Available online at www.sciencedirect.com
ScienceDirect
Sensors and Actuators B 129 (2008) 67–71
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

The gas sensing properties of single-walled carbon nanotubes deposited on an aminosilane monolayer

Thu Hong Tran, Jin-Woo Lee, Kyongsoo Lee, Yang Doo Lee, Byeong-Kwon Ju *

Display and Nanosystem Laboratory, College of Engineering, Korea University, Seoul 136-713, Republic of Korea

Received 14 May 2007; received in revised form 17 July 2007; accepted 18 July 2007
Available online 2 August 2007

Abstract

This paper presents our study on the effects of an aminosilane monolayer on the gas sensing properties of single-walled carbon nanotubes (SWCNTs). A gas sensor for nitrogen dioxide (NO_2) detection was fabricated by conventional photolithography process on an oxidized silicon wafer functionalized with 3-aminopropyltriethoxysilane (APTES). Such a CNT-based gas sensor was found to result in high sensitivity and fast response time compared with the sensor fabricated on a non-silanised surface. The amine groups in the APTES monolayer, electron donating in nature, played a role of charge transfer to the semiconducting SWCNTs, and hence the amount of electrons transferred from SWCNTs to NO_2 molecules increased. Our results suggest that the APTES intended originally for selective placement of individual SWCNTs could be used to enhance the gas sensing properties of the SWCNTs.

Keywords: Single-walled carbon nanotubes (SWCNTs); Nitrogen dioxide (NO_2); Self-assembled monolayer (SAM); Gas sensor; Electron donation

1. Introduction

Ever since the discovery in 1991 [1], carbon nanotubes (CNTs) as new materials with outstanding properties are promising for a variety of potential applications especially in the field of gas sensing. CNTs-based gas sensors have received much attention because they offer the possibility of excellent sensitivity, low operating temperature, rapid response time and sensitivities to various kinds of gases. A CNT, with a large surface-to-volume ratio, as well as remarkable electrical properties and the interesting relationship between their geometric structure and electronic properties, is a strong candidate for gas sensing. Electron donating and withdrawing molecules such as NO_2, NH_3, O_2, etc. either transfer electrons to or withdraw electrons from SWCNTs. This gives the SWCNTs more charge carriers or holes, respectively, and increases or decreases, dramatically, the conductance of SWCNTs [2–4].

However, up-to-date, the lack of a simple and reliable process to deposit CNTs in a controlled way is holding back CNTs-based gas sensors for practical applications. Recently, an approach named "surface-programmed assembly" based on patterns of a self-assembled monolayer (SAM) of molecules with positively charged and neutral terminal groups, 3-aminopropyltriethoxysilane (APTES) and 1-octadecyltrichlorosilane (OTS), respectively, was reported [5]. Burghard et al. first reported that the surfactant-stabilized nanotubes can be specifically adsorbed onto the amino silanised SiO_2 surface [6]. More recently, selective placement of large numbers of SWCNTs into nanolithographically defined regions of APTES was reported by Choi et al. [7] and later by Lewenstein et al. [8]. The self-assembled CNTs and nanowires (NWs) relied on the polar and non-polar or hydrophilic and hydrophobic SAM patterns have been studied by a number of researchers [5–15]. On the SiO_2 surface, hydrophilic surface molecular patterns are utilized to assemble and align CNTs and NWs over a large surface area, while hydrophobic surface molecular patterns are utilized to avoid any unwanted adsorption of CNTs and NWs. The functionalized surface by the hydrophilic amino-terminated ($-NH_2$) SAM has a high selectivity in which long SWCNTs can be seen bending to align well with the APTES

* Corresponding author at: School of Electrical Engineering, College of Engineering, Korea University, 5-1 Anam-Dong, Seongbuk-Gu, Seoul 136-713, Republic of Korea. Tel.: +82 2 3290 3237; fax: +82 2 921 0544.
E-mail address: bkju@korea.ac.kr (B.-K. Ju).

0925-4005/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2007.07.104

patterns and no nanotubes seem to adhere on non-silanised SiO_2 as shown by Liu et al. [13] and Valentin et al. [16].

Patterning the SAM, which can be done with photolithography, plasma etching and backfilling techniques, ion-beam, e-beam, atomic-beam or scanning probe microscopy lithography, was successfully reported elsewhere in [5–15]. Controlled deposition of CNTs carried out using the SAM features, owing to the simplicity of the processing steps, has opened a new way for the development of CNTs-based electronics devices. However while the use of silanised patterns for CNTs' selective deposition has increased, the influence of APTES on the characteristics of these devices was evaluated in only a few studies. So far, only one study of Auvray et al. was reported on the role of chemical interface SWCNTs/APTES on the device transport properties of CNT field effect transistors [17].

In this letter, we report on our investigation of the effects of a $-NH_2$ functionalized SiO_2 surface on the gas sensing properties of SWCNTs. The uses of a patterned aminosilane monolayer as templates turn out to improve the gas sensor characteristics. SWCNTs which play a role as a sensing material of a resistive gas senor are in contact with electrodes and deposited directly on the SiO_2 bare surface or via the APTES SAM. We investigated the characteristics of the sensors when exposed to NO_2 and discussed the function of the amine groups on APTES monolayer.

2. Experimental

The SWCNT powder (purchased from Iljin Nanotech Co. Ltd.) has properties of 1–1.2 nm in average diameter, 5–20 μm length and ~90% purity (prepared by an arc-discharge process). The CNTs were used without further purification. Prior to the SWCNTs manipulation, 8 mg of the sample was ultrasonically dispersed in 40 ml dimethylformamide (DMF) for 4 h (at a pulse cycle: 1 s on, 1 s off and at 200 W). The resulting solution was diluted to 20 mg/L. The DMF organic solvent was chosen to debundle the SWCNTs ropes because the amine groups can easily attach to the surface of the nanotubes providing a uniformly suspended SWNT solution [13,16]. Fig. 1(a) and (b) shows the schematic diagram of the sensor without the surface treatment and the illustration of silanization process of the sensor with surface treatment. The fabrication of the interdigitated electrode (IDE) was carried out using a conventional photolithographic method with a finger width of 10 μm and a gap size of 10 μm. The interdigitated electrode fingers were made by an e-beam evaporating the 30 nm Ti and 200 nm Au on a layer of SiO_2 which was grown thermally on top of a silicon wafer, as shown in Fig. 1(a). Then, the substrate modification as shown in Fig. 1(b) was accomplished by adopting an APTES 99% purchased from Aldrich Co. monolayer in vapor phase on its surface after the fabrication of electrodes. The wafer was first carefully cleaned; soaked in acetone for 5 min, soaked with ultrasonic agitation for 5 min twice, rinsed in deionized water, and dried by a nitrogen blow. Following this, the wafer was further cleaned by microwave plasma ash for 10 min in order to enhance the quality for the APTES monolayer. It was found that the thickness of the APTES layer was important because CNTs did not seem to adhere to the surface if there was more than one monolayer of APTES [16]. Then, the wafer was placed in a sealed container in the presence of APTES, and put in an oven at 130 °C for 3 h. After cooling, the wafer was washed carefully first with ethanol and then with water for the removal of all not chemically bound silane. A quantity of 0.05 μL of a 20 mg/L SWCNT–DMF solution was drop deposited in the area between microelectrodes using a hot plate. We experimentally found that the resistances of the SWCNTs at room temperature typically ranged from several kΩ to several hundreds of kΩ, depending on the density of the SWCNTs across the IDE fingers. In our experiments, the resistance value was controlled to about a few kΩ. This resistance was performed after removal of the solvent DMF. The SWCNTs, on the IDE, were dried under vacuum at 350 °C for 9 h to remove the DMF residue. The morphology of SWCNTs was observed by scanning electron microscopy (SEM, Hitachi S-4300). The sensor output was measured by using a source meter (Keithley 2400) and LabVIEW (National Instruments Corp., Austin, TX) software. The gas concentrations of the NO_2 mixture were 10 ppm and 50 ppm. N_2 was used to purge gas. The chamber was first filled with N_2 gas then NO_2 was introduced. During the experiments, the gas sensor was placed in a sealed chamber through a vacuum at a pressure of 1×10^{-3} Torr. The gas was introduced at a pressure of 5×10^{-3} Torr in the vacuum system. The whole process and all the measurements were carried out at room temperature. Fig. 2 shows a schematic of the experimental setup for measurement of the gas sensing behavior.

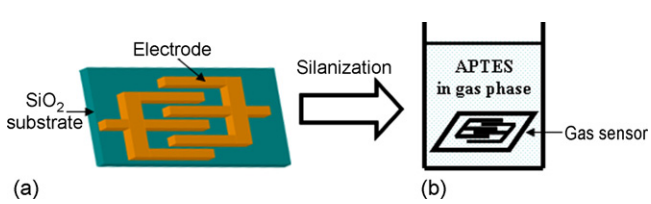

Fig. 1. (a) A schematic view of the gas sensor without surface treatment and (b) illustration of silanization process of the sensor with surface treatment.

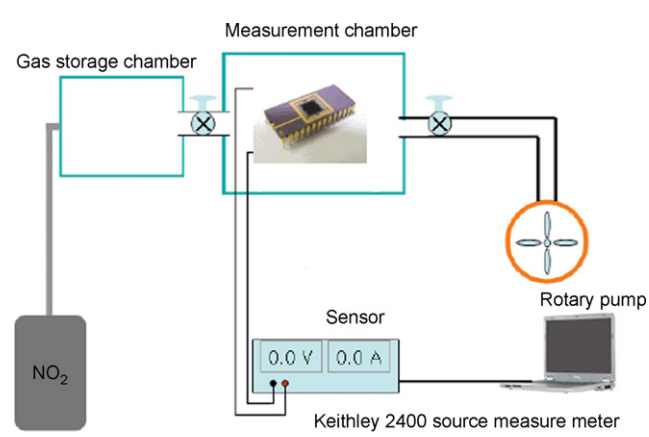

Fig. 2. A schematic of the experimental setup for the measurement the gas sensor behavior.

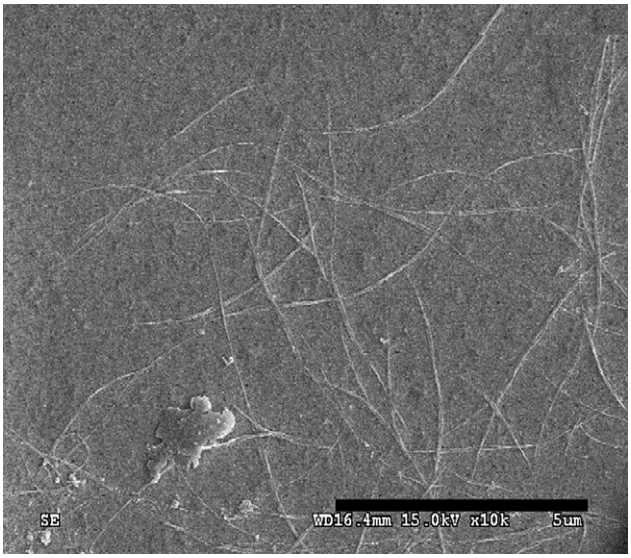

Fig. 3. SEM image of the SWCNTs after drying deposited on the APTES monolayer.

3. Results and discussions

A surface treatment by APTES was found to result in a two times higher relative resistance changes and faster response time for the SWCNTs-based gas sensor compared with the sensor fabricated on a non-silanised SiO_2 surface. Fig. 3 shows the SEM image of SWCNTs adhesion on the APTES monolayer. The SEM images of the interdigitated electrode and SWCNTs on the bare and treated surface crossed the microelectrodes are shown in Fig. 4(a)–(c), respectively. The SEM observation was conducted after removing DMF at 350 °C in an oven for 9 h. The SEM images revealed that the density of the SWCNTs on APTES was significant. The sensor relative resistance change (R_r) is defined as $R_r = [(R - R_0)/R_0] \times 100$. R_0 is the resistance of the SWCNTs when exposed to ambient N_2 and R represents the resistance upon exposure to NO_2. Fig. 5(a) shows the plots of the relative resistance change versus time of the SWCNTs upon exposure to 10 ppm NO_2, resulting from the bare and treated surfaces. Similar results were obtained for 50 ppm NO_2 detection experimentally, as shown in Fig. 5(b). The improved relative resistance changes after 200 s under gas exposure of the gas sensor with the surface treatment, compared to those without the surface treatment, were calculated and are represented in Table 1. The relative resistance changes of the SWCNTs are improved from $R_r = 21\%$ to 53% under exposure of 10 ppm NO_2 and from $R_r = 30\%$ to 74% under exposure of 50 ppm NO_2. We defined the response time as the time for 90% total resistance change. It can be seen from Fig. 5(a) and (b) that the response time of the gas sensor in the case of the bare surface was slow (hundreds of seconds), while the response time of the gas sensor in the case of the treated surface was fast (a few seconds). The much faster response of the treated sensor than the normal sensor indicates that the chemical potential barrier against gas adsorption is lower. The reason for this might be that the characterization of the APTES layer and the interaction of the APTES with the sidewall of SWCNTs gave easier accessibility during adsorption.

Table 1
Relative resistance changes of the gas sensor with and without surface treatment after 200 s upon gas exposure

Relative resistance changes (%)	NO_2 (10 ppm)	NO_2 (50 ppm)
Silanised surface	53.5	75
Un-silanised surface	21.1	30.6

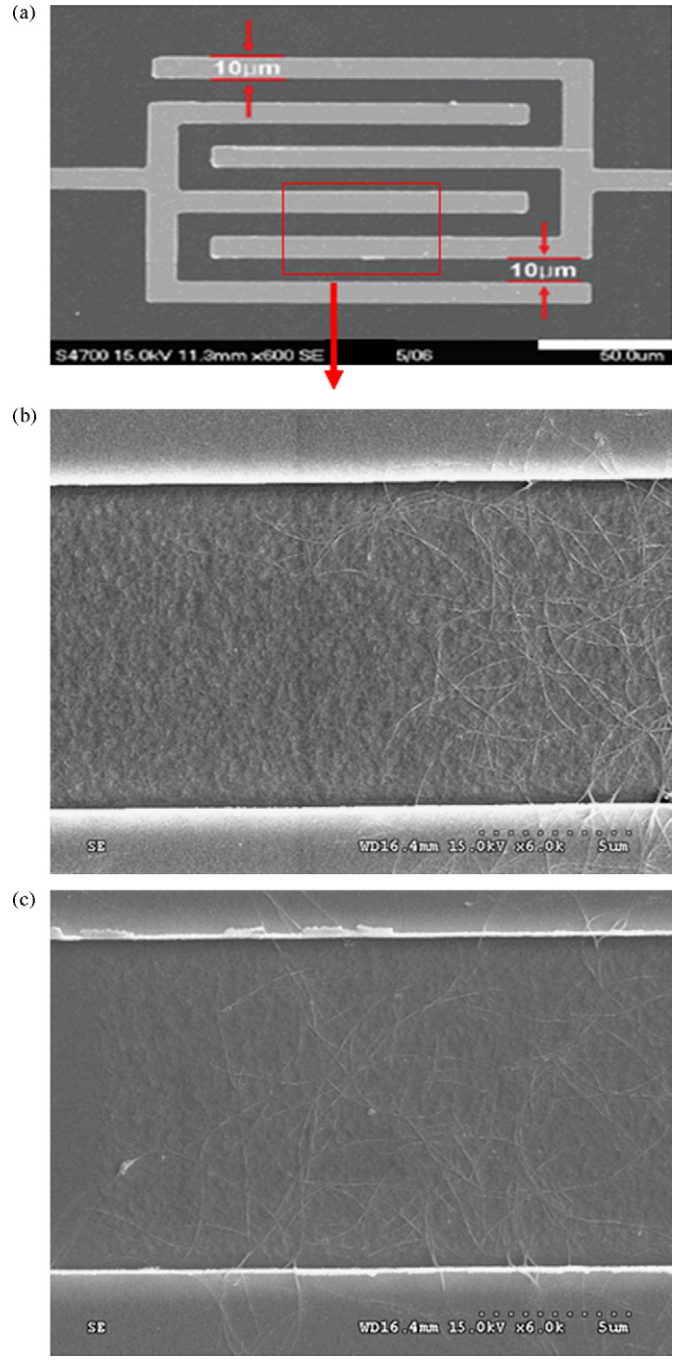

Fig. 4. SEM images of the (a) interdigitated electrodes, SWCNTs after drying (b) across the two electrodes on the bare surface and (c) across the two electrodes on the treated surface.

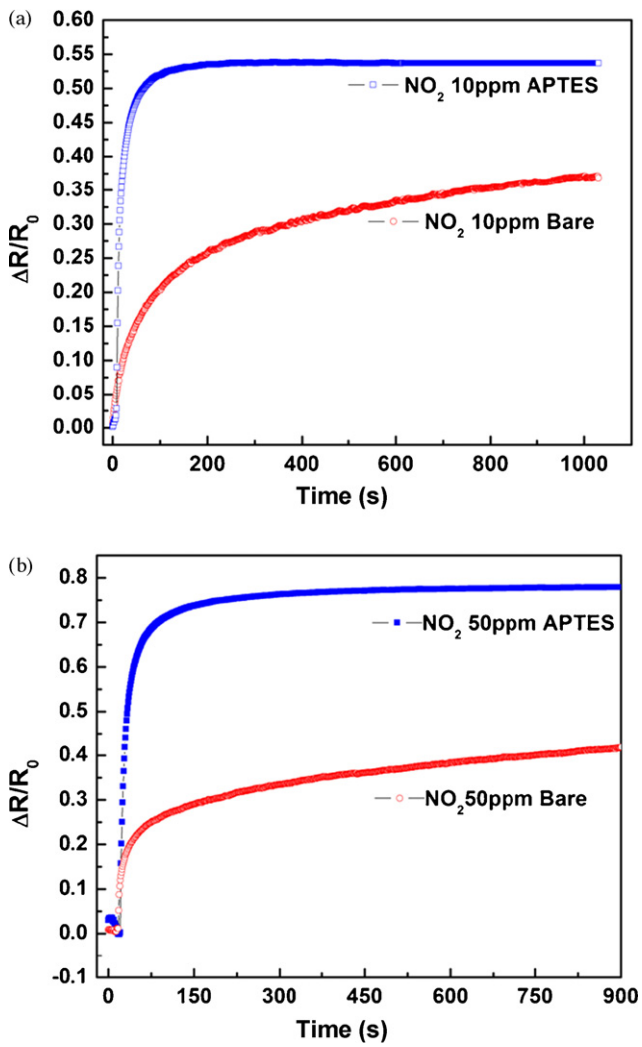

Fig. 5. Relative resistance changes vs. time of the SWCNTs on a bare and treated surface upon exposure to (a) 10 ppm NO_2 and (b) 50 ppm NO_2.

The SWCNTs adhered on the bare surface as well as on the treated surface exhibited a typical p-type electrical property while decreasing the electrical resistance upon exposure to a NO_2 atmosphere, as shown in Fig. 6. In order to investigate the effect of APTES to the desorption process of our sensors the experiment was carried out at room temperature without heating treatment. Fig. 6 shows the resistance changes when the sensors were exposed to 50 ppm NO_2 for three cycles as a function of time. As seen in Fig. 6, the surface treatment by the APTES monolayer did not affect the recovery time, the recovery time being even a little worse than the sensor without surface treatment. The –OH groups on a bare SiO_2 surface turn to the $–NH_2$ groups of the APTES monolayer on the treated surface after modification, as schematically shown in Fig. 7(a)–(c) shows the energy band diagram of the individual p-type semiconducting SWCNT on un-silanised and silanised SiO_2, respectively, under exposure to NO_2 molecules. The NO_2 molecules attached to the walls of the SWCNTs acted as electron acceptor molecules. The interaction between the amine groups of the APTES and the semiconducting SWCNTs has been reported by Kong and Dai [18]. Electron donating due to the amine-terminating group

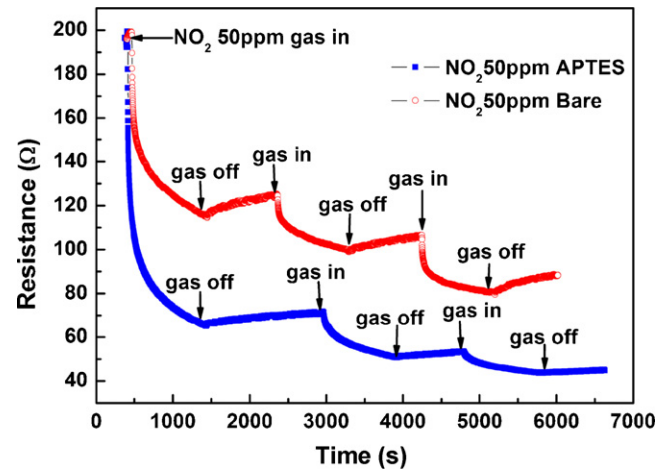

Fig. 6. Resistance changes vs. time of the SWCNTs on a bare and treated surface upon exposure to 50 ppm NO_2 at room temperature for three cycles.

($–NH_2$) on the monolayer will transfer electrons to SWCNTs, thereby giving more charge carriers to the SWCNTs. Therefore, it is reasonable to consider that the amine groups introduced on the surface caused an enhancement of charge density in the SWCNTs and hence increased the amount of electron transfer between SWCNTs and gas molecules which increased the hole current of p-type SWCNTs. Moreover, when a gas sensor is put in an environment containing some kinds of gas molecules, the molecules are adsorbed onto the SWNTs, the APTES SAM and the metal electrodes. The metal/SWNTS interface is similar to the case without surface treatment. However, in the case with surface treatment, the presence of the APTES monolayer close to the NT/metal interface may result in an increased dipole density and thus a more substantial Schotkky barrier lowering,

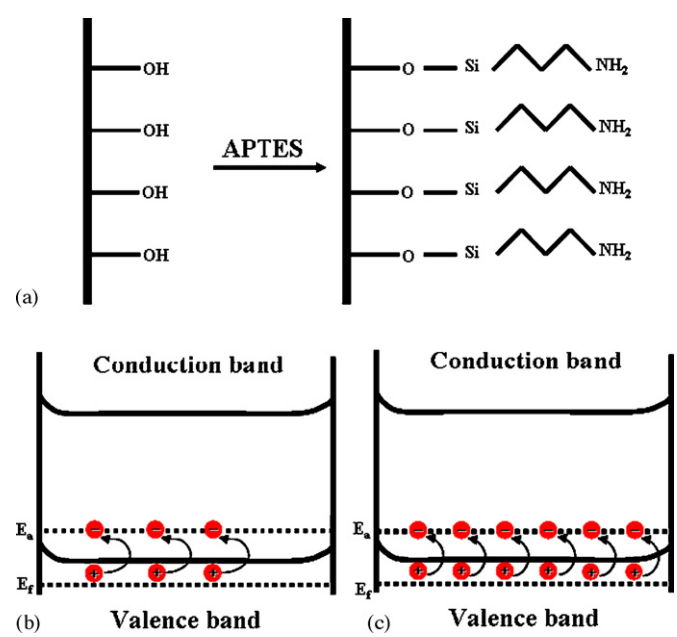

Fig. 7. (a) The silanization of the SiO_2 surface by APTES. An energy band diagram of the individual semiconducting p-type SWCNT on (b) un-silanised and (c) silanised SiO_2 upon exposure to NO_2 gas molecules.

as reported by Auvray et al. [17], which leads to the better improvement of gas sensitivity.

4. Conclusions

In conclusion, we fabricated a gas sensor based on SWCNTs with and without surface treatment with an aminosilane SAM. We investigated the electrical resistance response of the SWCNTs on the bare SiO_2 surface and on the surface treated with the APTES monolayer to ppm level of NO_2 at room temperature. The SWCNTs adhered to the bare surface as well as on the treated surface exhibited a typical p-type electrical property of a decrease in resistance upon exposure to the NO_2 atmosphere. The relative resistance changes of the SWCNTs to NO_2 in the case of the APTES-treated surface were twice larger than the case without surface treatment under the same conditions. The surface treatment by the APTES did not affect the recovery time of the gas sensor. A significantly fast response time of the sensor with the APTES-treatment was observed when exposed to 10 ppm or 50 ppm NO_2. The interaction between the SWCNTs/APTES and the gas molecules was also discussed. These results showed that the method for selective deposition of CNTs relied on the SAM patterns can be further optimized for better performance of gas sensing. Thus, the method has high potential for gas sensor applications.

Acknowledgements

This work was supported in part by MIC and IITA through the IT Leading R&D Support Project. The authors thank the government for financial support.

References

[1] S. Iijima, Helical microtubules of graphitic carbon, Nature 354 (1991) 56–58.
[2] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai, Nanotube molecular wires as chemical sensors, Science 287 (2000) 622–625.
[3] O.K. Varghese, P.D. Kichambare, D. Gong, K.G. Ong, E.C. Dickey, C.A. Grimes, Gas sensing characteristics of multi-wall carbon nanotubes, Sens. Actuators B: Chem. 81 (2001) 32–41.
[4] J. Li, Y. Lu, Q. Ye, M. Cinke, J. Han, M. Meyyappan, Carbon nanotube sensors for gas and organic vapor detection, Nano Lett. 3 (2003) 929–933.
[5] S. Myung, M. Lee, G.T. Kim, J.S. Ha, S. Hong, Large scale "surface-programmed assembly" of pristine vanadium oxide nanowire-based devices, Adv. Mater. 17 (2005) 2361–2364.
[6] M. Burghard, G. Duesberg, G. Philipp, J. Muster, S. Roth, Controlled adsorption of carbon nanotubes on chemically modified electrode arrays, Adv. Mater. 10 (1998) 584–586.
[7] K.H. Choi, J.P. Bourgoin, S. Auvray, D. Esteve, G.S. Duesberg, S. Roth, M. Burghard, Controlled deposition of carbon nanotubes on a patterned substrate, Surf. Sci. 462 (2000) 195–202.
[8] J.C. Lewenstein, T.P. Burgin, A. Ribrayro, L.A. Nagahara, R.K. Tsui, High-yield selective placement of carbon nanotubes on pre-patterned electrodes, Nano Lett. 2 (2002) 443–446.
[9] H. Ko, S. Peleshanko, V.V. Tsukruk, Combining and bending of carbon nanotube array with confined microfluidic flow on patterned surfaces, J. Phys. Chem. B 108 (2004) 4385–4393.
[10] J.W. Im, M. Lee, S. Myung, L. Huang, S.G. Rao, D.J. Lee, J. Koh, S. Hong, Directed-assembly of single-walled carbon nanotubes using self-assembled monolayer patterns comprising conjugated molecular wires, Nanotechnology 17 (2006) 3569–3573.
[11] H. Ko, V.V. Tsukruk, Liquid-crystalline processing of highly oriented carbon nanotube arrays of thin-film transistors, Nano Lett. 6 (2006) 1443–1448.
[12] Y. Wang, D. Maspoch, S. Zou, G.C. Schatz, R.E. Smalley, C.A. Mirkin, M. Cowley, Controlling the shape, orientation, and linkage of carbon nanotube features with nano affinity templates, Proc. Natl. Acad. Sci. U.S.A. 103 (2006) 2026–2031.
[13] J. Liu, M.J. Casavant, M. Cox, D.A. Walters, P. Boul, W. Lu, A.J. Rimberg, K.A. Smith, D.T. Colbert, R.E. Smalley, Controlled deposition of individual single-walled carbon nanotubes on chemically funtionalized templates, Chem. Phys. Lett. 303 (1999) 125–129.
[14] A.W. Harant, S.G. Wipple, K. Douglass, C.N. Bowmana, Micropatterning organosilane self-assembled monolayers with plasma etching and backfilling techniques, Amer. Vac. Soc. 23 (2005) 354–358.
[15] C.K. Harnett, K.M. Satyalakshmi, H.G. Craighead, Low-energy electron-beam patterning of amine-functionalized self-assembled monolayers, Appl. Phys. Lett. 76 (2004) 2466–2468.
[16] E. Valentin, S. Auvray, J. Goethals, J. Lewenstein, L. Capes, A. Filoramo, A. Ribayrol, R. Tsui, J.P. Bourgoin, J.N. Patillon, High-density selective placement methods for carbon nanotubes, Microelectron. Eng. 61–62 (2002) 491–496.
[17] S. Auvray, V. Derycke, M. Goffman, A. Filoramo, O. Jost, J.P. Bourgoin, Chemical optimization of self-assembled carbon nanotube transistors, Nano Lett. 5 (2005) 451–455.
[18] J. Kong, H. Dai, Full and modulated chemical gating of individual carbon nanotubes by organic amine compounds, J. Phys. Chem. B 105 (2001) 2890–2893.

Biographies

Thu Hong Tran received her BS degree from the Department of Electrical Engineering, Vietnam National University, Hanoi, in 2001. Currently, she is a master candidate in the Department of Electrical Engineering, Korea University. Her current research interests include the application of carbon nanotubes to bio- and chemical- sensors.

Jin-Woo Lee received his PhD degree from the Department of Mechanical Engineering, Seoul National University in 1999. He worked in Max-Planck Institute for micro-structural physics, Germany and in Watter-Schottkey Institute of Technische Universitat Munchen, Germany. He joined Korea University as a research professor from 2006 for the development of nanoscale sensor and Bio MEMS.

Kyongsoo Lee received his MS degree from the Department of Electrical Engineering, Korea University in 2007. Currently, he is a doctor course candidate in the Nano Device Research Center, Korea Institute of Science and Technology, KIST. His current research interests include the carbon nanotube sensor, nanoimprint lithography and fuel cell.

Yang Doo Lee received his BS and MS degrees from the Department of Materials Science and Engineering, Pukyong National University in 1997 and 1999, respectively. He received his PhD degree in the Department of Materials Science and Engineering from Korea University in 2007. He has been a postdoctoral research of Korea University with his main interest in field emission device, sensor and carbon nanotube-based nanosystems.

Byeong-Kwon Ju received the ME in electronics engineering from University of Seoul in 1988 and PhD in semiconductor engineering from Korea University in 1995. In 1988, he joined the Korea Institute of Science and Technology (KIST), Seoul, where he was engaged in development of mainly silicon micromachining and micro-sensors as a principal research scientist. In 1996, he spent 6 months as a visiting research fellow at Microelectronics Centre, University of South Australia, Australia. Since 2005, he has been an associate professor of Korea University with his main interest in flexible electronics (OLED, OTFT), field emission device, MEMS (Bio and RF) and carbon nanotube-based nanosystems.