View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by Ulster University's Research Portal

Superior electrochemical performance of CN_x nanotubes using $TiSi_2$ buffer layer on Si substrates

Wei-Chuan Fang and Jin-Hua Huang
Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan

Chia-Liang Sun and Li-Chyong Chen[a)]
Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan

P. Papakonstantinou
School of Electrical and Mechanical Engineering, University of Ulster, Newtownabbey, County Antrim BT37 OQB, Northern Ireland, United Kingdom

Kuei-Hsien Chen
Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan

(Received 27 April 2005; accepted 31 October 2005; published 12 January 2006)

On-chip growth of vertically aligned nitrogen-containing carbon nanotube (CN_x NT) arrays was demonstrated. The nanotubes were grown by microwave plasma-enhanced chemical-vapor deposition on different types of silicon substrates (n, p, n^+, p^+) using a few nanometer thick Fe layer as a catalyst and a Ti buffer layer. The effects of the Ti thickness on the electrochemical (EC) characteristics of the CN_x NT arrays were studied. It was found that for a Ti thickness of 20 nm, while vertically aligned CN_x NTs were produced on all Si substrates, an almost ideal Nerstian behavior was observed only on highly conductive n^+ and p^+ substrates. As the Ti buffer thickness increased to 200 nm, good electrical contacts were established at the bottom end of the CN_x NTs and fast electron kinetics were then attainable on all kinds of Si substrates. Nevertheless, the use of thick buffer layers inhibited directional growth. Oxidation treatment of the catalyst Fe layer prior to nanotube growth proved efficient for achieving directional CN_x NT formation. Pretreatment of the Ti buffer layer at a temperature of 800 °C, leading to the formation of $TiSi_2$, was appropriate for achieving simultaneously enhanced current density and fast electron kinetics comparable to those of CN_x NTs on bulk Ti electrodes. The Si-based micro-EC platform established in this work has superior current collection efficiency and is amenable for fundamental EC studies and energy applications. © *2006 American Vacuum Society.* [DOI: 10.1116/1.2141627]

I. INTRODUCTION

Carbon nanotubes (CNTs) have attracted considerable attention in the area of energy production and storage.[1–4] For the time being, the applications include microelectromechanical systems (MEMSs), nanoelectromechanical systems (NEMSs), microrobots, and implantable medical devices.[5,6] For the micropower devices of these applications, thin-film batteries[7–10] still do not have sufficient power density to launch these applications. At present, the only solution is to use microsupercapacitors[11,12] (μ-SCs) to enhance pulse current and extend the lifetimes of these devices. Moreover, for purposes of integration and miniaturization, the μ-SCs need to be fabricated on Si substrates using modern semiconductor technology. The current trend of development is to adapt the nanotechnology to obtain a microelectrochemical system whose process readily integrates into an on-chip unit. Meanwhile, the study of the intrinsic electrochemical (EC) properties of carbon nanotubes suffers from the difficulties in fabricating small-resistance Ohmic contacts[13,14] between the nanotube and the metal electrodes. To fully exploit the benefit of high conductivity or even ballistic transport properties in CNTs, the contact resistance should be minimized.

The goal of this work is to establish an EC platform of well-aligned carbon nanotubes on a Si substrate with fast electron-transfer kinetics and current density comparable to that on bulk Ti foils. As will be described, the incorporation of a $TiSi_2$ (Refs. 15–19) buffer layer between the silicon substrate and the Fe catalyst layer is ideally suited for that purpose. The $TiSi_2$, which serves as the electrical contact, has not only low electrical resistance but also has superior anticorrosion ability in EC environments.[20,21] Meanwhile, we also report on the EC characteristics of CN_x NT arrays grown on different kinds of Si substrates (n, p, n^+, p^+) with various thicknesses of the Ti buffer layer. Subsequently, heat treatment of the Ti buffer layer was another parameter investigated to optimize simultaneously the EC behavior and nanotube alignment.

II. EXPERIMENTAL PROCEDURES

CN_x NTs were grown by microwave chemical-vapor deposition on four different types of (100) silicon substrate (n, p, n^+, p^+) using an 8-nm-thick Fe layer as a catalyst and Ti as the conduction layer. Ti layers with thicknesses of 20 and 200 nm were deposited on the Si substrates by electron-

[a)]Author to whom correspondence should be addressed; electronic mail: chenlc@ccms.ntu.edu.tw

beam evaporation. The conduction layer not only was used to prevent the formation of Fe silicides, which would otherwise impede the formation of carbon nanotubes, but also to promote the electron transfer between the CN_x NTs and the Si substrate. Thermal oxidation in air at 350 °C of the Fe catalyst layer led to the formation of iron oxide, which inhibited the formation of Fe–Ti alloys. Prior to CN_x NT growth, hydrogen-plasma treatment (2 KW, 10 min) was employed for cleaning the substrate and forming fine carbon onion-encapsulated metal particles.[22] Except for the Ti buffer-layer thickness, all samples were grown under identical conditions, namely, microwave power of 2 KW, gas flow rates of $CH_4/H_2/N_2$=20/80/80 SCCM (standard cubic centimeter per minute), total pressure of 45 torr, substrate temperature of 1000 °C, and deposition time of 10 min. In another series of experiments, the 200-nm-thick Ti layer was annealed for 2 h in a vacuum of 9.8×10^{-3} torr, and subsequently CN_x NTs were grown under identical conditions as above. For reference purposes, CN_x NTs were also grown on bulk Ti foils.

The formation of the $TiSi_2$ phase upon annealing of the Ti layer was identified by a Rigaku x-ray diffractometer. A JEOL-6700 field-emission scanning electron microscope (FESEM) was employed to probe the surface morphologies. Electron-transfer kinetics inclusive of the EC reversibility, called Nerstian behavior from peak separation (DEp), within anode-cathode and reactivity from current density were performed by cyclic voltammetry (CV) in a μAutolab Potentialstat/Golvanostat Type III in a three-electrode setup using Pt wire as the counterelectrode and Ag/AgCl/3*M* KCl (207 mV vs SHE at 25 °C) as the reference electrode. The EC results were averaged from three individual samples with the same condition. Each sample was examined for 10 cycles. Contact was established through the front surface of the samples. The redox system used was as follows: 1 mM $Fe(CN)_6^{4-}$ in 1*M* H_2SO_4 solution made from $K_4Fe(CN)_6$.

III. RESULTS AND DISCUSSION

In order to identify the role of the substrate on the electron-transfer kinetics, CN_x nanotubes were grown under identical conditions on different types of (100) silicon substrates (n, p, n^+, p^+) using an 8-nm-thick Fe layer as a catalyst and a 20 nm Ti as a buffer layer. Insets in Fig. 1 present typical cross-section views of CN_x NTs grown on different types of Si substrates. As evident from these images, all nanotubes deposited on these four different types of Si substrates have similar morphology. However, the height of CN_x nanotubes ranged from 3 to 5 μm. This variation may come from uncontrollable factors on the growth conditions. Detailed structure analyses (not shown here) revealed that these aligned nanotubes were produced by tip growth, as well as the root growth mechanism.[22]

EC reactivities of Ti-buffered CN_x NTs on different Si substrates examined by cyclic voltammetry are shown in Figs. 1(a)–1(d). The DEp values at 5 mV/s were 83, 69, 83, and 74 mV on n, n^+, p, and p^+ types, respectively. It is found

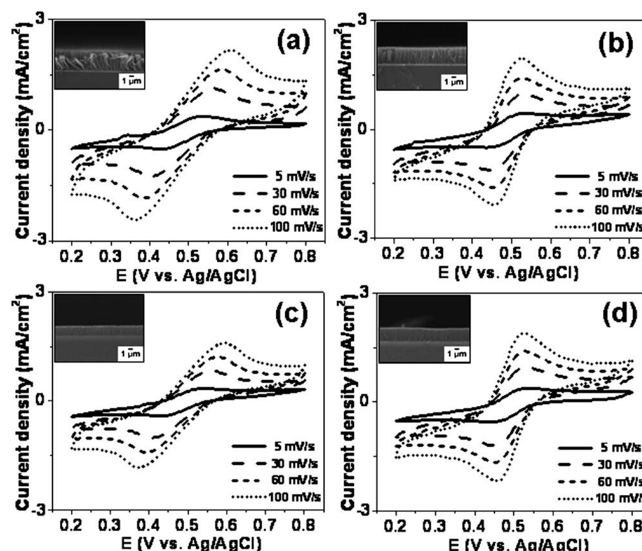

FIG. 1. Cyclic voltammograms of CN_x NTs grown on Ti-(20 nm) buffered (a) n-type, (b) n^+-type, (c) p-type, and (d) p^+-type Si substrates. Insets are corresponding scanning electron microscope (SEM) cross-section views of CN_x NTs.

that the electrical conductivity of the Si substrate plays a major role in these measurements. Both n^+ and p^+ substrates serve as effective conductive paths, facilitating fast electron-transfer kinetics. In addition, the current densities on n- and p-Si substrates are slightly lower than those on n^+- and p^+-Si substrates. An apparent phenomenon can be seen that the 20 nm Ti buffer layer does not provide sufficient isolation from the substrate effects. To overcome the effect of the substrate, we have increased the thickness of the Ti buffer layer to 200 nm.

Moreover, we have also studied the effect of thermal oxidation of the catalyst layer on surface morphologies of CN_x NTs. The cross-section views of CN_x NTs with a thermally oxidized catalyst layer on n-Si substrates with 20 and 200 nm of Ti thicknesses are shown in Figs. 2(a) and 2(b). Corresponding CN_x NTs not subjected to catalyst pretreatment are shown as inserts in Fig. 2. It is obvious that for a Ti thickness of 20 nm, a good degree of alignment on the CN_x NTs can be attained with and without oxidation of the catalyst layer. However, as the Ti thickness is raised to 200 nm, the alignment has significantly deteriorated in the case of the nonoxidized sample. The poor alignment associated with the thick buffer layer will affect the uniformity of subsequent oxide loading for μ-SC development. In contrast, the alignment improved significantly after the oxidation process. These results illustrate the importance of both buffer-layer thickness and catalyst pretreatment on the alignment of nanotube growth. It is insinuated that at higher Ti thickness the Ti and Fe atoms have a greater chance to dissolve mutually and form alloys, thereby decreasing the active catalyst surface area and inhibiting oriented growth. Once the Fe layer was thermally treated in air,[23] high-density iron-oxide nanoparticles were created. These nanoparticles inhibited the formation of Fe–Ti alloys and enhanced the direction growth.

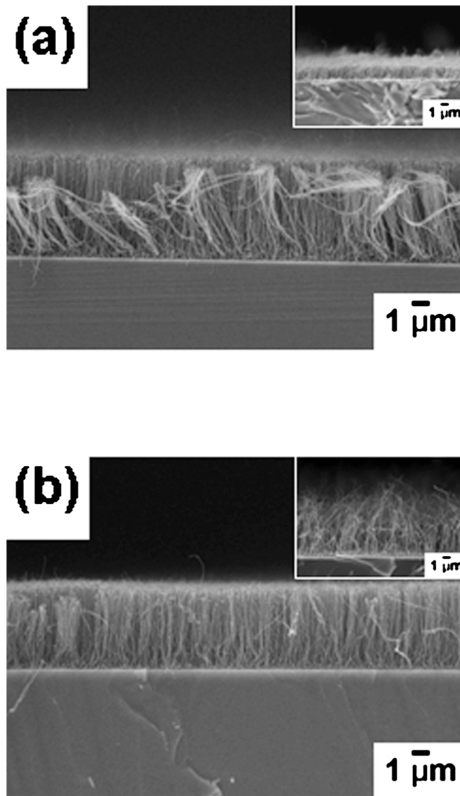

FIG. 2. Cross-section morphologies of SEM show CN_x NTs grown with thermally oxidized catalyst on *n*-type Si with a Ti buffer-layer thicknesses of (a) 20 nm and (b) 200 nm. The insets are their counterparts without thermal oxidation.

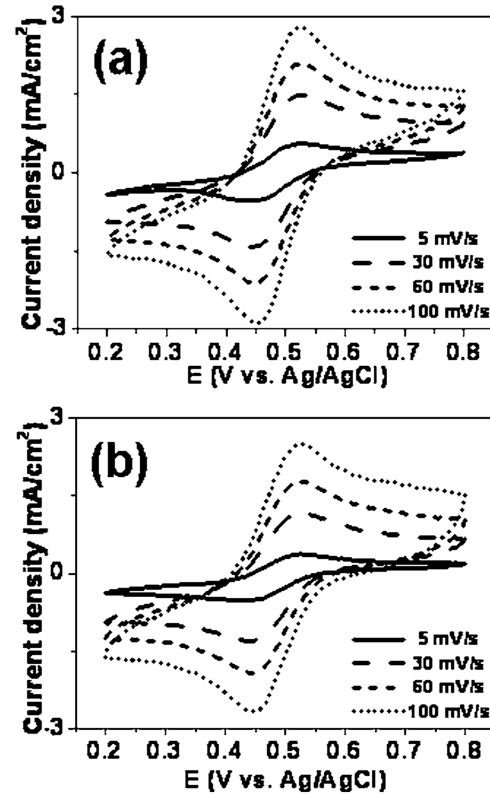

FIG. 3. Cyclic voltammograms of CN_x NTs grown with a 200-nm-thick Ti buffer layer on (a) *n*-type and (b) n^+-type Si substrates.

It is therefore concluded that the oxidation step plays an important role in surface morphologies of CN_x NTs.

According to the results of Figs. 1(a) and 1(b), the anode-cathode current densities on *n*- and n^+-Si substrates are 1.6–1.4 and 1.8–0.8 mA/cm^2 at the Ti thickness of 20 nm. At the thicker layer of 200 nm, the corresponding current-density values calculated from Figs. 3(a) and 3(b) are 2.5–2.5 and 2.2–2.0 mA/cm^2. Therefore, much higher current densities can be achieved on a 200 nm Ti buffer layer, irrespective of the substrate type. Nearly ideal electron-transfer kinetics[24] were attained on both 200 nm Ti samples and on n^+ Si with a 20 nm Ti buffer layer. The results demonstrate that enhanced Faradaic response with ideal electron-transfer kinetics can be achieved employing thick Ti buffer layer, hence eliminating the effect of the substrate.

Although a better EC performance was shown, using Ti as buffer layer electrochemically was unstable against reaction with Si substrate. Eventually, the better approach is to use $TiSi_2$ in place of Ti. Prior to the growth, vacuum annealing of the Ti-coated Si substrate at 800 °C for 2 h was carried out to form the $TiSi_2$ phase, which was verified by x-ray diffraction (XRD) characterization, as shown in Fig. 4. Moreover, as depicted in the inset of Fig. 4, subsequent directional growth of CN_x NTs on such a substrate has also been achieved. It is worth noting that $TiSi_2$ is a preferred choice for use as a contact and interconnect material in microelectronics because it exhibits low resistivity and excellent chemical stability.

EC reactivities of CN_x NTs on $TiSi_2/n$-Si and Ti foils are shown in Figs. 5(a) and 5(b). The Ti foil plays the role of an ideal bulk conductor and is used here as a reference for purposes of comparison. Both samples exhibited very similar characteristics, namely, a current density of 2.5 mA/cm^2 at the scan rate of 100 mV/s and a DEp value of 69 mV at 5 mV/s. In other words, the electrochemical performance of CN_x NTs on $TiSi_2/n$-Si is as good as that on Ti foils. Peak-current density as a function of the scan-rate root is plotted in Fig. 5(c). A linear relationship between peak-current (i_c/i_a) values and $v^{1/2}$ was observed at scan rates between 5 and

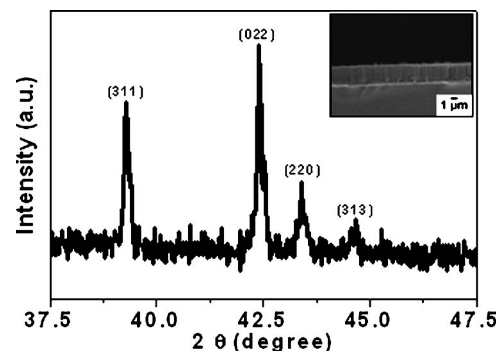

FIG. 4. XRD pattern shows $TiSi_2$ phase formation. The SEM image of CN_x NTs on $TiSi_2/n$-Si is shown in the inset.

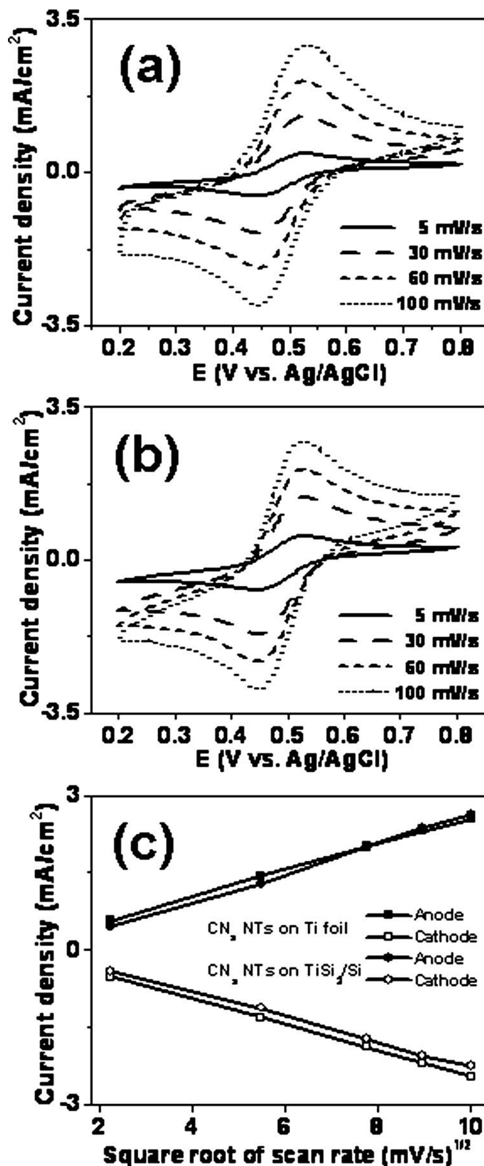

FIG. 5. Cyclic voltammograms of CN_x NTs on (a) $TiSi_2/n$-Si and (b) Ti foils. (c) The peak-current densities as a function of the square root of scan rate for both anode and cathode.

100 mV/s for both samples, indicative of reactions limited by semi-infinite linear diffusion of reactants to the electrode surface.

IV. CONCLUSIONS

In summary, the optimized electrochemical performance of arrayed nitrogen-containing carbon nanotubes (CN_x NTs) on Si substrates using $TiSi_2$ as a buffer layer has been investigated. We used ferricyanide as the molecule probe to study the electrochemical properties of CN_x NTs on different types of Si substrates with Ti buffer layers 20- and 200 nm thick. The use of a 20 nm Ti buffer layer would give rise to vertically aligned growth of CN_x NTs. However, the electrochemical performance was quasireversible only on n^+- and p^+-Si substrates. Increasing the thickness of the Ti buffer layer to 200 nm, the EC performance became independent of the type of the substrate. Nevertheless, the use of thick buffer layers inhibited directional growth. Oxidation treatment of the catalyst Fe layer prior to the growth could efficiently improve the alignment of CN_x NTs. Pretreatment of the Ti buffer layer at high temperature led to the formation of $TiSi_2$ which displayed ideal Nerstian behavior and current densities comparable to that of CN_x NTs on bulk Ti electrodes. With this work, we have successfully developed a Si-based micro-EC platform with superior reactivity and good alignment for current collection and energy applications.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support for this project from the National Science Council (NSC) and Ministry of Education (MOE) in Taiwan.

This paper was presented at the First International Workshop on One Dimensional Materials, January 10–14, 2005, National Taiwan University, Taipei, Taiwan.

[1]M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996).
[2]G. L. Che, B. B. Lakshmi, E. R. Fisher, and C. R. Martin, Nature (London) **393**, 346 (1998).
[3]W. Z. Li, C. G. Liang, W. J. Zhou, J. S. Qiu, Z. H. Zhou, G. Q. Sun, and Q. Xin, J. Phys. Chem. B **107**, 6292 (2003).
[4]C. Niu, E. K. Sichel, R. Hoch, D. Moy, and H. Tennent, Appl. Phys. Lett. **70**, 1480 (1997).
[5]K. Shokoohi, J. M. Tarascon, and B. J. Wilkens, Appl. Phys. Lett. **59**, 1260 (1991).
[6]B. J. Neudecker, N. J. Dudney, and J. B. Bates, J. Electrochem. Soc. **147**, 517 (2001).
[7]R. B. Goldner, T. Y. Liu, and S. Slaven, J. Electrochem. Soc. **143**, L129 (1996).
[8]D. R. Baker and M. W. Verbrugge, J. Electrochem. Soc. **146**, 2413 (1999).
[9]J. M. McGraw, C. S. Bahn, and P. A. Parilla, Electrochim. Acta **45**, 187 (1999).
[10]J. B. Bates, N. J. Dudney, and B. Neudecker, Solid State Ionics **135**, 33 (2000).
[11]S. V. Golod, V. Y. Prinz, and P. Wagli, Appl. Phys. Lett. **84**, 3391 (2004).
[12]J. H. Sung, S. Kim, and K. H. Lee, J. Power Sources **133**, 312 (2004).
[13]Y. H. Lee, K. H. An, J. Y. Lee, and S. C. Lim, in *Encyclopedia of Nanoscience and Nanotechnology*, edited by H. S. Nalwa (American Scientific, New York, 2004).
[14]B. E. Conway, *Electrochemical Supercapacitors-Scientific Fundamentals and Technological Applications* (Kluwer Academic, New York, 1999).
[15]D. S. Yu, C. H. Huang, A. Chin, C. X. Zhu, M. F. Li, B. J. Cho, and D. L. Kwong, IEEE Electron Device Lett. **25**, 138 (2004).
[16]Y. H. Wu, W. J. Chen, S. L. Chang, A. Chin, S. Gwo, and C. Tsai, IEEE Electron Device Lett. **20**, 200 (1999).
[17]C. Y. Lin, M. W. Ma, A. Chin, Y. C. Yeo, C. X. Zhu, M. F. Li, and D. L. Kwong, IEEE Electron Device Lett. **24**, 348 (2003).
[18]V. S. Neshpor and G. V. Samsonov, Sov. Phys. Solid State **2**, 1966 (1960).
[19]S. P. Muraka and D. B. Fraser, J. Appl. Phys. **51**, 350 (1980).
[20]S. P. Muraka, *Silicides for VLSI Applications* (Academic, New York, 1983).
[21]V. Kolotyrkin, V. Knyazheva, O. Yurchenko, Y. Kolosvetov, and T. Toyanovskaya, Prot. Met. **28**, 418 (1992).
[22]L. C. Chen, C. Y. Wen, C. H. Liang, W. K. Hong, K. J. Chen, H. C. Cheng, C. S. Shen, C. T. Wu, and K. H. Chen, Adv. Funct. Mater. **12**, 687 (2002).
[23]Y. H. Wang, J. Lin, C. H. A. Huan, and G. S. Chen, Appl. Phys. Lett. **79**, 680 (2001).
[24]P. T. Kissinger and W. R. Heineman, *Laboratory Techniques in Electrochemical Chemistry* (Marcel Dekker, New York, 1988).