCNT network. (b) TEM image of the acid-treated CNT. (c) SEM image of the laser-irradiated CNT network. (d) TEM image of cleaved CNT after laser irradiation.

the Fourier transform infrared (FTIR) spectrometer (IFS/66, Bruker equipped with a 1064-nm excitation source) and X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI-1600).

III. RESULTS AND DISCUSSION

After the chemical oxidation step, the CNT solution was sprayed onto the quartz substrate. Fig. 1(a) shows the SEM image of the top view of as-sprayed CNT network. As can be seen, the distribution of CNTs is highly uniform. Moreover, the sidewalls of CNT were partially etched by the strong acid to exhibit incomplete crystal structures as pointed out by the arrow, shown in Fig. 1(b). The SEM image of the laser-irradiated MWCNT network is shown in Fig. 1(c). As compared with the as-sprayed network, the tube diameters of the laser-irradiated MWCNTs were obviously expanded, and most of the originally discrete CNT contacts formed a continuous film. To further investigate, the HRTEM image is shown in Fig. 1(d). Under the proper laser irradiation, the CNTs absorbed the laser power and began to cleave initially from the defect sites at the most outer sidewall, resulting in the graphite layers and CNT hybrid structures. Moreover, the CNTs would be ablated under a high laser energy irradiation, and the conducting paths would be interrupted, resulting in the degradation of electrical characteristics.

Fig. 2(a) and (b) shows the FTIR analyses of the as-sprayed and the laser-irradiated CNT networks for confirming the stretching bonds of functional groups. For the as-sprayed MWCNTs, the peak around 3000–3650 cm^{-1} is assigned to the C–H bonds of carboxylic group stretching, ascribing to the structure defects formed during the oxidation [7]. The peak at 2060 cm^{-1} is attributed to the C = C bond stretching. The laser-irradiated CNT network contains plenty of carbon dangling bonds at the boundary of unzipped sidewall layers, and these dangling bonds mostly connected with hydrogen atoms because of the lowest binding energy [8]. In addition,

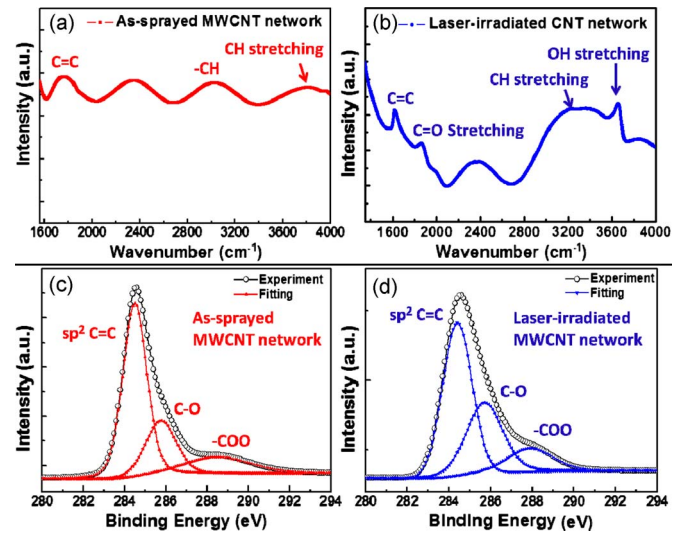


Fig. 2. FTIR spectra of (a) the as-sprayed and (b) the laser-irradiated MWCNT networks. The XPS spectra of (c) the as-sprayed and (d) the laser-irradiated MWCNT networks.

the FTIR results in Fig. 2(b) demonstrated the elevated COOH bonding at 3000–3340 cm^{-1} which is in accordance with the expanding graphene layers, implying the raising C–H bonding. The new peak at 3650 cm^{-1} is assigned to the OH bonding, suggesting the binding of the dangling bonds at the boundary of graphite and the hydroxyl groups dissociated from the water molecules. The peaks around 2360 cm^{-1} were assigned to the CO_2 presented in the chamber [9]. Moreover, the I_D/I_G ratios measured from Raman spectroscopy to be 1.55, 1.66, and 1.81, and the monotonically increased ratios, correspond to the elevated dangling bonds or defects. Furthermore, the chemical bonding of the as-sprayed and laser-irradiated CNT networks was analyzed by XPS spectra. Fig. 2(c) shows the main $\text{C}1s$ peak spectrum of as-sprayed CNT network which was identified into a strong peak at 284.2 eV assigned to the C = C sp^2 structure, C–O bonds (285.8 eV), and C = O bonds (288.8 eV) [10], owing to the strong oxidation. Fig. 2(d) shows the XPS $\text{C}1s$ spectrum of the laser-irradiated CNT network. The C–O bonding and C = O bonding exhibit magnified peak intensities as compared to the oxidized CNT network.

The fabricated MWCNT pH sensing membrane is shown in Fig. 3(a). The $I_{DS}-V_{REF}$ characteristics in the linear region of the laser-irradiated CNT network are shown in Fig. 3(b). The sensing properties are associated by the potential-determining ions in the PBS buffer solution (i.e., H^+ and OH^- ions). As the pH values of the buffer solution are increasing, there exists a threshold voltage shift positively because of the decreasing surface potential. The inset of Fig. 3(b) shows the $I_{DS}-V_{REF}$ characteristics in the linear region for the as-sprayed and laser-irradiated CNT networks at $pH = 3$. The sensitivity of pH sensors can be extracted from the threshold voltage shift, i.e.,

$$\begin{aligned} \text{sensitivity} &= \frac{V_{T(\text{EGFET})}(pH') - V_{T(\text{EGFET})}(pH)}{pH' - pH} \\ &= \frac{\Delta V_{T(\text{EGFET})}}{\Delta pH}. \end{aligned}$$

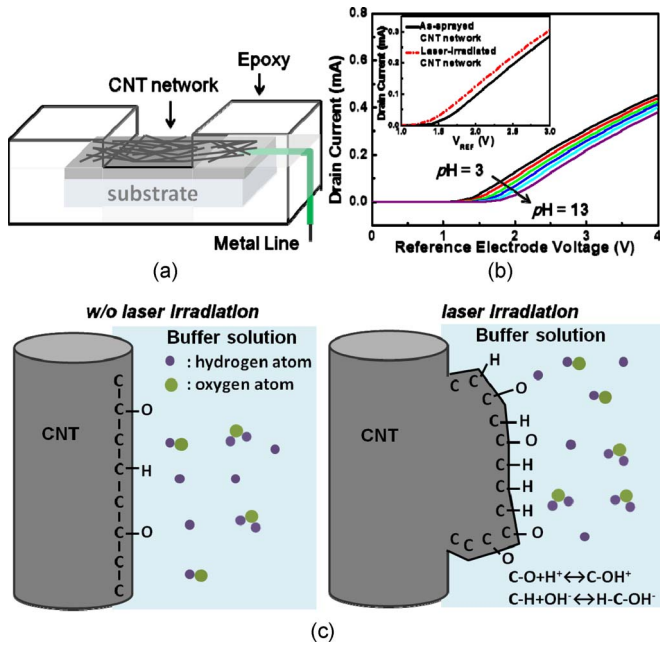


Fig. 3. (a) Fabricated MWCNT pH-EGFET. (b) $I_{DS}-V_{REF}$ (reference electrode potential) characteristics in the linear region of the laser-irradiated MWCNT network, and the inset displays the $I_{DS}-V_{REF}$ curves for the EGFET pH sensors of without laser (as sprayed) and laser-irradiated networks at $pH = 3$. (c) CNT network sensing mechanism: (Left) Without laser-irradiated CNT network and (right) laser-irradiated CNT network.

For comparison, the extracted sensitivity and linearity of the as-sprayed network without laser treatment were calculated to be 35.5 mV/pH and 0.9510, respectively. The sensitivity and linearity values of the laser-irradiated CNT network were enhanced to be 50.9 mV/pH and 0.9978, correspondingly. The sheet resistance of the as-sprayed CNT network was measured to be 8.94 k Ω /sq. After the laser irradiation, the resistance was reduced to be 1.5 k Ω /sq. For the as-sprayed MWCNT network, the electrical transporting would be seriously deteriorated by the discrete CNT contact intertube junctions. However, for the laser-irradiated network, the expanding CNT layers broadened the conducting paths, therefore improving the electrical characteristics and the contact with the substrate. After the proper laser energy irradiation, the MWCNT network unzipped into numerous graphite layers, and these dangling bonds at graphite edges would partially form functional groups such as carbonyl and C-H bonds [8]. Therefore, in the acidic environment, the C-O bonds adsorbed H⁺ ions [11] and elevated the pH sensing surface potential. On the other hand, in the alkaline solution, the C-H bonds would adsorb OH⁻ ions forming H-C-OH bonding [12], hence increasing the threshold voltage of pH sensors. The sensing mechanisms of the as-sprayed and laser-irradiated CNT networks are shown in Fig. 3(c). After acid oxidation, the oxidants would partially damage the structure of CNTs and bond oxygen and hydrogen containing functional groups [7] at the outer sidewalls of CNTs. The oxidized CNTs still remained as complete structures, but the CNTs with high surface-to-volume ratios could absorb the H⁺ and OH⁻ ions only by the functional group bonding at the outer sidewalls, as shown in Fig. 3(c). Moreover, after the laser irradiation, part of the CNTs cleaved into graphite layers, and the elevated dangling

bonds at graphite layers and the inner shells of MWCNTs could also assist the ion bonding, therefore improving the sensing properties. As compared to the as-sprayed MWCNT network, the superior sensing properties of laser-irradiated CNT network were attributed to the reduced sheet resistance and further uniform surface sensing sites for ion bonding.

IV. CONCLUSION

A novel pH-EGFET with the CW laser-irradiated CNT network as both the contact electrode and sensing membrane has been investigated. With the chemical oxidation, the MWCNTs were bounded with functional groups and possessed hydrophilic properties. After the appropriate laser power irradiation, MWCNTs were cleaved into multilayer graphite structures. Therefore, the laser-irradiated MWCNT network exhibited improved electrical and sensing characteristics. The laser-irradiated CNT network without metal layers has demonstrated superior pH sensing characteristics of the sensitivity of 50.9 mV/pH and linearity of 0.9978 in a wide sensing range. It is attributed to the improved conductivity and the abundant sensing sites for ion bonding. Therefore, the laser-irradiated MWCNT network presents excellent chemical tolerance, mechanical flexibility, and sensing properties, making it a promising material for the future applications in flexible and transparent biosensors.

REFERENCES

- [1] P. Bergveld, "Development of an ion-sensitive solid state device for neurophysiological measurement," *IEEE Trans. Biomed. Eng.*, vol. BME-17, no. 1, pp. 70-71, Jan. 1970.
- [2] J. Van Der Spiegel, I. Lauks, P. Chan, and D. Babic, "The extended gate chemical sensitive field effect transistor as multi-species microprobe," *Sens. Actuators*, vol. 4, pp. 291-298, Jan. 1983.
- [3] K. S. Lee, J. H. Kwon, S. L. Moon, W. S. Cho, B. K. Ju, and Y. H. Lee, "pH sensitive multiwalled carbon nanotubes," *Mater. Lett.*, vol. 61, no. 14/15, pp. 3201-3203, Jun. 2007.
- [4] N. Ferrer-Anglada, M. Kaempgen, and S. Roth, "Transparent and flexible carbon nanotube/polypyrrole and carbon nanotube/polyaniline pH sensors," *Phys. Stat. Solid. (B)*, vol. 243, no. 13, pp. 3519-3523, Nov. 2006.
- [5] L. Zhao, T. Nakayama, H. Tomimoto, Y. Shingaya, and Q. Huang, "Functionalization of carbon nanotubes with a pH-responsive molecule to produce a pH sensor," *Nanotechnology*, vol. 20, no. 32, p. 325 501, Aug. 2009.
- [6] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis, and C. Galiotis, "Chemical oxidation of multiwalled carbon nanotubes," *Carbon*, vol. 46, no. 6, pp. 833-840, May 2008.
- [7] S. M. Yuen, C. C. M. Ma, Y. Y. Lin, and H. C. Kuan, "Preparation, morphology and properties of acid and amine modified multiwalled carbon nanotube/polyimide composite," *Compos. Sci. Technol.*, vol. 67, no. 11/12, pp. 2564-2573, Sep. 2007.
- [8] Y. G. Hwang and Y. H. Lee, "Adsorption of H₂O molecules at the open ends of singlewalled carbon nanotubes," *J. Korean Phys. Soc.*, vol. 42, no. 92, pp. S267-S271, Feb. 2003.
- [9] M. Heese, H. Meier, and B. Zeeh, *Spectroscopic Methods in Organic Chemistry*. New York: G. Thieme, 1997, ser. Thieme Foundations of Organic Chemistry.
- [10] S. E. Baker, W. Cai, T. L. Lasseter, K. P. Weidkamp, and R. J. Hamers, "Covalently bonded adducts of deoxyribonucleic acid (DNA) oligonucleotides with single-wall carbon nanotubes: Synthesis and hybridization," *Nano Letters*, vol. 2, no. 12, pp. 1413-1417, Dec. 2002.
- [11] D. E. Yates, S. Levine, and T. W. Healy, "Site-binding model of the electrical double layer at the oxide/water interface," *J. Chem. Soc. Faraday Trans. 1*, vol. 70, pp. 1807-1818, Nov. 1974.
- [12] A. Denisenko, A. Aleksov, and E. Kohn, "pH sensing by surface-doped diamond and effect of the diamond surface termination," *Diam. Relat. Mater.*, vol. 10, no. 3-7, pp. 667-672, Mar.-Jul. 2001.