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Gas sensing properties of single-wall carbon nanotubes dispersed with dimethylformamide

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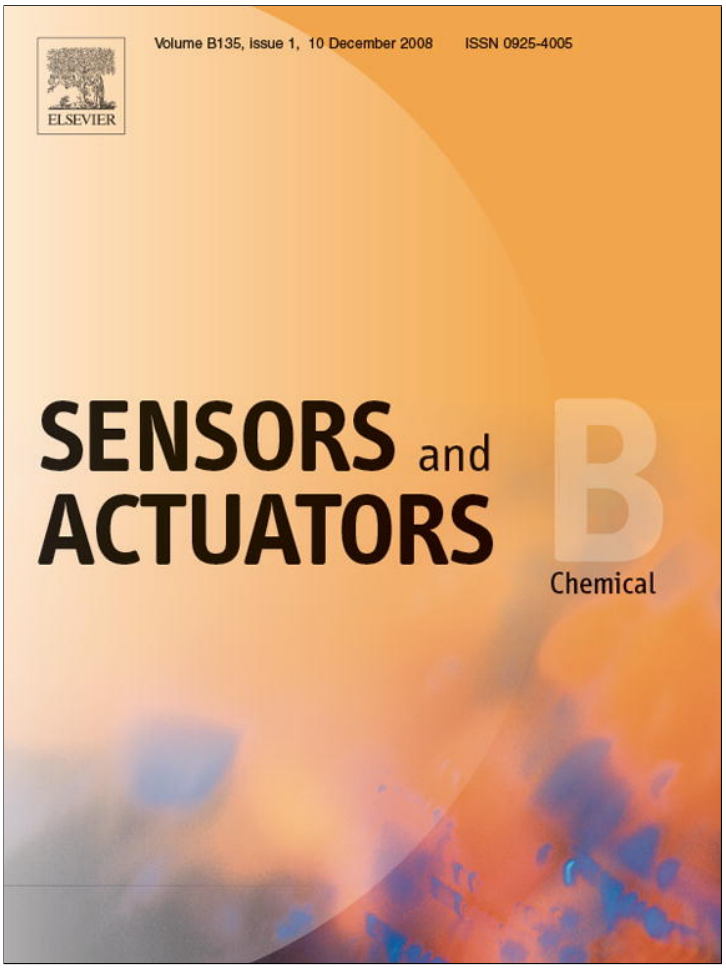
Abstract

For NO_2 gas sensing, we deposited single-walled carbon nanotubes (SWCNTs) on a pair of interdigitated electrodes (IDEs) by using a simple casting method. In order to achieve well-dispersed SWCNTs, we dispersed the as-grown SWCNT powder into dimethylformamide (DMF). We selected DMF as one of the candidate materials to ravel the entangled SWCNT bundles because the amide group could easily attach to the surface of the nanotubes. The resultant SWCNTs were well separated. However, the SWCNTs dispersed in DMF required a heat treatment to eliminate the DMF molecules adsorbed on the surface of the SWCNTs. Therefore, we heated the SWCNTs on the IDEs to 350 °C for 1, 2, 3, and 5 h, to remove the outer DMF adsorbed layers. The assembled sensors were exposed to NO_2 of 3 and 10 ppm concentrations. We attributed the NO_2 gas sensing to the direct charge transfer from the physically adsorbed molecules to the individual p-type semiconducting SWCNTs.

Keywords: Carbon nanotube; Nitrogen dioxide; Gas sensor; Dimethylformamide



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ABSTRACT

For NO_2 gas sensing, we deposited single-walled carbon nanotubes (SWCNTs) on a pair of interdigitated electrodes (IDEs) by using a simple casting method. In order to achieve well-dispersed SWCNTs, we dispersed the as-grown SWCNT powder into dimethylformamide (DMF). We selected DMF as one of the candidate materials to ravel the entangled SWCNT bundles because the amide group could easily attach to the surface of the nanotubes. The resultant SWCNTs were well separated. However, the SWCNTs dispersed in DMF required a heat treatment to eliminate the DMF molecules adsorbed on the surface of the SWCNTs. Therefore, we heated the SWCNTs on the IDEs to 350 °C for 1, 2, 3, and 5 h, to remove the outer DMF adsorbed layers. The assembled sensors were exposed to NO_2 of 3 and 10 ppm concentrations. We attributed the NO_2 gas sensing to the direct charge transfer from the physically adsorbed molecules to the individual p-type semiconducting SWCNTs.

1. Introduction

Carbon nanotubes rank among the most exciting new materials in modern science and engineering. Since Iijima first discovered carbon nanotubes, the past 10 years have witnessed significant progress in both carbon nanotube synthesis and information acquisition, revealing the electrical, mechanical, and chemical properties of the nanotubes. This progress has largely been driven by the exciting science involved, numerous proposed applications of the results indicating unique electronic properties, and the nanometer size specificity of the nanotubes. Single-wall carbon nanotubes are ideally suited for low-dimensional physics, including studies on electron-electron interactions, electron-lattice interactions, electron localization, and band structures. Nanotubes have great potential to be used as nano-scale electronic devices such as field effect transistors, single-electron transistors, and nano-scale p–n junctions. In addition, carbon nanotubes are becoming promising candidates in scope tips, field emitters, and chemical sensors [1–5]. Dai and co-workers were the first to demonstrate that semiconducting single-wall carbon nanotubes act as rapid and sensitive chemical sensors at ambient temperature. They found that the conductivity of the semiconducting SWCNTs changed rapidly by several orders of magnitude upon exposure to nitrogen dioxide and ammonia. Theoretical studies have also predicted significant changes in the electronic properties of carbon nanotubes caused by gas adsorption. These results provide the motivation of applying carbon nanotubes as gas sensors to detect sub-ppm concentrations of oxidizing gases such as NO_2, O_3, and Cl_2 [6–11].

In this study, we demonstrate a simple SWCNT sensor platform with extended application to the sensitive detection of gas molecules. In this platform, SWCNTs form a network or mesh on interdigitated electrodes using a solution casting process, providing a large enough density of SWCNTs for sensor performance. To form a good dispersion, the SWCNTs were dispersed in dimethyl formamide (DMF) until the sample was completely suspended in the solvent. NO_2 was detected with fast response down to the ppm level under room-temperature operation.

2. Experimental

A pair of interdigitated electrodes was fabricated using a conventional photolithographic method with a finger width of 10 μm and a gap size of 10 μm. The interdigitated electrode finger was made by e-beam evaporating 30 nm Ti and 200 nm Au on a layer of silicon dioxide (SiO_2) thermally grown on top of a silicon wafer (Fig. 1).

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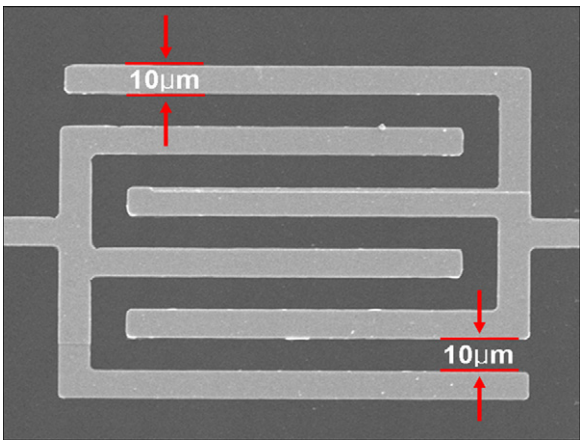

Fig. 1. An SEM image of interdigitated electrodes.

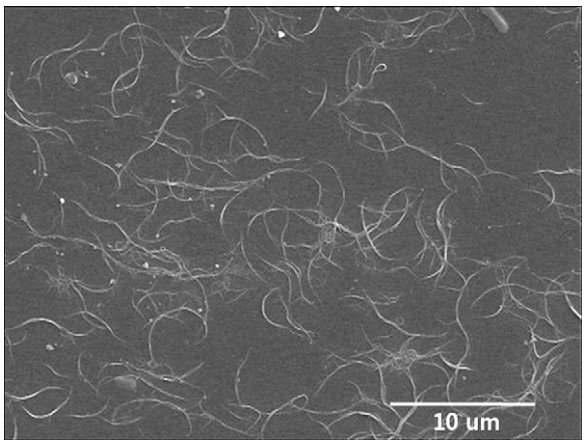

Fig. 3. An SEM image of SWCNTs dispersed with DMF.

Dispersion experiments were carried out using purified SWCNTs. The SWCNT powder used (purchased from Iljin Nanotech Co. Ltd.) had grains of 1–1.2 nm diameter on average, 5–20 μm in length, and ~90% purity (prepared by an arc-discharge method). The purified SWCNTs of 2 mg were then sonically dispersed in dimethylformanide (DMF) of 40 mL to form a suspension (at a power of 200 W and a pulse cycle of 1 s on and 1 s off for 2 h). DMF is known to generate a stable dispersion of carbon nanotubes with extended applications to the sensitive detection of NO_2. The DMF was chosen to untangle the SWCNT bundles because the amide group could easily attach to the surface of nanotubes, providing a uniformly suspended solution of SWCNTs in DMF [12,13].

The SWCNT/DMF solution (0.1 μL) was drop-deposited onto the substrate. This ensured good-quality deposition of SWCNTs on top of the substrate. The density of the SWCNTs across the interdigitated electrodes could be adjusted by varying the concentration of SWCNTs in a DMF solution. There have been advances in this technology that enable the assembly and characterization of SWCNTs in nanoelectronic devices. This technology has a means of suspending individual nanotubes in solution. Such suspensions are also very stable and can be stored at room temperature for several months without precipitation. In Fig. 2, we illustrate images of suspensions of SWCNTs dispersed in DMF and acetone. We observed that the dispersion of SWCNTs in DMF was homogeneous, while the acetone suspension was phase separated with coagulated SWCNTs appearing at the bottom of a vial after 2 months. Thus, the use of DMF provides an opportunity for manipulation of individual nanotubes into nanostructures and nanodevices. However, in this technology, a heat treatment is required to eliminate the DMF molecules adsorbed on the SWCNTs. The DMF-adsorbed SWCNTs cannot detect gas molecules. The heat treatment adjusted the electrical resistance of the SWCNTs and optimized the sensor response to NO_2. Therefore, the samples of SWCNTs drop-deposited onto the substrate were heated to 350 °C for 1, 2, 3, and 5 h, in vacuum to desorb the DMF adsorbed layers.

3. Results and discussion

3.1. Determining optimal heat treatment

Fig. 3 shows a network of nanotubes bridging the electrode fingers after dropdeposition of an SWCNT/DMF solution, followed by evaporation of DMF. A highly concentrated solution gave denser SWCNTs bridging the interdigitated electrodes, as shown in Fig. 4, yielding the highest conductivity of the sensing film. The samples were then subjected to heat treatment at 350 °C for 1, 2, 3, and 5 h, as described in Section 2. The initial resistance of the samples heat treated for four different periods was about a few hundred ohms in every case. Then, we made an in situ measurement of electrical resistance variation by cycling the chamber atmosphere from a vacuum to 10 ppm NO_2 at room temperature. The gas was introduced at a pressure of 5×10^{-3} torr in the vacuum system. The electrical resistance of the SWCNTs was measured using a Keithley 2400

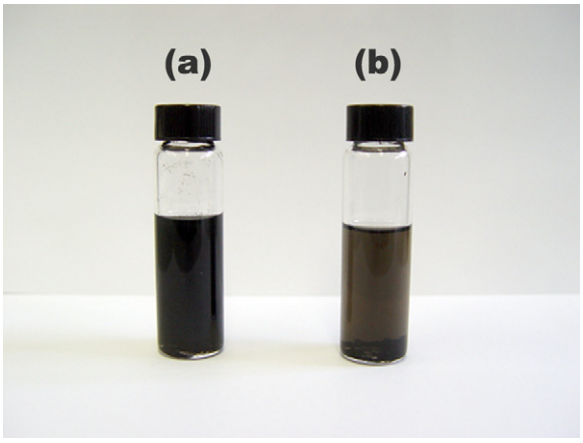

Fig. 2. Aqueous solutions of (a) SWCNT/DMF (20 mg/L) and (b) SWCNT/acetone (20 mg/L).

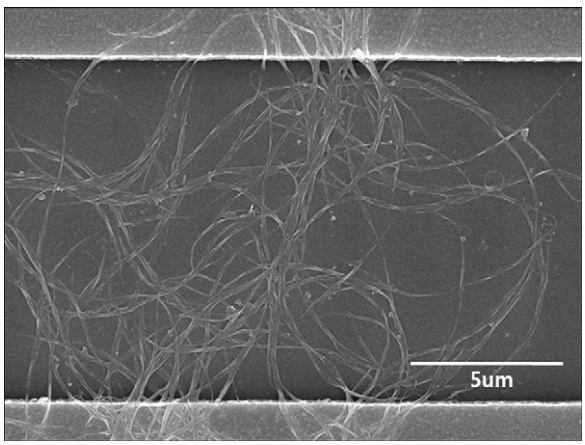

Fig. 4. An SEM image of SWCNTs across two Pt electrodes without heat treatment.

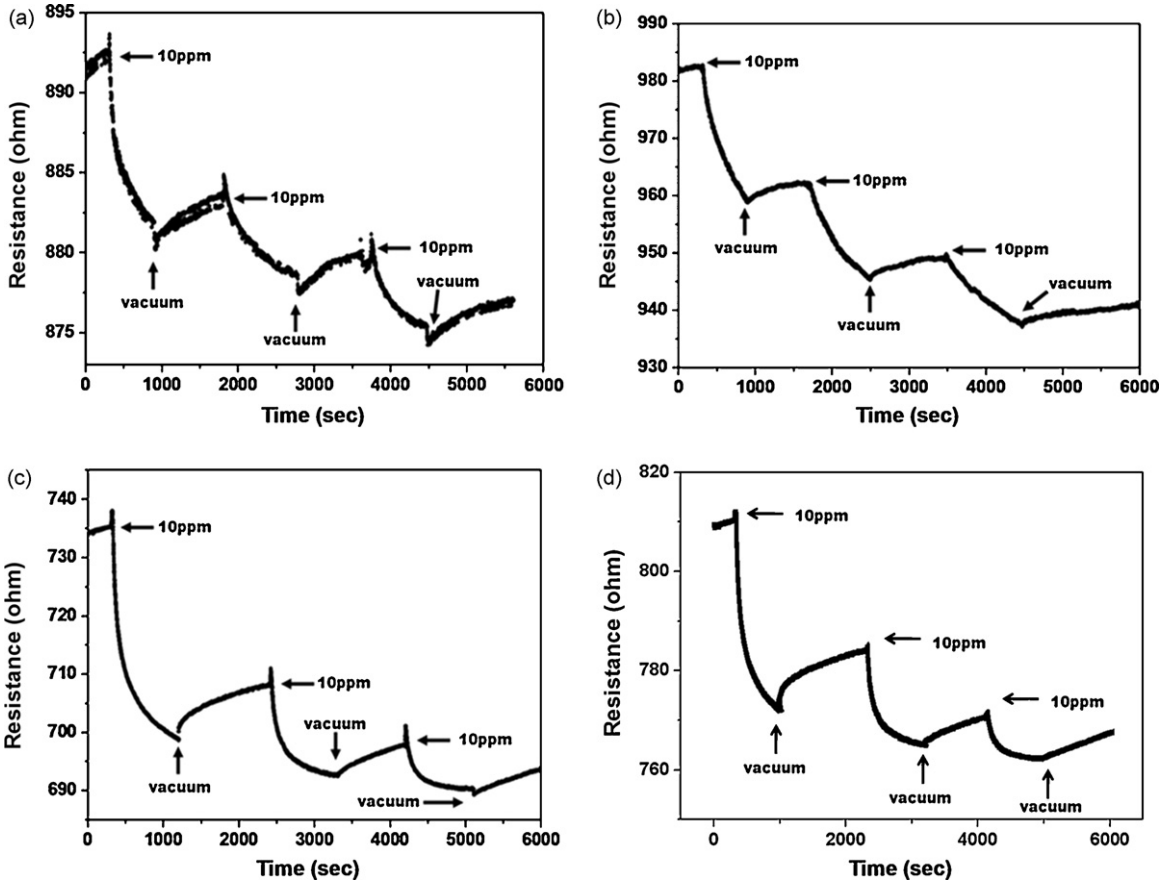

Fig. 5. Resistance changes of the sensors heat treated at 350 °C for (a) 1 h, (b) 2 h, (c) 3 h, and (d) 5 h when exposed to 10 ppm NO_2.

series source meter and was recorded as a function of the operating time.

Fig. 5(a)–(d) show the resistance changes of the sensors heated at 350 °C for 1, 2, 3, and 5 h, respectively. The response transients were recorded during three short exposures to 10 ppm NO_2 in vacuum at room temperature. The exposure to NO_2 rapidly decreased the resistance of the SWCNTs.

Fig. 5 clearly demonstrates that the sensor heated for a longer time has a significantly higher response. In Fig. 5(a), it is seen that the response transients are rather noisy. This may be because the DMF molecules used as a solvent were remained and was not perfectly desorbed by the heat treatment at 350 °C for 1 h. If the DMF molecules are remained adsorbed, the SWCNTs could not detect stably the NO_2 gas molecules because the DMF molecules may block the interaction sites with NO_2 molecules.

Fig. 5(b) shows the resistance changes of the 2-h heat-treated sample. The resistance changed in a better manner than for the 1-h heated sample. It is likely that this was caused by the removal of DMF molecules from the surface of SWCNTs. The degree of DMF removal and therefore the response should depend on the heating time. In our experiments, the optimal heating time was 3 h, as easily seen from Fig. 5(c). The resistance of this sample dramatically decreased when exposed to 10 ppm NO_2 probably because the DMF molecules were almost completely removed by the 3-h heat treat-

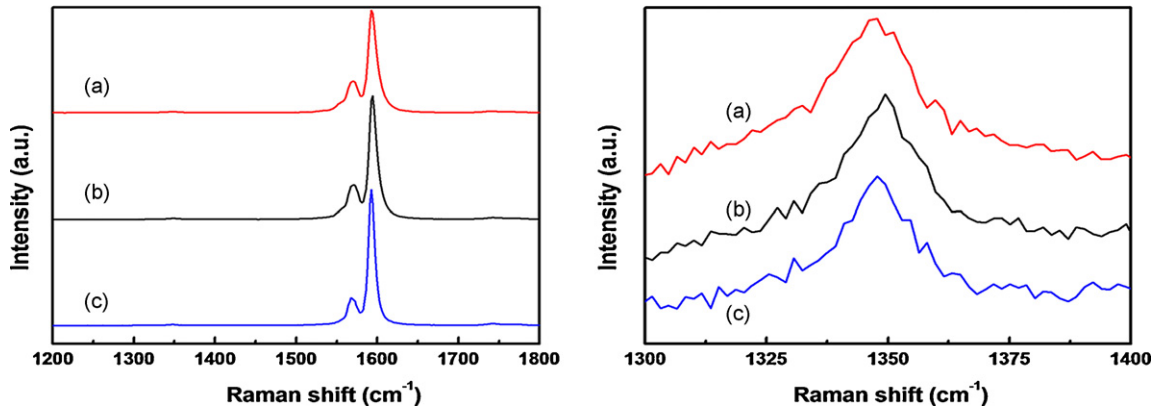

Fig. 6. Raman spectra showing the G-band (left) and D-band (right) features of (a) heat treated SWCNTs to remove DMF, (b) SWCNTs treated in DMF but without heat treatment, and (c) raw SWCNTs.

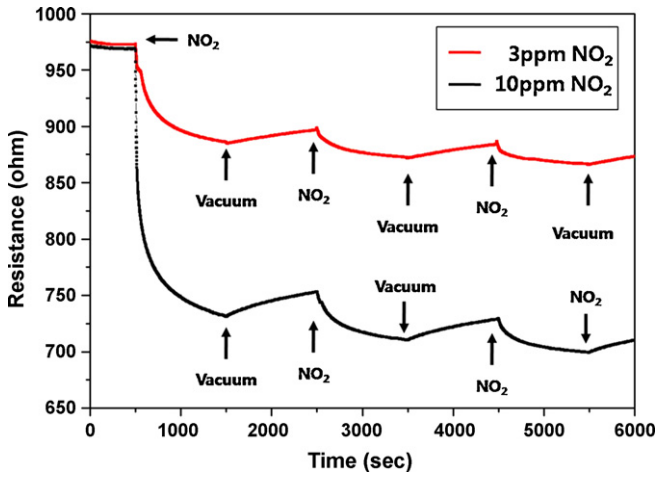

Fig. 7. Resistance change of the 4-h sonicated SWCNT sensor as a function of exposure time to NO_2 of 3 and 10 ppm.

ment. Almost similar results of NO_2 detection were obtained with the sensor heated for 5 h (Fig. 5(d)). Therefore, the 3-h sample, was selected as a representative in the following experiments. In Fig. 6, we compare the Raman spectra of the SWCNTs before and after heat treatment at 350 °C. The spectrum of the raw SWCNTs is also shown for comparison. Though the SWCNTs clearly displayed a resistance decrease after the heat treatment, the G- and D-bands in the Raman spectrum were almost unaffected. Therefore, it is suggested that no defect sites were created on the SWCNT wall after the dispersion in DMF or even by the heat treatment.

3.2. Response properties

In the above investigations, the response to 10 ppm NO_2 was small. It may be due to the reduced surface area of the SWCNTs. Here, we have to consider the side surface of the SWCNTs in a bundle. Namely, the response and recovery characteristics depend on how we can untangle the SWCNT bundles to utilize the side surface area of SWCNTs. Also, SWCNTs are usually in a bundle form where van der Waals forces make them gather. In other words, it is necessary to consider the undesirable reduction of surface area due to the formation of bundles. In fact, SWCNTs were ultrasonically dispersed in DMF for 2 h in the above experiment. When a longer time is employed for the ultrasonical treatment, it would lead to more pronounced untangling and hence to a good response to NO_2. To confirm this effect, the SWCNTs were ultrasonically treated for 4 h, and two NO_2 concentrations of 3 and 10 ppm were tested. Fig. 7 shows the dynamic responses of the 4-h sonicated SWCNT sensor at room temperature. When the sensor was exposed to the gas, the response increased rapidly in comparison with the 2-h sonicated sample in Fig. 5.

Exposure to NO_2 rapidly decreases the resistance of the SWCNTs. Similar behavior has been observed with individual SWCNT sensors. Theoretical and experimental studies have attributed this behavior to a charge transfer from the electron accepting NO_2 molecules to the SWCNTs. Because the semiconducting SWCNTs are hole-doped from environmental molecular oxygen, this charge transfer decreases the resistance of the SWCNTs by refilling the valence band of the p-type semiconducting SWCNTs [4,5]. The significantly lower response of SWCNTs observed, as compared to the previously reported results [7], can be explained by the different sensor configuration. The measurements in the previous report were conducted on selected semiconducting SWCNTs, whereas in the random network of SWCNTs of our sensor, both metallic and semiconducting nanotubes were present. The charge transfer from NO_2 to metallic nanotubes would not be expected to induce large changes in sensor resistance.

4. Conclusion

We demonstrated a sensor based on SWCNTs dispersed in a DMF solution for detecting NO_2 gas molecules at room temperature. DMF was chosen to untangle the SWCNT bundles because the amide group can easily attach to the surface of the nanotubes, providing a uniformly suspended solution of SWCNTs. The sensors, fabricated from a random network of SWCNTs/DMF, showed an improved response to NO_2 after heat treatment at 350 °C. The SWCNTs dispersed in DMF required the heat treatment to eliminate the DMF adsorbed on the surface of SWCNTs. Without heat treatment, they cannot detect NO_2 molecules effectively. The optimal heating time was 3 h. The NO_2 sensing of our sensor can be understood by intra- and inter-tube electron modulation in terms of charge-transfer mechanisms. The goal of this work was to assess the possibility of carbon nanotubes as an innovative NO_2 sensor for environmental applications. Moreover, this is a promising step toward the development of miniaturized devices with extensive analytical capabilities.

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Biographies

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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 microsensors 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.