Vertically aligned multiwalled carbon nanotubes (MWCNTs) as an interdigital electrode were fabricated to investigate AC response to NO₂ gas. The response mechanism was explained in terms of the polarization effect of gases, charge transfer by gas adsorption on CNT electrodes, and field emission current. The response was affected more by gas adsorption than by the polarization effect and field emission effect. We also found that capacitive response and the yield of device production can be significantly improved by a post-heat-treatment, which can be explained by the removal of adsorbents such as moisture and/or other functional groups on the CNT surface.

1. Introduction

Carbon nanotubes (CNTs) have been considered as a strong candidate for gas sensors. In single-walled carbon nanotubes, all of the carbon atoms are exposed to the surface. Therefore, the transport properties of CNTs are easily affected by gas adsorption, which makes them more sensitive than bulk materials. Since initial work done by Kong et al. and Collins et al., numerous studies have been conducted on the CNT-based sensors. In general, electrical properties, such as resistance and capacitance, and dielectric properties are modified by the presence of gas molecules on the CNT sensors. The conventional approach is to use the change in resistance to detect the presence of gas molecules. Devices of this kind are easy to fabricate and operate. Nevertheless, the realization of resistance-based sensors has been limited due to the simultaneous presence of metallic and semiconducting CNT channels, which degrades the sensitivity and the fabrication yield of such devices.

Random network CNT thin films have been used for DC and AC response. The charge transfer between gas adsorbents and CNTs was the main origin for DC response, while the gas polarization effect has been taken into account to explain the capacitance change in AC measurement. At the same time, vertically aligned multiwalled carbon nanotubes (MWCNTs) have been also introduced as an electrode to generate high gas sensitivity by gas ionization. Anode was formed on top of the vertically aligned MWCNTs in this case so that the strong field was applied to the tip of MWCNTs to generate ionized gases. Sensitivity in the range of ppb has been realized, which is quite promising for future commercialization. In general, the response to gases generally relies on charge transfer (resistive type), polarization (capacitive type), or field emission (ionization type). The effective mechanism and dominant factor among three effects will be different depending on the device structures. However, no detailed research has been tried to study three sensing mechanisms as a package so far. For this purpose, a vertically aligned MWCNTs sensor using AC measurement was constructed since all of the sensing mechanisms as mentioned could appear as a combination. In the case of capacitive response with vertical alignment, the MWCNTs seem to be more appropriate than the SWCNTs, since MWCNTs can act simply as an electrode due to their metallic nature to enhance the local field near the tip of CNTs, let alone their robustness of synthesis.

The purpose of our report is 2-fold: (i) to fabricate a CNT device to study the combined response mechanism by AC measurement and (ii) to improve the fabrication yield of devices with response. We fabricated interdigital electrodes with vertically aligned MWCNTs by using chemical vapor deposition (CVD). Distances between electrodes were optimized. This device with AC measurement incorporated three response mechanisms: polarization of gas molecules, charge transfer by gas adsorption on the surface of CNT walls, and field emission current. Thermal annealing of devices provided a method of improving AC response and the yield of production.

2. Experimental Methods

2.1. Capacitive CNT Sensor Fabrication and AC Measurements. A BNI-300 negative photoresist layer of 2.4 μm thickness was used to coat a 400 nm thick SiO₂/Si substrate. After development with a photomask, a patterned pair of 2 × 2 mm² interdigital Ti (300 nm)/Au (500 nm) electrodes was deposited by using electron beam evaporator, followed by further deposition of 13 nm thick aluminum as a buffer layer and 1 nm thick iron layer as a catalyst. Two parallel capacitor-type electrodes were formed with three different gap distances (2.5, 5.0, 10 μm), as shown in Figure 1a.

Vertically aligned MWCNTs on each electrode were synthesized by the decomposition of acetylene gas with use of plasma-enhanced chemical vapor deposition (PECVD) at 700 °C in Ar and H₂ environment. The catalysts residual was rarely found within the tubes, implying negligible sensing effect from catalysts. The fabrication process and the schematic sensor structure are shown in Figure 1a. The morphology of the synthesized nanotubes was then analyzed by field-emission scanning electron microscopy (FESEM JSM7000F, JEOL).
All measurements were performed at room temperature. NO\textsubscript{2} gas was diluted by N\textsubscript{2} to 20 ppm and introduced into a vacuum chamber where the sensor was loaded. Gas valves (dry air and NO\textsubscript{2}) were controlled by a data acquisition (DAQ) card from National Instrument. Two-point probe (source drain or working and counter electrode) capacitance measurement was conducted with use of a combination of impedance analyzer (Solartron 1260 FRA) and potentiostat (Solartron 1287), as shown in Figure 2.

These two instruments supplied AC bias of 3 V at 500 kHz across the interdigital electrodes, and measured AC current. Then, the current was analyzed with respect to the equivalent series RC circuit (as shown in Figure 3a). Before the growth of CNTs, the capacitance of gas sensor ranged below 1 pF/cm\textsuperscript{2}. Then, the capacitance increased to 100 pF/cm\textsuperscript{2} after deposition of CNTs. Such a large increase of capacitance is ascribed to the large surface area of CNT forests. Therefore, the contribution of SiO\textsubscript{2} layer to our device capacitance is negligible. In the case of three-point probe measurement, the reference electrode is connected to Si substrate like gate electrode in FET. However, in the case of two-point probe, the reference electrode was common with the working electrode. All of the data were recorded automatically through general purpose interface bus (GPIB) by a Labview interface.

The stable baseline capacitance was achieved in vacuum and marked as \( C_0 \). Steady-state capacitance of sensor upon exposure to NO\textsubscript{2} gas was recorded as \( C \). The capacitive sensitivity was then calculated:
Investigation of AC Response to NO$_2$ Gas

Figure 3. (a) Capacitance and resistance response of the sensor at a gap distance of 5 µm with 20 ppm NO$_2$ gas. The gas was taken up at 1000 s, and released at around 2200 s. The inset image is the equivalent circuit. Schematic of the gas sensing mechanism with NO$_2$ molecules: (b) charge transfer by gas adsorption, resulting in the change of electronic density of states near the Fermi level shift and (c) polarization effect.

\[
\frac{\Delta C}{C_0} \% = \frac{C - C_0}{C_0} \times 100
\]

The resistive sensitivity was calculated similar to this.

2.2. Post-Heat-Treatment and Gap Distance Optimization. Over 60 as-prepared samples with three different gap distances were characterized. We categorized 67 as-prepared samples into two: “good” samples with sensitivity higher than 10% and “bad” samples with sensitivity lower than 10%. To improve the sensitivity and production yield, post thermal annealing was done to the bad samples. The gap distance of 5 µm was used for this purpose. Since the rest of the structures were fixed during thermal annealing, the effect should be generalized even for devices with different gap distances. These samples were heated on a hot plate in air by increasing temperature from 100 to 450 °C. The temperature was increased 50 °C at every step and maintained for 30 min. Micro-Raman spectroscopy (Renishaw RM1000-Invia) measurement was done before and after heat treatment to investigate the heating influence to CNTs.

3. Results and Discussion

As shown in Figure 1b, the MWCNT arrays were highly dense and vertically aligned, the typical CNT length was 1–3 µm. The diameter ranged from 10 to 15 nm. A typical pair of interdigital electrodes is shown in Figure 1c. This structure is different from the previous, planar capacitive sensor. Figure 3a shows the changes of capacitance and resistance of the sensor with NO$_2$ gas uptake and release at a gap distance of 5 µm.

Our sensor can be considered as a series combination of the CNT resistor and capacitor between interdigital electrodes, as shown in the inset of Figure 3a. With an uptake of 20 ppm NO$_2$ gas, the capacitance increased by about 70%. Since the device consists of vertically aligned CNTs as an electrode, AC response should incorporate three different response mechanisms: (i) charge transfer by gas adsorption, (ii) polarization effect of gases between electrodes, and (iii) field emission current from the CNT tips. The first two factors are basically similar to the previous study with the planar CNT network. We simply summarize the sensing mechanism based in Figure 3b,c here: The Fermi level can be shifted down by the charge transfer from CNTs to NO$_2$ gas upon gas adsorption. This will modify the electronic density of states near the Fermi level, as shown schematically in Figure 3b. The NO$_2$ molecule has a permanent dipole moment and will generate an induced dipole moment in a strong electric field as shown in Figure 3c. Both of these two mechanisms will alter the capacitance eventually. Moreover, in the case of vertically aligned MWCNTs, the existence of field emission current should be taken into account. However, the field is applied perpendicular to the sidewalls of the CNTs. This is different from the emission from the CNT tip that exhibits a large field enhancement factor, although there might be some contributions to the capacitance near the tips. Therefore, the field emission effect is supposed to be negligible in our case. Nevertheless, the effect of ionized gases from the field enhancement near the local CNT surface should be considered in our case. The estimation of the field enhancement factor from the CNT sidewalls will be discussed later.

The recovery time is longer than 1 h at room temperature (partially shown in Figure 3a). By taking account of the full recovery time, the amount of desorbed molecules was about 30%. This means that approximately 70% of gas molecules are strongly adsorbed on the CNT surface. The large portion of gas adsorbates contributed to the capacitive sensitivity by a direct charge transfer causing a change in the density of states near the Fermi level of the CNTs. This contribution was much larger than the 10% in the previous study. The remaining 30% were desorbed and contributed to the polarization effect by changing a dielectric constant in the medium. This discrepancy is a consequence of the higher field enhancement factor in the previous work that induces stronger polarization effect and property difference between volatile organic compounds and NO$_2$ gas. Gas response can be obtained from the resistance measurement, as shown in Figure 3a. The resistance decrease after gas uptake is exclusively caused by the charge transfer from CNTs to NO$_2$, which will increase the hole concentration of CNTs.

To test practicability of our structure under AC measurement, over 60 as-prepared samples with three different gap distances were characterized. It was found that about 40% of the devices (24 out of 67 devices) had the capacitive sensitivity above 10% right after fabrication. However, the remaining 60% of the
devices showed no response to the exposed gas. Thus, we adopted an idea of thermal annealing to improve the response. Figure 4a shows a typical example of the capacitive response improvement by a simple annealing of sample before measurement. A 5 µm gap distance device that showed undetectable sensitivity initially on average sensitivity and conversion percentage after heat-treatment in air. The inset shows the G band downshift of 6.2 cm⁻¹ in Raman microscopy with an excitation laser of 633 nm after heat-treatment at 350 °C for 30 min.

The reason for the capacitive sensitivity and yield improvement by post thermal annealing under AC measurement, however, cannot be simply deduced from the resistance-type sensor, which was explained by the microstructural rearrangement of the tube structure in the previous report. Raman spectroscopy measurement was then done to understand the underlying mechanism of the response improvement. The G-band of the CNTs in Raman spectroscopy near 1598.7 cm⁻¹ was shifted down to 1592.5 cm⁻¹ after 350 °C annealing. This is the evidence of removal of p-type adsorbents (for instance moisture and/or functional groups such as hydroxyl and carboxyl groups). These p-type adsorbents as mentioned above may interact with the NO₂ molecule first, and alleviate the effect of intrinsic dipole moment of the NO₂ molecule. As a consequence, the capacitive response is minimized. On the other hand, such ambient adsorbents can be removed near 200 °C. The relatively high annealing temperature near 350 °C to produce the best yield suggests some additional effect. In general, thermal annealing improves the contact between CNTs and metal electrodes around 650 °C for 30 s to avoid CNT damage. In our case, the annealing was done for a long time of 30 min. In addition, the change of the D-band (data not shown) in Raman spectra was not appreciable, indicating no annealing effect to the defects on the CNT walls. Initially saturated defects by adsorbents could be activated to enhance sensitivity. Nevertheless, the decrease in the capacitive response and conversion percentage near 400 °C is ascribed to possible damage to the nanotube walls, since the annealing was done in air. Our results show that the presence of moisture and/or functional groups is in fact detrimental to the detection of NO₂ gas. The capacitive response of NO₂ molecules to the CNT surface is affected by the presence of water molecules or some other functional groups. In addition, the probable contact improvement between metal and CNTs also affects the sensitivity and production yield.

Figure 5 shows the capacitive sensitivity and yield of devices as a function of gap separation distance. Smaller gap distances improved sensitivity, demonstrating the existence of the polarization effect. Nevertheless, the difference from larger gap distance was not so significant. After heating the 5 µm samples, both sensitivity and yield were improved, as indicated by two arrows in Figure 5. The percentage of devices with a sensitivity of less than 15% decreased from 57% to 23%, whereas that with a sensitivity of 15-30% increased from 24% to 48%. It is also intriguing to see that the recovery time was independent of the gap distance (data not shown). This suggests that gas molecules were not broken down by the current electric field range. The breakdown voltage of gases (1% SF₆ and 99% N₂, which is supposed to be higher than that of 20 ppm NO₂) is about 7 MV/m. Since the local electric field near the CNT surface can be expressed as

$$E_{\text{local}} = \gamma E_{\text{external}}$$  (2)
where \( E_{\text{external}} \) is the applied field, therefore eq 2 can be written as

\[
E_{\text{local}} = \gamma \frac{3 \text{ V}}{5 \mu\text{m}} < 7 \text{ V/\mu m}
\]  

(3)

Thus \( \gamma < 12 \). The field enhancement factor from the sidewall CNTs is much smaller than that from the CNT tips.\(^{18,19}\) This suggests that the polarization effect is not strong under the currently used bias (3 V), which is in agreement with our analysis of the capacitive sensitivity in Figure 2. Here we summarize the origin of dominant charge transfer effect: (1) long recovery time implies that gases are strongly adsorbed on the CNT surface and charge transfer plays an important role; (2) weak local field induces a small polarization effect; and (3) weak local field strength near the tip strongly suggests negligible field emission current.

4. Conclusions

We have constructed capacitive NO\(_2\) gas sensor of high sensitivity with vertically aligned MWCNTs acting as electrodes to study the combined response mechanism by AC measurement. The sensing mechanism incorporates charge transfer, polarization of gas molecules, and field emission current. We infer in our case that the charge transfer plays a more important role than the polarization and field emission effect. Annealing as a post-heat-treatment can improve the capacitive response and production yield by removing the preexisting adsorbents and possibly improving the contact between metal and the CNT. Our optimization procedure shows that shorter gap distance gives better AC response and thus production yield of the sensor is improved due to the enhanced polarization effect. Improvements related to the recovery time and gas selectivity are under investigation.

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References and Notes

(15) Since our MWCNTs have diameters ranging from 10 to 15 nm, the electronic density of states of MWCNTs is rather graphite-like than SWCNTs-like. Nevertheless, charge transfer due to gas adsorption will occur and thus the Fermi level will be shifted. The electronic density of states near the Fermi level will accordingly change and the quantum capacitance as well.

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