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**Development of an ozone gas sensor using single-walled carbon nanotubes**Youngmin Park<sup>a</sup>, Ki-Young Dong<sup>a</sup>, Jinwoo Lee<sup>a</sup>, Jinnil Choi<sup>a</sup>, Gwi-Nam Bae<sup>b</sup> and Byeong-Kwon Ju<sup>a</sup>, <sup>a</sup>Display and Nanosystem Laboratory, College of Engineering, Korea University, Seoul, Republic of Korea<sup>b</sup>Center for Environmental Technology Research, Korea Institute of Science and Technology, Republic of Korea

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**Abstract**

This study deals with the fabrication of an ozone gas sensor using single-walled carbon nanotubes (SWCNTs) as sensing material. The SWCNTs are dispersed by N,N-dimethylformamide (DMF). The CNT-DMF solution was dropped between interdigitated electrodes' fingers to fabricate ozone gas sensor. For ozone environment, a commercial ozone generator was introduced. To improve sensor response, the deposited carbon nanotubes network was thermally treated at high temperature in a furnace. The sensor exhibits high sensitivity to ozone gas at concentration as low as 50 ppb, and fast response time, which is promising for future commercialization of carbon nanotubes based ozone gas sensor.



## Development of an ozone gas sensor using single-walled carbon nanotubes

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### ABSTRACT

This study deals with the fabrication of an ozone gas sensor using single-walled carbon nanotubes (SWCNTs) as sensing material. The SWCNTs are dispersed by N,N-dimethylformamide (DMF). The CNT-DMF solution was dropped between interdigitated electrodes' fingers to fabricate ozone gas sensor. For ozone environment, a commercial ozone generator was introduced. To improve sensor response, the deposited carbon nanotubes network was thermally treated at high temperature in a furnace. The sensor exhibits high sensitivity to ozone gas at concentration as low as 50 ppb, and fast response time, which is promising for future commercialization of carbon nanotubes based ozone gas sensor.

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### 1. Introduction

Seriousness of increasing atmospheric pollution resulting from industrialization has led to significant interest in sensing toxic gases. Various studies of gas sensors for detection of different kinds of hazardous gases have been conducted. Research has also been focused on sensing materials whose properties allow fast response and high sensitivity to certain gases. Since it was reported that the electrical properties of carbon nanotubes (CNTs) change by adsorption of gases, CNT-based gas sensors have been studied [1]. However, although many results of noxious gases detection including NO<sub>x</sub> [2], CO [3], NH<sub>3</sub> [4], volatile organic compounds (VOC) [5] were reported, there have been few research results involving ozone gas detection by CNT sensors. Ozone at the ground level, indirectly discharged from auto exhaust, is one of the harmful pollutants and the greenhouse gases. It is also the main cause of photochemical smog and atmosphere contamination. According to the air quality standard established by the U.S. environmental protection agency in 2008, ozone is required to have a concentration lower than 75 ppb.

A UV adsorption method is the standard method for ozone detection [6]. Although this method is reliable and has a high sensitivity, it has drawbacks in the complexity of the apparatus with high cost and large detector size. On the other hand, the ozone sensors based on metal oxide thin film, which utilizes an electrochem-

ical detection method, have also been developed with ZnO [7], WO<sub>3</sub> [8], InO<sub>3</sub> [9], etc. used as sensing materials. They have advantages such as compact size and high sensitivity; however, there is a severe limitation due to their high operational temperature [10]. In order to overcome these disadvantages, studies of ozone detection with SWCNT-based gas sensors have been conducted. In an existing research study of ozone detection, SWCNT film, grown by chemical vapor deposition (CVD), was used to detect ozone gas, but showed a limitation due to a long response time of 200 min [11,12].

In the present study, we developed a SWCNT-based gas sensor for ozone detection with a concentration down to 50 ppb at room temperature. Commercial SWCNTs were dispersed in N,N-dimethylformamide (DMF) and deposited over electrodes with conventional interdigitated design. To enhance the performance, a heating component was integrated into the gas sensor.

### 2. Experiment

Our sensor consists of an interdigitated Pt electrode on the top and a Pt microheater at the bottom. The electrodes are 20 μm in width with gap size of 20 μm and 200 nm in thickness. Electrical insulating layers are stacked between the electrodes and the microheater. The layers consist of oxide–nitride–oxide (O–N–O) structure. The silicon substrate was etched away by using an anisotropic etchant (KOH) to achieve the thermal isolation of the substrate. SWCNTs (purchased from Iljin Nanotech Co. Ltd.) have properties of 1–1.2 nm in average diameter, 5–10 μm in length and ~90% in purity (prepared by an arc-discharge process). No further purification was performed on the as-received SWCNTs. A

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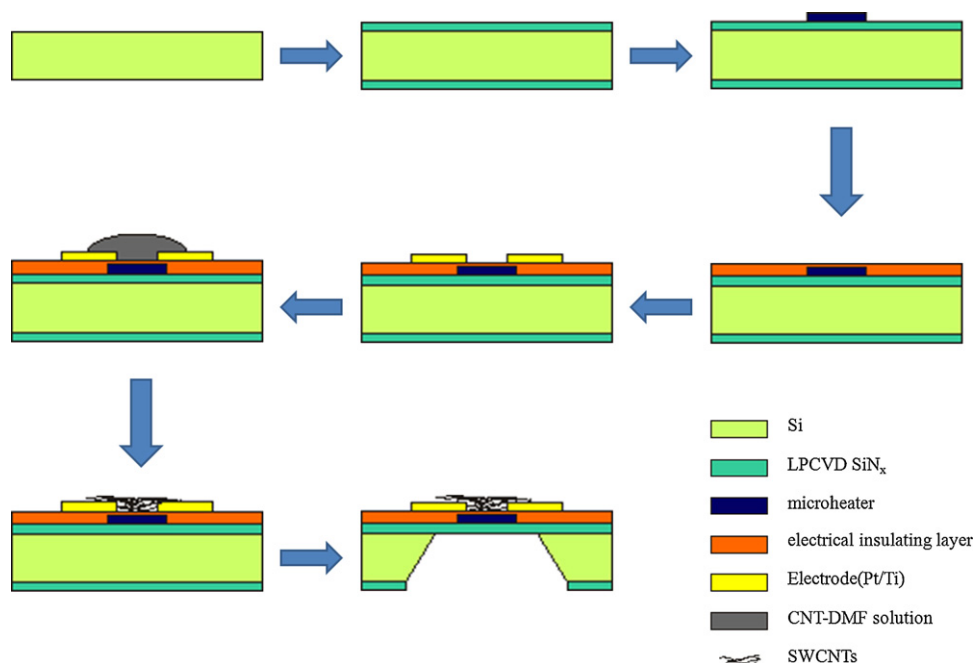


Fig. 1. Schematic diagram of CNT-based sensor fabrication. CNT solution was dropped and evaporated in room temperature.

stable suspension of SWCNTs in DMF was prepared by sonicating the SWCNTs in DMF at a concentration of 0.02 wt% for 4 h (at a pulse cycle: 2 s on, 2 s off, and at 200 W). Then, the SWCNT-DMF solution was dropped using a syringe between the interdigitated Pt electrodes fabricated by MEMS process. It was experimentally found that the resistance of the SWCNTs network ranged from several k $\Omega$  to several tens of k $\Omega$ , depending on the density of the SWCNTs across the interdigitated electrodes. In these experiments, the resistance was measured after the organic solvent DMF was removed by evaporation. Two types of the sensor samples were fabricated. Sample 1 was dried at room temperature after dropping the SWCNT-DMF solution. For sample 2, additional heating in furnace at 350 °C for 30 min was performed. The whole processing steps of our sensor fabrication are shown in Fig. 1, briefly.

A test gas of ozone was produced by a commercial ozone generator. Fig. 2 shows our measurement system. When the ozone gas generated from the ozone generator was introduced into the measurement chamber, the changes in resistance of SWCNTs were automatically monitored by LABVIEW software and KEITHLEY

2400. The effect of thermal treatment was investigated by comparing the responses of sample 1 and sample 2 at 1 ppm ozone gas. We also measured the changes in resistance of the CNT sensor when it was exposed to ozone gases with five different concentrations of 50, 100, 200, 500 ppb, and 1 ppm, sequentially. A dry air was used as carrier gas in order to obtain different concentration. The ozone generator that we used produced ozone by projecting UV to dry air. The concentration of the ozone could be controlled by the ozone generator up to 1 ppm. Every experimental process was performed at room temperature except for the recovery stages. The microheater and a rotary pump were utilized only for the recovery processes, providing self heating. The ozone gas was injected into the measurement chamber at a flow rate of 4 L/min. In addition, a dry filter was set up between the measurement chamber and the ozone generator in order to remove the influence of environmental humidity during the experiment.

### 3. Results and discussion

Fig. 3 shows the fabricated sensor, where Fig. 3(a)–(c) are the images of packaged sensor chip, heater and electrode, diaphragm, respectively. Fig. 3(d) is the SEM image of the dispersed SWCNTs by DMF. The DMF organic solvent was chosen as a dispersing agent for SWCNTs because the amide groups of DMF can be easily adsorbed to the nanotubes wall to debundle the SWCNTs and provide a uniformly suspended SWCNT solution [13,14]. We experimentally found that the resistance value of the SWCNTs network was increased from 3.4 to 4.8 k $\Omega$  after thermal treatment. This phenomenon will be discussed later.

Fig. 4 shows the result of ozone detection using sample 1. In our experiment, the sensor response,  $S$ , was defined by  $S = \Delta R/R_0 \times 100$ , where  $\Delta R = R_t - R_0$ .  $R_t$  and  $R_0$  were the resistance values of the sensor with and without ozone gas exposure, respectively. When 1 ppm ozone gas was introduced to the measurement chamber, the sensor response was changed by 9.8% for 500 s. After that, a 2% recovery was obtained by degassing the chamber for 500 s. During the second cycle, with the same concentration of ozone and the same period of gas injection and degassing, the change of the sensor response was 11%. This change was a little bit more than that of the first cycle. At

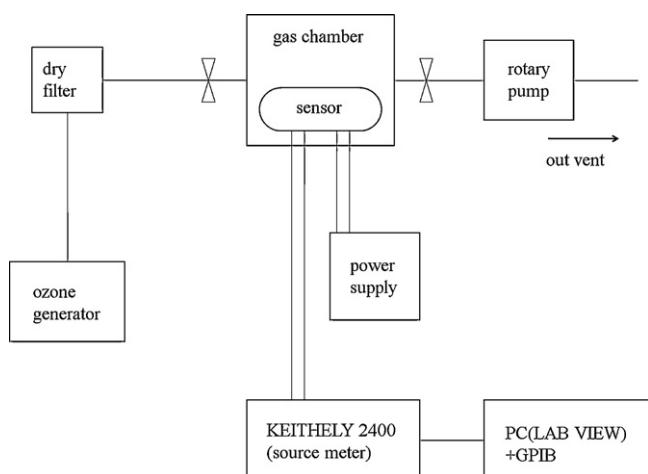
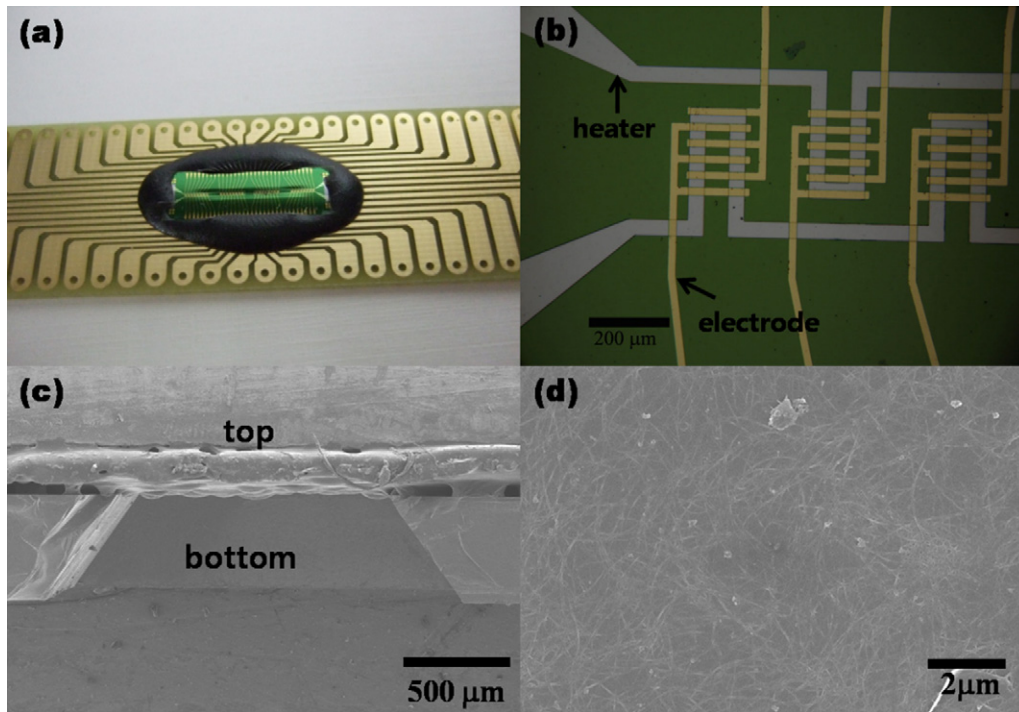


Fig. 2. Schematic diagram of experimental setup.



**Fig. 3.** Sensor and dispersed SWCNTs images: (a) fabricated sensor chip and (b) electrode and heater image. (c) SEM image of diaphragm cross-section and (d) SEM image of the dispersed SWCNTs.

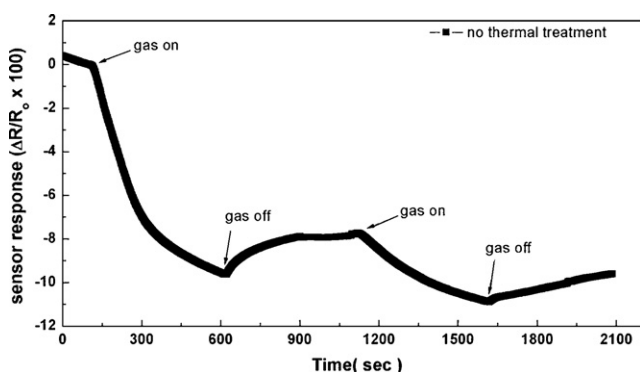
the second recovery stage, the sensor response decreased back to 9.8%.

As reported in the literature [11,15], the mechanism of the resistance change of SWCNTs exposed to ozone gas is as follows: an O<sub>3</sub> molecule has one unpaired electron and is a strong oxidizer. Upon O<sub>3</sub> adsorption, electron transfer is likely to occur from the CNTs being exposed to O<sub>3</sub> because of the electron-withdrawing power of the O<sub>3</sub> molecules. The O<sub>3</sub> adsorption depletes electrons from the CNTs resulting in an increase of the concentration of conducting holes, which are the majority carrier in the CNT networks. This leads to the decrease in resistance observed in the experiment [11]. However, as shown in Fig. 4, there is a limit in recovery only by degassing the chamber. This is probably because the chemisorption binding between O<sub>3</sub> molecules and SWCNTs are too strong to break by degassing [16] and because the oxidation due to ozone may form carbonyl or alcohol group on the nanotube surface [17].

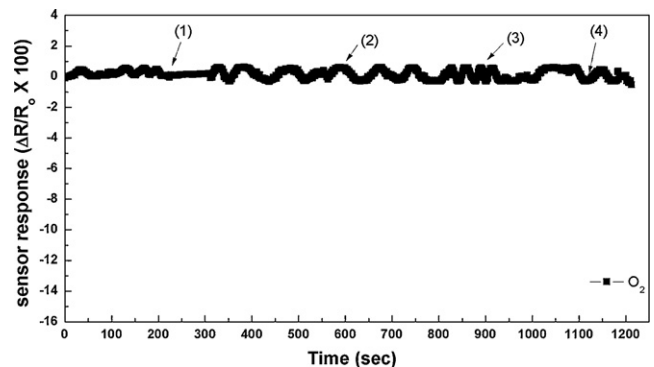
Our gas detection system is a static type so that the pressure inside the gas chamber changes during an experiment. The temperature of our sensor can also vary during recovery because of the

heating operation by a microheater. In addition, there is a possibility for oxygen in ozone environment to have an effect on our sensor response. The effects of these factors were explored through several experiments on ozone sensing results. The sensor resistance varied little as the pressure and the temperature in gas chamber changed by injecting and evacuating O<sub>2</sub> gas and turning on a microheater (Fig. 5), respectively. Furthermore, though the sensor resistance showed fluctuating tendency when exposed to oxygen, a resistance variation of the sensor was much less than that when exposed to ozone (Fig. 5). These findings confirm the validity of our sensor response to ozone.

Fig. 6 shows the responses of sample 1 and sample 2 at 1 ppm of ozone gas. The improved responses of the sensor under ozone gas exposure after the thermal treatment, compared to those before thermal treatment, were calculated and are itemized in Table 1. In the case of sample 1, the sensor response was 9.8% for 500 s. In comparison, sample 2 was saturated within almost a 100 s after exposure to ozone gas. It was recognized that the sensor response was 14.7% which was an increased value compared to the sample



**Fig. 4.** Response of the SWCNT-based sensor to O<sub>3</sub> of 1 ppm without thermal treatment.



**Fig. 5.** Sensor response to oxygen: (1) and (3), oxygen injection to gas chamber; (2) and (4), turning on a microheater and outgassing the gas chamber by using rotary pump.



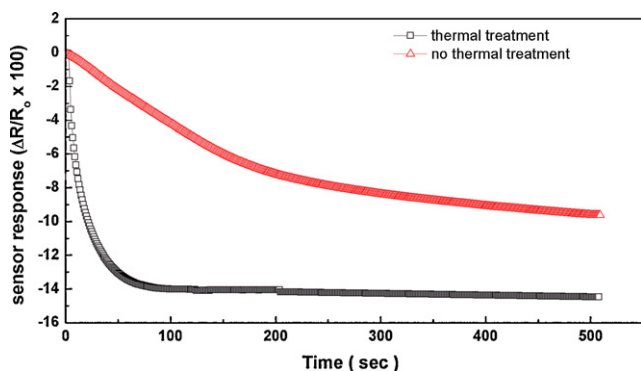


Fig. 6. Comparison of the sensor response before and after thermal treatment. The thermal treatment was performed in furnace at 350 °C for 30 min.

without the thermal treatment. Although the data given at Table 1 are the experimental values of two samples, and thus could raise reproducibility issue, we obtained just slightly different experimental results for each sensor sample and unchanged tendency. It confirmed that the sample with thermal treatment showed more improved sensor response (relative resistance change and response time) than that without the treatment. In accordance with the gas detection principle, where the concentration change of majority carrier in p-type semiconducting SWCNT is derived and the electrical conductance is changed on ozone gas exposure, results from Fig. 6 will be explained further below. As reported previously, the structural rearrangement within the SWCNT bundles occurs and the electrical properties of the SWCNTs change from semiconducting behavior to metallic response as the temperature is increased [18]. It was also reported that the electrical properties of the SWCNTs changed from metallic back to semiconducting behavior, when the temperature exceeded 300 °C and cooled back to room temperature [19]. It seems that the ratio of the p-type semiconducting SWCNT increased in the CNT network which had both metallic SWCNT and p-type semiconducting SWCNT on the basis of the fact that the resistance of the SWCNTs is increased and its electrical properties are returned to the semiconducting behavior. The increase in sensor response to ozone gas supports that the CNT network became a more responsive sensing material of the gas after the thermal treatment.

Fig. 7 shows the response of sample 2 being continuously exposed to the ozone gas with various concentrations. Our sensor showed high sensor response for ozone gas even at 50 ppb. The sensor was saturated nearly 200 s after being exposed to 50 ppb of ozone gas. After saturation, we stopped the ozone gas injection. Recovery was conducted by turning on a heater and degassing the ozone gas in the chamber with a rotary pump. The responses for the various concentrations were easy to distinguish. As the concentration of the ozone gas introduced to the chamber increased, the variation of the sensor resistance also increased. When 50, 100, 200, and 500 ppb of ozone gases were injected, it was observed that the sensor response was changed by 11.1, 12.3, 13.3, and 14.1%, respectively. When the sensor was reacted to 1 ppm of ozone after 500 ppb of that, the sensor resistance variations was almost same to each other. Consequently, it seemed that the sensor was saturated.

**Table 1**  
Comparison of the gas sensor performance before and after thermal treatment on 1 ppm ozone gas.

	Before thermal treatment (sample 1)	After thermal treatment (sample 2)
Relative resistance changes (%)	9.8	14.7
Response time (s)	500	100

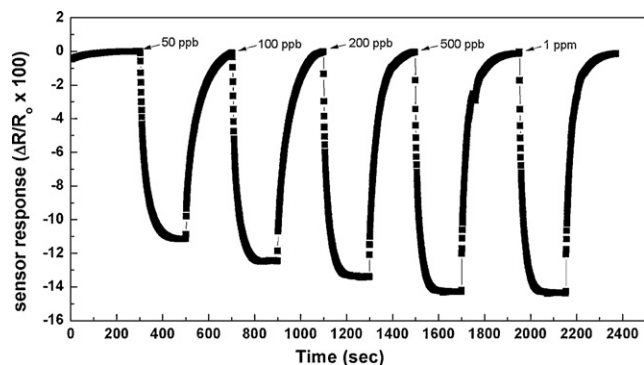


Fig. 7. Response of the SWCNT-based sensor at various O<sub>3</sub> concentration. The concentrations of O<sub>3</sub> gas were 50, 100, 200, 500 ppb, and 1 ppm, sequentially. The microheater and the rotary pump were used for recovery.

#### 4. Conclusion

We demonstrated ozone detection using SWCNT networks. The SWCNT networks utilized as a sensing material were deposited across the interdigitated electrode's fingers after being dispersed with DMF in a solution form. The SWCNT networks were sensitive to ozone down to 50 ppb. Upon exposure to ozone gas, the resistance of the SWCNT-based sensor decreased with an increase in concentration of the ozone gas, which states that the SWCNTs have p-type semiconducting property at room temperature. Our sensor showed a rapid response as well as a fast recovery. The SWCNT networks with thermal treatment exhibited an improvement in sensor response. This result clearly shows that an SWCNT-based gas sensor can be a good candidate for sensitive ozone detection, surpassing existing methods due to its high sensitivity, simplicity in fabrication and compact size.

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