Multiwall Carbon Nanotube Gas Sensor Fabricated Using Thermomechanical Structure

Woo-Sung Cho, Seung-Il Moon, Yang-Doo Lee, Yun-Hi Lee, Jung-Ho Park, and Byeong Kwon Ju

***Abstract*—We address a multiwall carbon nanotube (MWCNT) gas sensor that has an enhanced reproducibility. The sensor consists of a heater, an insulating layer, a pair of contact electrodes, and an MWCNT-sensing film on a micromachined diaphragm. The heater plays a role in the temperature changes to modify the rates for desorption of gases on the sensing surface during sensor operation. Gas sensor responses of MWCNT-film to NO_2 at room temperature are reported. We show that the sensor exhibits a reversible response with a time constant of a few minutes at thermal treatment temperature of 130 °C.**

***Index Terms*—Gas sensor, multiwall carbon nanotube (MWCNT), nitrogen dioxide (NO_2), recovery.**

I. Introduction

INTEREST in nano-materials has been growing rapidly for the past several years. Carbon nanotubes (CNTs) are especially promising as new materials for a variety of potential applications [1]. Existing electrical sensor materials include semiconducting metal oxides [2], silicon devices [3], [4], and carbon black-polymer composites [5]. Semiconducting metal oxides have been widely used for NO_2 and NH_3 detection. These sensors operate at high temperatures (200 °C to 600 °C) to achieve enhanced chemical reactivity between molecules and the sensor materials for substantial sensitivity. Conducting polymers and organic phthalocyanine semiconductors have also been investigated for NO_2 sensing. The former exhibits limited sensitivity, whereas the latter tends to have very high resistivity (sample resistance of > 10 giga-Ohms).

Recently, CNT-based gas sensors [6]–[13] have received considerable attraction because of their outstanding properties, such as faster response, higher sensitivity, lower operating temperature, and a wide variety of gases that may be detected compared with the other types of gas sensor. Up-to-date reported studies on possible applications of carbon nanotubes as gas sensors have been focused either on isolated single wall carbon nanotubes (SWCNTs) or on SWCNT mats [6]. Theoretical studies have predicted significant changes in the electronic properties of carbon nanotubes because of gas adsorption. These results lead to the application of carbon nanotubes as gas sensors to detect sub-ppm concentrations of oxidizing gases like NO_2, O_3 and CO. However, it takes a long time for the CNT-based gas sensors fabricated to recover owing to the small diffusion barriers of gases on CNT surfaces [14].

This letter reports on the fabrication of the sensor composed of a heater, a diaphragm, a contact electrode, and a directly grown MWCNT-sensing film on a thermally insulated dielectric diaphragm [15], [16] to improve recovery characteristics. Following a description of the integrated structure and the MWCNT deposition process, the characteristics of the sensor when exposed to NO_2 are presented.

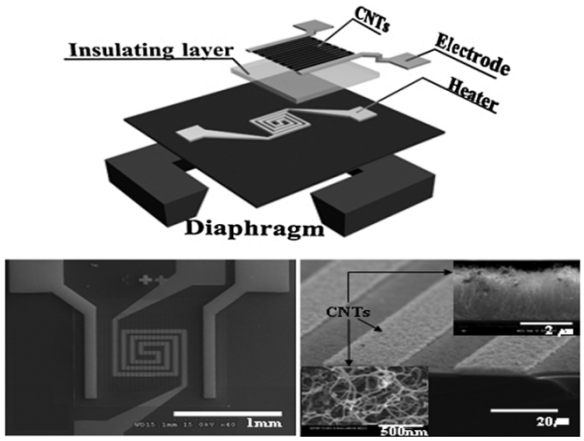

Fig. 1. Top: Schematic of the sensor. Bottom: FE-SEM micrograph of a sensor (left) and an MWCNT-film pattern (right).

II. Fabrication

A silicon substrate, 3×3 mm^2 wide and 450 μm thick, was etched from the back side to form a square diaphragm, 1.5×1.5 mm^2 wide and 20 μm thick, for the MWCNT gas sensor. On top of it, a chrome (Cr) heater, a pair of electrodes, and a gas-sensing film of MWCNT, 1.05×1 mm^2 wide, were attached.

Fig. 1 shows a FE-SEM micrograph of the integrated structure on a thermally insulated dielectric diaphragm that reduces thermal gradient and a schematic diagram of the sensor. The starting material was a (100) p-type double-sided polished silicon wafer with a thickness of 450 μm. A silicon wafer was doubly coated with silicon oxide (SiO_2, 150 nm) and silicon nitride (Si_3N_4, 150 nm) by thermal oxidation and low-pressure chemical vapor deposition (LPCVD), respectively. These dielectric layers were used as a diaphragm (front side) as well as passivation layer (backside) during etching. A heater, an insulating layer, a catalyst metal (cobalt, 8 nm) for the direct growth

Manuscript received February 25, 2005; revised April 21, 2005. This work was supported in part by the Nano Core Technology Project of the MOST (III), Korea and in part by the KRF Project under Grant 2004-05-C00060. The review of this letter was arranged by Editor K. T. Kornegay.

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Digital Object Identifier 10.1109/LED.2005.851095

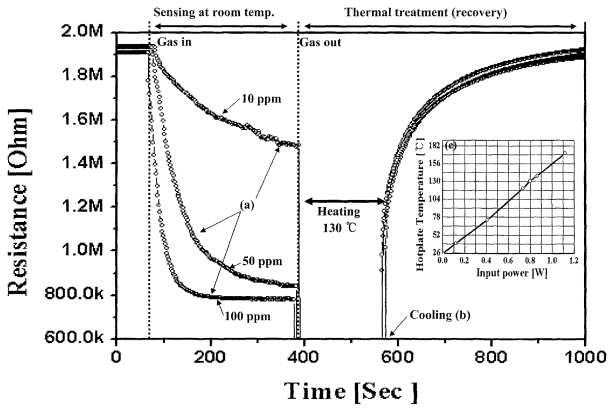

Fig. 2. Resistance changes of the sensor at NO_2 concentrations ranging from 10 to 100 ppm. (a) Resistance change of the MWCNT-film after exposure to NO_2 gas at room temperature. (b) Resistance change of the MWCNT-film after heating and out-gassing. (c) Plot of ambient temperature as a function of input power to Cr heater.

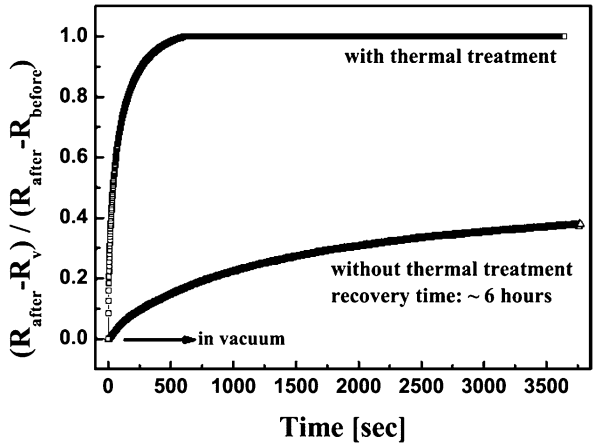

Fig. 3. Recovery time of sensor with thermal treatment and without thermal treatment in vacuum. R_v is resistance change with the variation in time after out-gassing.

of MWCNTs, and a pair of electrodes were patterned on the front side of the wafer by lift-off. The backside of the wafer was removed by anisotropic KOH etching to obtain a 20 μm thick square diaphragm.

The MWCNT-film was deposited by thermal chemical vapor deposition (Thermal CVD). The thermal CVD method to synthesize the MWCNTs used in this work has been reported earlier [1], [17]. The MWCNTs were grown by the pyrolysis of cobalt (Co) and acetylene (C_2H_2) gas under an argon (Ar)/hydrogen (H_2) atmosphere. The substrate was loaded onto a quartz boat inside the thermal CVD quartz reactor. The temperature of the thermal CVD chamber was raised to the process temperature of 750 °C within 10–20 min by the halogen lamps after evacuation down to 10^{-3} torr. During this step, the substrate was firstly treated under a hydrogen (H_2) gas environment for nearly 10 min to activate the surface of the catalytic metal and to prevent the corrosion of the catalytic metal and Cr electrode metal due to the residual gases. During the growth, the total pressure of the chamber was constantly kept at 20 torr and the flow rate of the hydrocarbon source, C_2H_2, was 5 sccm and that of the ammonia (NH_3) was 80 sccm. After the MWCNT growth, the chamber was purged continuously with a mixture of H_2 and Ar until the chamber temperature reached room temperature.

III. Results and Discussion

We observed *in situ* measurement of electrical resistance by cycling chamber atmosphere from NO_2 to vacuum $(\geq 10^{-3}$ torr) at room temperature. The gas was introduced at a pressure of 5×10^{-3} torr in the vacuum system. While chamber atmosphere changed from NO_2 to vacuum, we carried out thermal treatment of an MWCNT-film, using a heater. The thermal treatment process consisted of heating of the "as-deposited" MWCNT-film from 25 to 130 °C and then cooling of it back to 25 °C. The resistance of the film was measured using a Keithley 2400 series source meter that records electrical resistance as a function of the operating temperature.

Fig. 2 shows the dynamic gas response of MWCNT-film to NO_2 concentrations ranging from 10 to 100 ppm. Curve (a) represents the NO_2 response of the film at room temperature. While NO_2 gases were evacuated from a chamber, curve (b) represents the response of the film to NO_2 during cooling of the film from 130 to 25 °C. (c) Plot of ambient temperature as a function of input power to Cr heater. The gas sensitivity S is defined as the ratio between resistance R_{after} in gas and R_{before} in vacuum $(10^{-3}$ torr), i.e., $S = R_{\text{after}}/R_{\text{before}}$.

A plot of the active area temperature of the diaphragm versus input power applied to the Cr heater is shown in Fig. 3(c). The region where the resistance of the sensing layer is measured by means of suitable contacts is commonly referred to as the "active area." This plot exhibits a thermal efficiency of about 0.18 °C/mW for the active area in air. The active area temperature is measured using thermocouple.

At 100-ppm NO_2, the resistance of an MWCNT-film is found to decrease from 1.8 to 0.8 MΩ $(S \approx 2.5)$ in ~ 2 min. The sensitivity of the response to the gas molecule seems to be related to the amount of electron charge transfer and the nature of the surface interaction of the gas and MWCNT [1], [6]. The small resistance change is due to the presence of semiconducting MWCNTs dispersed among the predominant metallic MWCNTs because MWCNTs grown by CVD are not generally a single character of metallic or semiconducting but include both types. In most cases, they show typical properties of metallic MWCNTs. Gas sensing characterizations of an MWCNT showing p-type semiconducting property were carried out [1], [6], [12]. Also, the inner tubes in CNT ropes are blocked from interacting with NO_2 because the molecules are not expected to intercalate into CNT ropes [6].

During the adsorption process of NO_2 gas on a SWCNT surface, NO and NO_2 bind weakly with low diffusion barriers making it possible for the formation of NO_3 with strong binding energy and long life on a SWCNT surface [14]. These phenomena match well with the corresponding long recovery time seen in the NO_2 sensing experiments [6].

The operating temperature of 130 °C activated the desorptive process that results in fast recovery from the MWCNT-film. During the cooling of the film from 130 to 25 °C in vacuum $(10^{-3}$ torr), the resistance slightly increases. When the NO_2 concentration increases and decreases stepwise in this range, the sensor response is reproducible and stable. It is interesting to

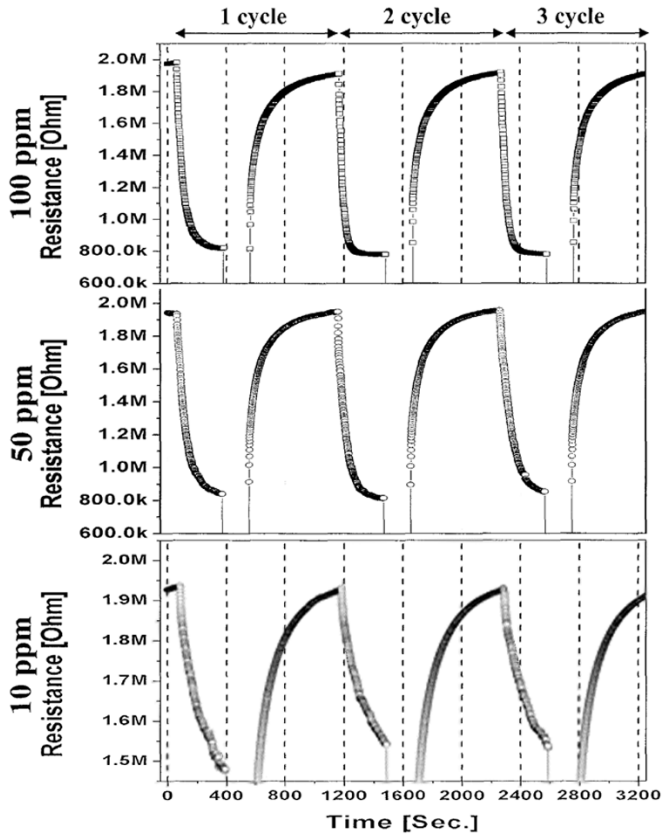

Fig. 4. Resistance changes of the sensor as a function of time when exposed to three cycles of a sequence of NO_2 and its concentrations ranging from 10 to 100 ppm.

note that recovery time of the sensor in this work is a few minutes, while sensors based on resistance changes of single walled nanotube ropes exhibit a recovery time of 8–12 h after exposure to higher NO_2 concentration (200 ppm of NO_2) [6].

Fig. 3 shows resistance change versus time during NO_2 gases were evacuated from a chamber. We define the recovery time as the time for $\sim 90\%$ total resistance change. The resistance of an MWCNT-film without thermal treatment was observed slow recovery ($\sim$ 6h), but the resistance of an MWCNT-film with thermal treatment was observed fast recovery $(\sim 10\ \mathrm{min})$. These characteristics were acquired with the sensor mounted in the same vacuum system that was used to directly grow the MWCNT-film.

To investigate the reproducibility of sensor, the sensor is tested three sensing cycles by repeating sensing and recovery. Fig. 4 shows the resistance of the MWCNT-film as a function of time when exposed to three cycles of a sequence of NO_2 exposure (sensing) and evacuation (recovery) and NO_2 concentrations ranging from 10 to 100 ppm. It is found that the device does not have much sensitivity decay during the sensing cycles, which proves that the sensing characteristics are repeatable. It turns out that if the thermal cycle of heating and cooling is maintained within the temperature range of 25–130 °C, sensor response is always reversible.

Finally, if we consider the long-term stability of the electrical response and that drift phenomena often reported in the case of many metal oxide sensors are due to the grain growth and chemical instability of the surface metal ions [18], we may presume that CNT sensors are more stable since they are not affected by mass transfer phenomena or by the change of the chemical nature of the surface carbon.

IV. Conclusion

An MWCNT gas sensor has been realized by the integrated structure on a micromachined diaphragm fabricated and then thermal CVD growth of an MWCNT sensing film. The sensor exhibits a resistance decrease in response to NO_2 exposure and the recovery of CNT thin films can be improved only by the proper selection of thermal treatment protocols. These characteristics show the possibility as a sensor in integrated sensor systems capable of gas analysis.

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