FABRICATION OF GAS SENSOR USING SINGLE-WALLED CARBON NANOTUBES DISPERSSED IN DICHLOROETHANE

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The single-walled carbon nanotube (SWCNT)-field effect transistor (FET) gas sensor was fabricated by spin-coating SWCNTs dispersed in dichloroethane (DCE) solvent on silicon substrate. Raman spectra revealed that walls of the nanotubes were well preserved without much damage during DCE treatment. The sensitivity of the gas sensor was strongly dependent on the series resistance. The sensitivity was maximized in the reasonable contact resistance between nanotubes and electrodes. This was attributed to the suppression of the dark current. The SWCNT gas sensor revealed typical p-type characteristics with respect to NO$_2$ and NH$_3$ gases. The small-bundled SWCNTs increased accessibility of gases to nanotubes and therefore increased the sensitivity of the nanotube gas sensor. The response time was shortened particularly in the case of NO$_2$ gas compared to the previous report.

Keywords: Single-walled carbon nanotubes; gas sensor; dichloroethane; sensitivity.

1. Introduction

Isolated single-walled carbon nanotubes (SWCNTs) have been used in electronic devices such as field effect transistor (FET) and gas sensor because of their unique properties. In particular, SWCNT-FET type of gas sensor has revealed superb sensitivity at room temperature due to a drastic change in the electrical conductivity upon various gas adsorptions. Despite such advantages, the presence of both metallic and semiconducting carbon nanotubes on the patterned electrodes is a critical bottleneck in the application of SWCNT-gas sensor. In addition, the yield of electrode formation of SWCNT-FET gas sensor has been still lower compared to that of the conventional gas sensor. Because of this, the real application of large scale arrays of SWCNT-FET gas sensor is still limited.

Recently, another approach has also been reported with SWCNT-gas sensor which was based on nanotube network film using dispersed SWCNTs in organic solution such as dimethylformamide (DMF). The SWCNTs network was fabricated by using a solution casting process on the patterned electrodes. The contact resistance between the SWCNTs network and electrode decreased effectively over a large area. Moreover, the sensitivity of SWCNT-gas sensor was enhanced with NO$_2$ gas adsorption due to abundant active sites of SWCNT surfaces. This method was simple and straightforward to developing inexpensive gas sensors. However, the sensitivity of nanotubes gas sensor was still lower than that of conventional gas sensor due to low dispersibility of nanotubes with DMF solvent.

In this paper, we have introduced dichloroethane (DCE) to enhance dispersibility of SWCNTs and demonstrated a simple SWCNT-sensor that combines the advantages of both single nanotube transistors and random network nanotube sensors with extended application to the sensitive detection of NO$_2$ and NH$_3$ gases. The hydrophobic
nanotubes were well dispersed in nonpolar DCE solvent. The SWCNTs formed a random network on the prepared electrodes using a solution-casting process. A random network with well dispersed nanotubes provided good accessibility for gas and vapor adsorption to all SWCNTs including semi-conducting tubes. A reasonable contact resistance was necessary for a high sensitivity of gas sensor to suppress the dark current.

2. Experimental Details

The pristine HiPCO SWCNTs were purchased from CNI (Carbon Nanotechnologies Inc.).

Figure 1(a) presents the schematic diagram of the sample preparation procedure. The remaining metal (metal oxide) content was 1.7 wt% from thermogravimetric analysis in air. The pristine SWCNTs were immersed in DCE (surface tension 32.6 mN/m) without additives. The sample of 0.1 mg was further sonicated in DCE of 100 ml for 15 h. After centrifuging the sample at 27 460 g for 3.5 h, supernatants were dropped on the pre-patterned SiO\(_2\) substrate. The electrode pattern was obtained on the SiO\(_2\) substrate by using conventional photolithography process, as shown in Fig. 1(a). The separation distance between metal electrodes was about 5 µm. The molybdenum (Mo) electrodes were deposited using RF (Radio Frequency) magnetron sputter at 4 × 10\(^{-6}\) Torr with a thickness about 50 nm. Well dispersed SWCNTs in DCE were dropped onto the patterned electrodes (Mo), as shown in Fig. 1(a). After the drop each sample was dried in air overnight. The sample morphology between the two electrodes was observed by field emission scanning electron microscopy (FE-SEM) (JSM6700F, JEOL). The sample was composed of 12 pairs of electrode arrays. Figure 1(c) presents a typical FESEM morphology. SWCNTs were randomly oriented between electrodes. The density of SWCNTs was controlled by controlling CNT amounts in the solution. In order to characterize the sensitivity, selectivity and response time of the gas sensor, this sample was exposed to various NO\(_2\) gas concentrations from 50 to 2000 ppm.

3. Results and Discussion

Figure 2(a) presents the AFM image of the individually dispersed SWCNTs spin-casted on SiO\(_2\) substrate. Nanotubes were well dispersed with relatively small diameters with peak values near 2 nm, as shown in Fig. 2(b). In the current approach, the dispersion of SWCNTs was achieved by a solution of nanotubes in a nonpolar solvent, in good contrast with nonsoluble nanotubes in a polar solvent. In particular, the nonpolar solvent with halogen groups enhances the solvation of nanotubes by increasing the binding energy between nanotubes and solvent molecules. Another advantage of using DCE is that its boiling temperature is 83°C, much lower than 202°C and 153°C of respective organic NMP and DMF solvents, which can be easily removed by vaporization after treatment. Another point to address is that the boiling temperature of DCE (32.6 mN/m) has smaller surface tension than water (72.3 mN/m), revealing a better wettability of nanotubes. The most probable height (diameter) was duplicated near 1.6 and 3 nm, where the latter could be
a bundle composed of two or three nanotubes. Although the dispersed SWCNTs in DCE solution seemed to be quite stable, the aggregation did occur microscopically. Figure 3 presents the resonant Raman spectra with two excitation energies of 633 and 514 nm. The diameters of the grown SWCNTs ranged from 0.8 to 1.3 nm, determined from the radial breathing modes (RBMs). By taking the areal intensity of RBMs, we extracted information for metallicity of the grown SWCNTs. The sample contained both metallic and semiconducting nanotubes. The sensitivity of the nanotube gas sensor was measured by exposing various concentrations of NO₂ gas (500, 1500 and 3000 ppm), as shown in Figs. 4(a) and 4(b). The sensitivity of SWCNT-gas sensor is defined as the resistance (or conductance) difference between after and before gas exposure \([R_m - R_0]/R_0\), where \(R_m\) and \(R_0\) are the measured and the initial resistances, respectively. Five different FETs were successfully connected after spray. The resistance was dropped with gas adsorption, giving negative values in the sensitivity. The absolute sensitivity increased linearly with increasing gas concentration. In fact, this phenomena is similar to that of the conventional CNT sensor, which clearly revealed the p-type characteristics with NO₂ gas. Another thing to note was that the sensitivity was strongly dependent on the initial resistance. In Fig. 4(a), the initial resistances of each FET were 62.3 kΩ, 120 MΩ, 108 kΩ, 1.2 MΩ and 6.7 MΩ from the top curves. Figure 2(b) presents
Fig. 4. (a) Sensitivity changes as a function of NO\textsubscript{2} gas concentration at 500, 1500 and 3000 ppm (black dotted circle: sensitivity at gas concentration of 1500 ppm); (b) sensitivity changes as a function of initial resistance at NO\textsubscript{2} gas concentration of 1500 ppm (black dotted circle: higher sensitivity at 6.7 MΩ of initial resistance); (c) sensitivity changes as a function of low NO\textsubscript{2} gas concentration at 50, 100, 150 and 200 ppm; (d) sensitivity changes as a function of initial resistance.

the change of the sensitivity at 1500 ppm as a function of initial resistance. It was found that the sample with an initial resistance of 6.7 MΩ revealed the highest sensitivity. Another set of devices also revealed the similar behavior even at low gas concentrations of less than 200 ppm. Their dependence on the initial resistance was also presented in terms of gas concentration in Fig. 4(d). In this case, an initial resistance of 2 MΩ resulted in the highest sensitivity. This value was about seven times higher than that obtained by the previous spin-casting approach.\textsuperscript{7} In our approach, SWCNTs were dispersed in DCE, whereas the previous work used DMF for SWCNTs dispersion. This indicates that the SWCNTs were dispersed in DCE better than in DMF. Well-dispersed SWCNTs can increase the specific surface area of SWCNTs, providing easy accessibility for gas adsorption. To yield high sensitivity, a reasonable initial resistance was required to suppress the dark current. Too many SWCNTs over percolation limit lower the resistivity of the device but the dark current is expected to be too large to distinguish the resistivity difference upon gas adsorption. This will in turn reduce the sensitivity.

To calculate the sensitivity of SWCNT-gas sensor, the initial resistance can be defined as the total resistance (R\textsubscript{T}) of a sensor which is composed of the contact resistance (R\textsubscript{C}) between nanotubes and metal electrodes, and nanotube resistances in combination with metallic and semiconducting ones. The gases may be adsorbed at the interface that might change the work function at the contact, i.e., the Schottky barrier height as suggested earlier.\textsuperscript{11–13} Another possibility is the change of carriers in the nanotubes due to charge transfer from nanotubes to gas adsorbates or vice versa depending on the gas species.\textsuperscript{14} Figure 5 presents a dynamical response upon gas exposure. The resistivity was drastically
dropped upon NO$_2$ gas exposure of 200 ppm, again revealing strong dependence on the initial resistance. The response time was obtained by defining the sensitivity that reached about 90% of the maximum sensitivity. The response time was about 5 min, independent of the initial resistance. This response time increased with decreasing the gas concentration (Fig. 5(c)). These values were faster than that of the previous works.\(^7\) The gas supply was terminated after saturation at about 15 min. Since the devices were operated at room temperature, the recovery time was relatively slow. In most cases, they were not fully recovered. This indicates that the adsorption energy of NO$_2$ gas is quite large, as suggested by the previous calculations.\(^{15}\) NO$_2$ has an unpaired electron and is known as a strong oxidizer. In case of NO$_2$ adsorption, charge transfer is likely to occur from an SWCNT to NO$_2$ due to strong electron negativity of NO$_2$ molecules. Therefore, the resistance (conductance) decreased (increased) with increasing exposure time of NO$_2$ gas, because SWCNTs were typically p-type transistor. As a result of hole-doping, the Fermi level of a semiconducting SWCNT was located above valence band, which was responsible for the observed resistance of semiconducting SWCNT samples at room temperature. On the other hand, the resistivity was increased with adsorption of NH$_3$ molecules. NH$_3$ acts as a donor due to strong electron affinity of SWCNTs. This neutralizes the acceptor, and thereby increases the resistivity of the device. Here we clearly confirm that the dispersed SWCNT-gas sensor with DCE solvent shows the superior selectivity with respect to NO$_2$ and NH$_3$ gases.

4. Conclusion
We have introduced a fabrication of SWCNT-gas sensor by using well dispersed SWCNTs in organic solvent without additives. The SWCNTS were dispersed in DCE solvent and simply spin-casted on
the pre-patterned electrodes. This method is very simple and straightforward compared to the conventional e-beam lithography approach. Furthermore, high sensitivity was obtained in the current approach by controlling the initial resistance. The sensitivity was seriously dependent on the initial resistance. A reasonable initial resistance is required to suppress the dark current.

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