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Gas sensor using a multi-walled carbon nanotube sheet to detect hydrogen molecules

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ABSTRACT

In this paper, a gas sensor with a fabricated multi-walled carbon nanotube (MWCNT) sheet, which can sense hydrogen (H_2) gas, is proposed and its output properties were evaluated. The key contribution of this study is a novel fabrication technique that introduces a simple transfer method. Easy transfer from initial substrate to another substrate, the simple process and integration ability, and low cost make CNT-based sensors more suitable for future nano-material based sensor. Moreover, the MWCNT sheet does not need a complex purification process to be used as a sensor, making it suitable for practical applications. The MWCNT-sheet gas sensor had a large surface area and many contact points; these facts were further confirmed through morphological analyses. In addition, the effects of thermal annealing and carrier gas flow on gas desorption were investigated in order to improve the recovery response of the gas sensor. It was found that a thermal annealing temperature of 100 °C and a larger flow (2000 sccm) of carrier gas recovered original resistance values, resulting in high performance, faster response time, and improved reproducibility for the MWCNT-sheet gas sensor.

1. Introduction

Ever since their discovery in 1991 by Ijima [1], carbon nanotubes (CNTs) have been intensively studied as a promising material for a variety of potential applications, such as flexible displays, sensors, and battery electrodes [2–6]. Recently, there have been many reports on CNT-based gas sensors due to their outstanding properties, which include fast response, high performance, and a wider variety of detectable gases in comparison with other types of gas sensors [7]. Due to their hollow core, large surface area, small size, and excellent mechanical and electronic properties, CNTs provide greater gas-sensing ability. In the near future, hydrogen (H_2) is expected to be widely used as an energy source for fuel cells. A H_2 gas sensor is necessary to ensure safe operation of hydrogen-based energy storage systems and facilities such as H_2 gas stations or fuel cell vehicles, since H_2 leakage may result in explosive accidents. To date, multi-walled carbon nanotube (MWCNT)-based gas sensors have been utilized to sense diverse gases such as NH_3, NO_2, CO_2, and O_2 [8–11]. MWCNT-based gas sensors can be operated by varying their electric properties, as carriers undergo adsorption or desorption with relation to available reaction sites in the CNTs. The electrical resistance of MWCNTs is dramatically altered upon exposure to target gases.

Currently, there are two methods for employing CNTs as an active layer. The first involves direct growth of CNTs on a sensor platform through controlled chemical vapor deposition (CVD), followed by connection with a metal electrode [12]. This fabrication method involves complex and expensive processing steps with low yield. The second method involves drop-casting or spraying CNTs in water or organic solvent on top of prefabricated electrodes using a micro-pipettor, followed by drying [13]. Although the second method is relatively easier than the former, it results in uneven dispersion of CNTs on electrodes, which can degrade sensor performance. Accordingly, simple, inexpensive, high yield, and reproducible fabrication techniques are definitely required for the success of CNTs-based sensors.

On the other hand, our previous papers [14–17] have reported MWCNT sheets from spin-capable MWCNT forests. These MWCNT sheets have a large surface area and show good adhesion to substrates. Such properties increase the utility of MWCNT sheets in gas sensor applications. In this paper, a MWCNT sheet-based gas sensor is introduced along with a simple, low-cost fabrication process that does not require manipulation of individual and/or bundles of CNTs or complex, expensive techniques such as photolithography. Moreover, the MWCNT sheet does not need a complex purification process to be used as a sensor, making it suitable for practical applications. Thermal annealing and carrier gas flow are considered to

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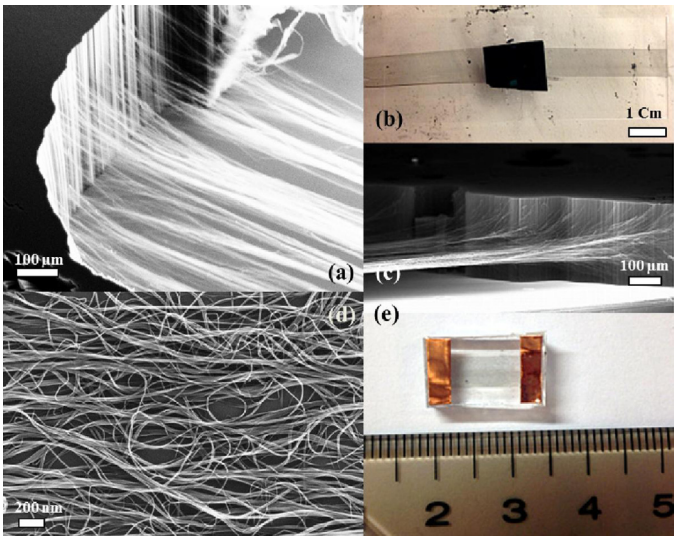

Fig. 1. SEM images and a photograph of (a) spin-capable CNTs showing good alignment of 430 μm MWCNTs, (b and c) CNTs sheet pulling from the CNT forest, (d) morphology of the CNT sheets, and (e) fabricated gas sensor.

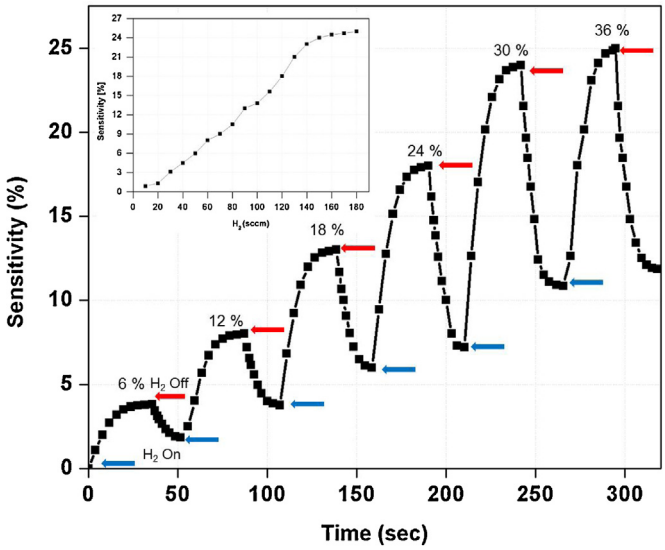

Fig. 2. Sensitivity of the gas sensor as a function of H_2 (inset) and time with respect to concentration. Blue and red arrows indicate on and off of H_2, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

improve recovery of sensitivity. One limitation of CNT-based gas sensors is their slow and imperfect recovery of original resistance values after turning off target gases due to high binding energy and/or strong interactions between gases and CNTs [11]. We found that a thermal annealing temperature of 100 °C and a larger carrier gas flow can enhance desorption of gas from CNTs. Based these results, the sensor has excellent gas characteristics upon repetitive exposure as well as a relatively fast response/recovery time.

2. Experimental details

2.1. Materials and sample preparation

An iron film was deposited on 330-μm thick p-type silicon wafers using electron beam (e-beam) evaporation. The thickness of the Fe films varied over a range of 5–6 nm and was monitored by a quartz-crystal sensor fixed inside the e-beam evaporation chamber. Catalyst annealing and CNT growth were performed in a vertical cylinder atmospheric-pressure chamber built by the authors. Flows of He (5 slm), C_2H_2 (100 sccm), and H_2 (100 sccm) were maintained using electronic mass flow controllers (MFCs). After purging the tube with He for 10 min, the chamber was ramped up to 780 °C over 15 min (ramping rate: 50 °C/min), after which growth of CNTs was carried out at 780 °C by adding acetylene gas to the flow for 5 min. Afterwards, the C_2H_2 and H_2 gas flows were turned off and the sample rapidly cooled. As shown in Fig. 1, the MWCNT sheets were directly pulled from a super-aligned MWCNT forest onto glass. In order to transfer other substrate, the tip of the MWCNT forest was manually pulled out using sticky bar and the gas sensor was prepared by soldering two electrical leads to the ends of the sheets on the glass substrate. After this process, the fabricated MWCNT sheets were immersed in nitric acid in order to functionalize their surface. The detail procedure was mentioned in a previous report [14–16].

2.2. Equipment set-up and characteristic measurements

The MWCNT sheet-gas sensor was prepared by directly soldering two electrical leads to the ends of the MWCNT sheets on the glass substrates. N_2 and H_2 were used as the carrier and target gases, respectively. The flow rates of N_2 and H_2 were controlled using MFCs. In order to test reproducibility, the inside of the chamber was purged with N_2 gas at high temperature (100 °C) after turning off H_2. A Keithley 2400 was used to measure the electrical resistance versus either time or concentration. The temperature was altered by adjusting the DC power supply voltage and was measured by a thermocouple.

3. Results and discussion

To evaluate gas-sensing characteristics, the sensor was introduced into a chamber at room temperature. The flow rate of the gas mixture was set to 500 sccm, and the H_2 concentration was controlled by a MFC. The sensitivity of the sensor was determined using the following equation:

$$\text{Sensitivity}\,(\%) = \frac{R - R_0}{R_0} \times 100 \quad (1)$$

where R and R_0 are the resistances of the sensor upon exposure to the H_2 and N_2 mixture and pure N_2 (R_0) gas, respectively. The response of the sensor to H_2 exposure is depicted in Fig. 2. The resistance of the MWCNT-sheet gas sensor was increased upon exposure to H_2 gas. This result was expected and can be explained by the following: an H_2 molecule is reducing agent that donates an electron to another species. Therefore, H_2 can play a role as an electron-donor and/or hole-acceptor. When the CNT gas sensor was exposed to H_2, electrons were transferred from H_2 molecules to the MWCNTs. H_2 then donated its electrons to the valence band of the MWCNTs, thereby decreasing the number of holes by recombination, reducing conductivity of MWCNTs, and increasing electrical resistance [18–20]. Therefore, it is reasonable to assume that MWCNTs are a p-type semiconductor.

We observed that the sensitivity of the gas sensor has relatively higher than that fabricated by drop-casting (dispersion) or spin-coating of CNTs [21,22]. It is well known that the sensing characteristics of the CNT gas sensor depend significantly on surface distribution and area. Sensors fabricated using dispersed CNTs on a substrate, either with randomly distributed CNTs of extremely low density or with overlapping CNTs of extremely low resistance, display much lower sensitivities [23,24]. Therefore, the large surface area and well aligned distribution promoted strong interactions between the MWCNTs and H_2 molecules, thereby improving sensor sensitivity. In other words, the excellent performance of the