Current Applied Physics 15 (2015) 377–382

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Different mechanism of capacitance change for gas detection using semiconducting and metallic single-walled carbon nanotubes

Seong Chu Lim [a, b, *], Jung Hyun Yoon [c], Dinh Loc Duong [a], Young Woo Cho [a], Tae Hyung Kim [b], Soo Min Kim [d], Ha Ryong Hwang [c], Young Hee Lee [a, b, *]

[a] Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Republic of Korea
[b] IBS Center for Integrated Nanostructure Physics, Institute for Basic Science (IBS), Daejeon 305-701, Republic of Korea
[c] WISE CONTROL Inc., R&D Division 199, Sanggal-dong, Giheung-gu, Youngin-si, Gyeonggi-do 446-905, Republic of Korea
[d] Korea Institute of Science and Technology, Eunhari san 101, Wanju-gun, Jeonbuk 565-905, Republic of Korea

ARTICLE INFO

Article history:
Received 6 December 2014
Received in revised form
11 January 2015
Accepted 19 January 2015
Available online 19 January 2015

Keywords:
Carbon nanotubes
Gas sensor
Quantum capacitance
Orientation polarization
Density of states

ABSTRACT

Semiconducting single-walled carbon nanotubes (s-SWCNTs) with lower absorption energy of NO_2 gas exhibited higher sensitivity than metallic SWCNTs. The result originated from quantum capacitance of s-SWCNTs, which was readily affected by charge transfer, whereas that of m-SWCNTs showed no change with even more transferred charges. However, m-SWCNT that were aligned polarize adsorbed gases on the surface by a local field that contributed the capacitance changes of m-SWCNT networks. This is a newly introduced detection mechanism of gas sensing using m-SWCNTs.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) have demonstrated superb responses to various gases due to the full utilization of a large surface area of exposed carbon that, as a consequence, facilitates direct interactions with foreign gases. In particular, the existence of π electrons on the SWCNT surface provides the best platform for sensors with reasonable adsorption energies and adsorption/desorption time [1,2]. Adsorption of gases in general involves changes in resistance, charge transfer, threshold voltage, dielectric constant, and capacitance [3–8]. For instance, a resistive-type gas sensor measures the conductance variation due to the charge transfer between CNTs and the target gases, whereas the change in dielectric constant cannot be measured directly with this approach.

Gas adsorption on CNTs has also been characterized by measuring the capacitance (C) [9–13]. Change in dielectric constant (ε) by the adhesion of gases with different ε on a sensing element, was reported to cause the capacitance change (ΔC). More specifically, the capacitance change originates from both polarization of gases due to a strong local electric field (C_d) and quantum capacitance (C_q) of the CNTs, although these effects compete with each other depending on the electrode geometries [14–16]. This is competing effect, together with dynamic behaviors in a capacitive-type sensor, is often advantageous in classifying and identifying target gases by simultaneously measuring both electronic and dielectric properties of the CNTs upon gas adsorption, as opposed to the resistive-type which measures only the electronic properties of the CNTs.

Analyses of the gas detection mechanism of SWCNTs have been often made ambiguous by the presence of both metallic (m-) and semiconducting (s-) SWCNTs in the channel. Since m-SWCNTs in the channel are expected to exhibit different responses from those of s-SWCNTs, use of a single type of SWCNT is highly desired. The capacitive responses of gas sensors can be stemmed from both charge transfer and dielectric constant change, separate tests with only s- and m-SWCNTs are desired to differentiate the two effects-charge transfer and dielectric constant change-between them, which has not yet been reported.

The purpose of this letter is to elucidate the underlying

* Corresponding authors. IBS Center for Integrated Nanostructure Physics, Institute for Basic Science (IBS), Daejeon 305-701, Republic of Korea.
E-mail addresses: seonglim@skku.edu (S.C. Lim), leeyoung@skku.edu (Y.H. Lee).

http://dx.doi.org/10.1016/j.cap.2015.01.013
1567-1739/

detection mechanism of the SWCNTs using separated metallic and semiconducting SWCNTs as a channel. We were able to observe different origins of the capacitance change in the metallic channel from that in the semiconducting channel. A remarkable quantum capacitance change of approximately 2500% was observed in s-SWCNTs, originating from a change in the electronic structures near the Fermi level rather than to charge transfers. On the other hand, in the case of m-SWCNTs, no appreciable quantum capacitance variation was observed due to the constant density of states (DOS) near the Fermi level. Instead, the capacitance was increased slightly by the polarization of gases due to strong local electric field in the case of aligned m-SWCNTs. This mechanism does not depend on the electronic structure, but local alignment of SWCNTs, which enables metallic SWCNTs to be used for gas detection.

2. Experimental

Highly purified arc-discharge SWCNTs were dispersed and separated into metallic and semiconducting ones using density gradient ultracentrifugation (DGU) [17]. The purity of the separated SWCNTs was characterized using UV–vis-IR absorption spectroscopy, as shown in Fig. 1(a). The pristine SWCNTs exhibited van Hove singularity peaks both from m- and s-SWCNTs, which were positioned near 700 nm (M_{11}) and 1000 nm (S_{22}), respectively. Optical images of each solution are presented in Fig. 1(b). Suppression of M_{11} peak intensity in s-SWCNTs and of S_{11} peak intensity in m-SWCNTs clearly demonstrated the efficiency of the DGU separation. Two separated solutions were dispensed on the interdigitated electrodes (Cr (10 nm)/Au (50 nm)) with a gap of 2.5 μm by the two different methods of drop casting and dielectrophoresis. The voltage applied for dielectrophoresis was about 5–10 V_{pp} at 10 MHz. Images of the as-prepared devices, presented in Fig. 1(c) and (d), exhibited different distributions of SWCNTs networks, i.e., a random network from drop-casting and an aligned network from dielectrophoresis. Both m-SWCNTs and s-SWCNTs were aligned parallel to the direction of the electric field, independent of the metallicity, which contrasts with the results of a previous report [18]. After deposing SWCNTs, the device capacitance increased by 3–4 orders of magnitude. We were not able to control the uniformity of density of SWCNTs, but the device capacitance was quite consistent under the same deposition conditions. The Raman spectrum shows a clear G-band near 1590 cm^{-1}, as shown in Fig. 1(e). In addition, a broad fluorescent spectrum was also observed due to the presence of surfactant introduced during the

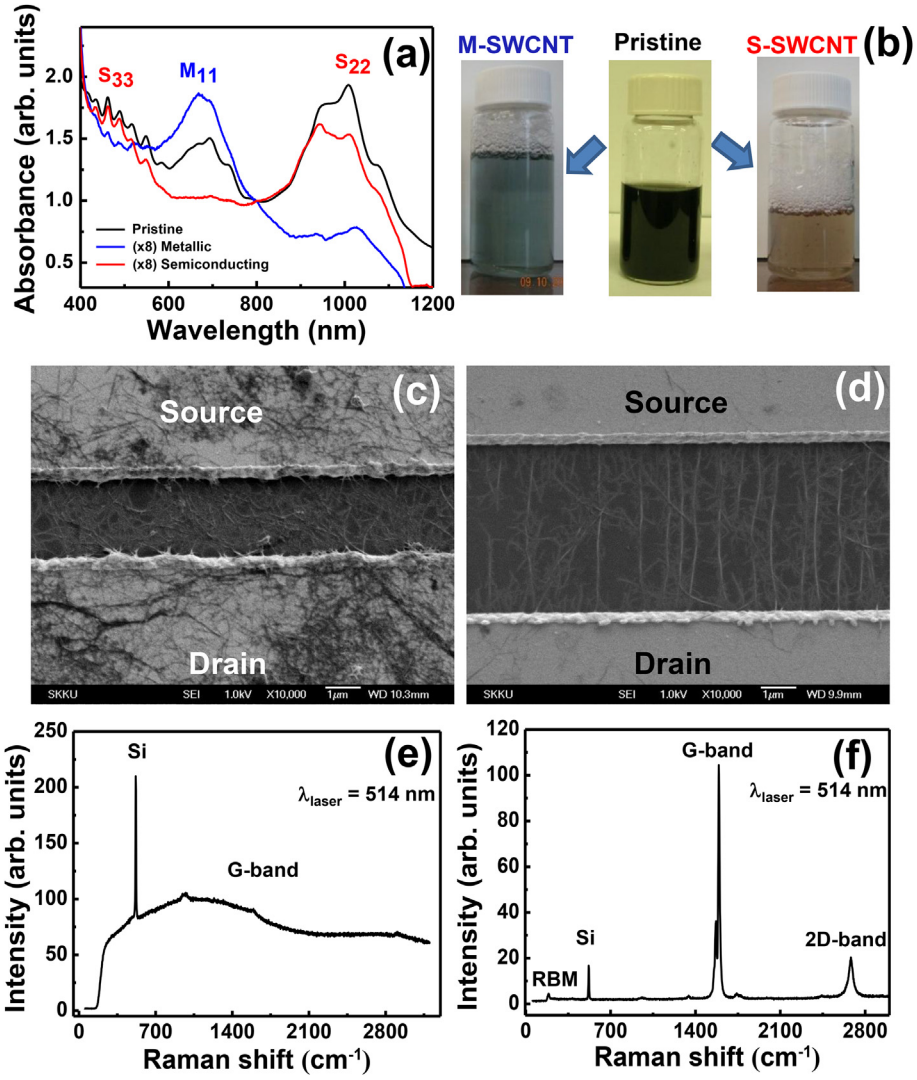

Fig. 1. (a) Absorption spectra and (b) corresponding optical images of the suspensions of pristine SWCNTs, s-SWCNTs, and m-SWCNTs. SEM images of s-SWCNT networks prepared with (c) drop-casting and (d) dielectrophoresis. Raman spectra (e) before and (f) after a rinsing with methanol.