

SIMPLE FABRICATION PROCESS OF A CHEMICAL SENSOR ON GLASS USING NANOTUBE AQUEOUS SOLUTION

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ABSTRACT

An FET-based chemical sensor was fabricated using single-walled or multi-walled carbon nanotube derivative solutions with one-step photolithography. The nanotube aqueous solution is dropped on pairs of source and drain electrodes that are fabricated with Au using chemical vapor deposition. After drying the nanotube solution, many bundles of nanotubes that bridge between the source and drain electrode were obtained. The effect of liquid potential on the current through the source and drain electrodes was monitored in a buffer using an Ag/AgCl gate electrode. The current decreased with increasing potential of the gate electrode, which indicated that the device showed p-type FET properties. Response of the single-walled carbon nanotube against the gate potential is stronger than that of multi-walled one. The current increased with increasing pH in the region of pH 7 to pH 3. We demonstrated a simple method for fabricating easily an FET-based sensor using nanotube properties.

KEY WORDS

CNT-FETs, pH, sensor, solution, glass

1. Introduction

Recently, biosensors and chemical sensors based on FET properties of nanotubes have been investigated. Many papers have reported detection of various reactions such as antigen-antibody interaction, avidine-biotin interaction, DNA, pH, single virus particles, and so on [1-8]. Nanotube-based FET can be fabricated through growth of a nanotube using chemical vapor deposition (CVD). Electric properties of the nanotubes, including a fabrication of a stable contact between a metal electrode and nanotube, are not easy to control. For that reason, CVD method sometimes requires strict growth conditions. High-temperature processing during nanotube growth restricts the choice of the kind of substrate. Although a nanotube-network FET, on which numerous nanotubes are connected to the source and drain, has also been fabricated using CVD method and has been investigated

as a biosensor by many research groups [6, 9, 10], an improved method for highly reproducible device production and a simpler preparation method are still required for use in biosensors.

For this study, we used a typical and classical method: merely dropping and drying a nanotube derived dispersion on a substrate [11]. One merit of this method is that similar electric properties of each sensor are contributed by averaging the properties of each nanotube because the number of nanotubes between the electrodes is greater than that of CVD method. However, raw carbon nanotubes can be dispersed in a strong acid or organic solvent such as chloroform and DMF. The organic solvent is easy to spread over substrates, thereby rendering it difficult to deposit the nanotube on any area by dropping the solution.

Controlled immobilization methods of nanotubes on a substrate have been well investigated to overcome this problem. One method is using a thin layer of 3-aminopropylsilane derivatives (APS) [12-14]. Recently, although other areas were protected from binding of nanotubes by organic molecules, nonspecific binding to a bare substrate was applied for fabricating a FET device [15]. These controlled immobilization methods can fabricate a small sensor whose sensing area can be down-scaled to less than 100 nm. However, these methods still entail a complex process. A simpler process might be required for wide use and application.

Nanotube-derived aqueous solutions were used in this study to prevent the CNT solution from spreading on the substrate. This eased deposit of nanotubes on an area: merely dropping the solution was sufficient to deposit them because of the surface tension between the substrate surface and buffer. Although a peptide-wrapped CNT network-FET and a surfactant coated CNT network-FET has been fabricated and electrical properties of the device was investigated using a back gate electrode in air [16, 17], application of the device in a buffer as a biosensor has not well been investigated. Preparation of the coated CNT was also required in their methods.

For this study, the nanotube solution was prepared using treatment with a mixture of acids. Then the acid

treated nanotubes solutions were dropped on pairs of source and drain electrodes that were fabricated from Au using chemical vapor deposition. We investigated the properties of the device by measuring I - V curves in a buffer.

2. Materials and Methods

From Sigma-Aldrich Corp., disodium hydrogen phosphate, multi-walled carbon nanotubes, 3-aminopropyltriethoxysilane, and dihydrogen sodium phosphate were purchased. Single-wall carbon nanotubes were purchased from Carbon Nanotechnologies Inc., USA. Sulfuric acid, nitric acid, hydrogen peroxide, sodium citrate dehydrate and sodium chloride were obtained from Kanto Chemical Co. Inc., Japan. Cover glass was purchased from Matsunami Glass Ind., Ltd., Japan. A photoresist (OFPR-800) was purchased from Tokyo Ohka Kogyo Co., Ltd., Japan.

2.1 Deposition of source and drain metallic electrodes

Patterns used for formation of metallic electrodes were fabricated on CNT-immobilized areas using a similar process to that used for formation of areas for immobilization. The distance between the source and drain electrode was 2–10 μm and the widths and lengths of electrodes were 6 μm and 5 mm, respectively. As metallic electrodes, a 30-nm-thick Cr film and a 50-nm-thick Au film were deposited using evaporation deposition.

2.2 Preparation of a nanotube derivative solution and its adsorption on silicon or glass substrate

Using a mixture of H_2SO_4 and HNO_3 , 0.5 mg of SW-CNTs or MW-CNT were washed for 1 h at room temperature. The mixture solution was centrifuged; then the residue was suspended in a mixture of H_2SO_4 , HNO_3 , and H_2O_2 for 1 h with ultra-sonication. The resultant black solution was diluted with water and subjected to dialysis with distilled water to adjust a neutral pH for the solution. The nanotube derivative solution was resonicated immediately before use. Using a micropipette, 2 μl of the solution was placed on the electrodes deposited substrate at room temperature for 10 min to evaporate the solution, followed by heating the substrate for 10 min at 150°C. The dropping area of the CNT solution was ca. ϕ 1 mm and the nanotube adsorbed area covered the region between the source and drain electrodes.

2.3 I - V measurements and pH measurement

To elucidate CNT properties in a solution, I_{ds} was measured in air or in 100 mM phosphate, 200 mM citrate buffer with 100 mM NaCl at pH 7.0 by applying -0.7 to +0.1 V to back gate or liquid gate (Ag/AgCl electrode). After immersion in buffer for at least 10 min, I_{ds} , the

current between the source and drain electrodes, data were plotted as a function of the gate (V) (I - V curve). A schematic model of the measurement is shown in Fig. 1.

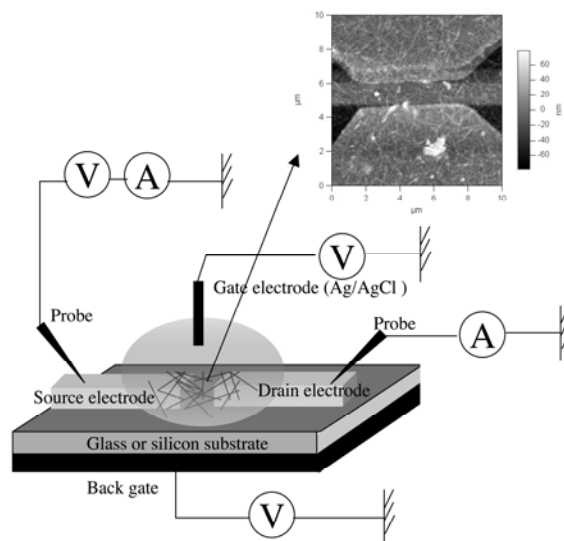


Figure 1. Schematic model of the measurement of I - V curves in the buffer or air. The gate potential was applied to the AgCl electrode in the case of the measurement in the buffer. Back gate was used in the measurement in air. The respective potentials applied to the source and drain electrode were 0.1 V and 0 V.

Effects of the pH on I_{ds} were measured by dropping various pH of the buffer on the CNT device. The potential between the source and drain electrode was 0.1 V and an Ag/AgCl electrode was used as the gate electrode and -0.3 V was applied to the gate electrode. To examine the CNT properties in air, CNT device was fabricated on a 100-nm silicon oxide layer with a 500- μm -thick silicon substrate. The back gate was contacted to the silicon substrate and I_{ds} , and was plotted as a function of the back gate potential. The potential between the source and drain electrode was +0.1 V.

A semiconductor characterization system (4155C; Agilent Technologies Inc.) was used to measure the I - V curves at room temperature.

3. Results and Discussion

The AFM images of the CNT derivatives closely resemble those of the images obtained by treating the SWCNT with a mixture of H_2SO_4 and H_2O_2 , however the length of each CNT bundle is shorter and the CNT bundle diameter is larger than 20 nm. After dropping the solution on the area between the source and drain electrode, CNTs were adsorbed on that area (inset of Fig. 1).

Electric properties of the devices prepared from SWCNT and MWCNT on the silicon oxide substrate were investigated using measuring I_{ds} - V_{gate} curves in air and 10

mM phosphate-citrate buffer (Fig. 2). In air, I_{ds} showed no back gate potential dependency in either the SW-CNT or the MW-CNT device. This result is consistent with those reported in the literature [18, 19]. Although dull FET properties was observed when the gate potential was applied from -40 to 40 V in one study [18], even when the back gate potential was increased to -20 to 20 V, no significant change in I_{ds} was observed (data not shown). In our case, byproduct carbon fragments by acid treatment, amorphous carbon, and poly-benzene derivatives, covered some part of the surface of the CNT bundles. These materials might prevent the back gate potential from running through from the back gate to CNT bundles.

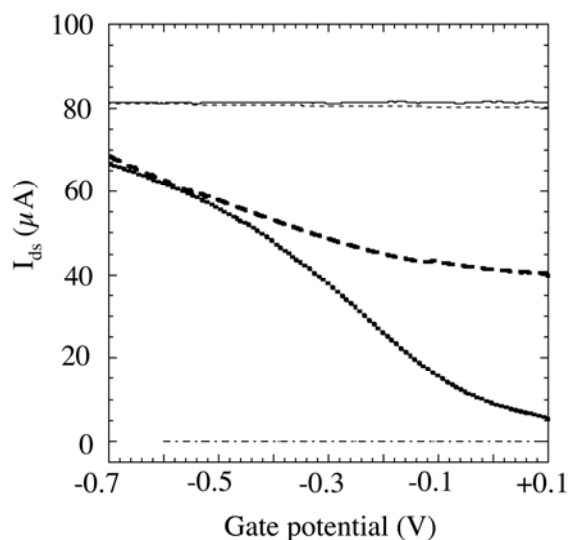


Figure 2. I - V curves in air and in the buffer. Solid and dotted lines respectively indicate the I - V curves produced by SW-CNTs and MW-CNTs. Thick and thin lines were measured in buffers and in air. Dashed lines show I - V curves in the case of no CNT between the source and drain electrode.

In the buffer, I_{ds} was strongly dependent on the gate potential in the case of the SW-CNT device, although only dull response was observed in the case of MW-CNT device. The current flow between the reference electrode and source drain electrodes or CNT via the buffer was less than 50 nA; the current might be negligible compared to the I_{ds} . These phenomena were observed 100% of the time in the case of SWCNT and 90% of the time in the case of MWCNT. In the buffer, water and electrolyte molecules accessed the CNT network surface, where the potential from back gate can not be transmitted well because of large capacitance of electrolyte compared to the capacitance of nanotube and silicon substrate. This result is consistent with the electrochemical properties of a single MW-CNT device, as reported by Kruger et al [19]. In addition, Rosenblatt et al. reported that the liquid gate is efficient for biosensors using CVD-prepared SW-CNT FET [20]. This result suggests that nanotube network devices prepared solely by depositing a CNT

solution on the electrodes show FET properties in the buffer.

The reason for not turning off I - V curves completely is the contribution from the occasional presence of nanotube bundles containing metallic nanotubes.

Investigation of the pH response to I_{ds} of MW-CNT network-FET or SW-CNT network -FET on a glass was carried out to evaluate the device as a pH sensor that might someday serve as a basic device for biosensors. Effects of pH on electron-transport properties of SW-CNT were assessed by measurement of its FET fabricated using CVD method on a silicon oxide substrate by Back et al. [21]. We also reported SW-CNT network-FET based pH sensor on a glass substrate using controlled immobilization of CNT on APS layer [22]. One of the typical I_{ds} - V_g curve of MW-CNT network -FET was shown in Fig.3. and the effect of pH change on I_{ds} of the MW-CNT network -FET is shown in Fig.4. The buffer solution at pH7 was dropped on the FET device at first. After FET signal was stable, the pH7 buffer was changed to pH6 buffer. The I_{ds} was decreased after changing the buffer. After signal showing stable, at the point indicated by arrows, the buffer solution was changed to other pH buffer. The I_{ds} was decreased with decreasing pH of the solution from pH 7.0 to pH 2.0. The decreasing of the I_{ds} could be explained by due to the adsorption of proton ion at the nanotube surface that could contribute to change the potential near the CNT to positive. The response of the signal against pH showed reproducibility. The potential changes near the nanotube were calculated from I - V curves (Fig. 3), as indicated in the right Y scale in Fig. 4. The potential change of the nanotube was estimated as ca. 25 ± 5 mV/pH unite from pH 7 to pH 3. This value is similar to the value reported using CVD-grown SW-CNT FET by Back et al.

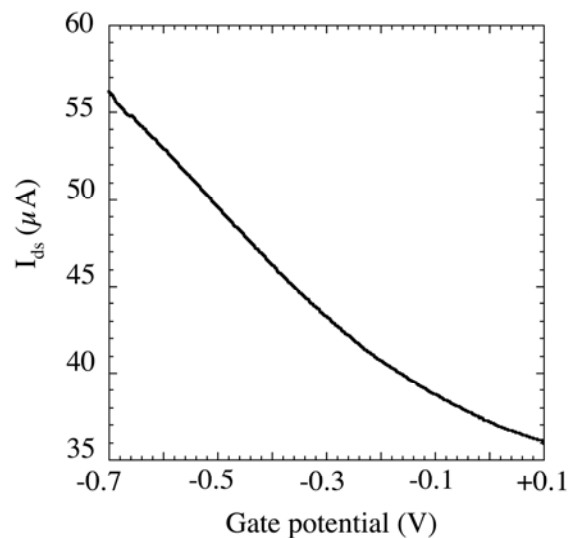


Figure 3. One of the typical I - V curve of MW-CNT in the buffer on the glass. The respective potentials applied to the source and drain electrode were 0.1 V and 0 V.

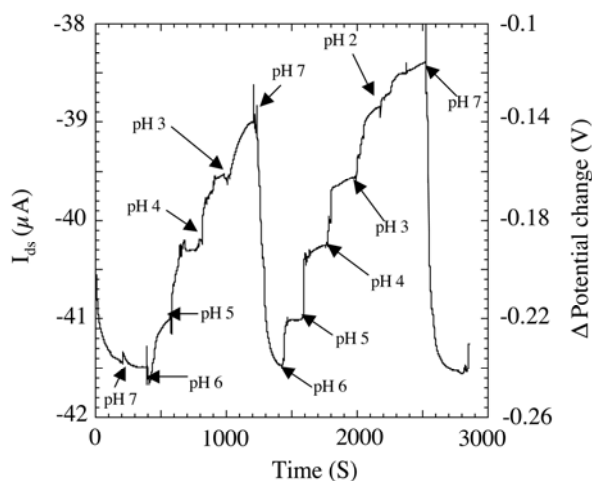


Figure 4. The effect of pH on I_{ds} of MW-CNT using the same device of Fig. 3 is shown in Fig. 4. The potential change was calculated from Fig. 3.

The SW-CNT network-FET also shows similar response against pH (data not shown) and the potential change of the nanotube against pH was estimated as 30 ± 10 mV/pH. These results suggest that the device might be applicable for use in pH sensors.

This device can be prepared very easily compared to the other method with more than 90% of the yield: within 20 min after preparation of an electrode deposited substrate and nanotube solution. Moreover, the choice of substrate is not restricted to those which can withstand heat processes for nanotube growth. For those reasons, this device might be applicable for use as a chemical sensor or biosensor.

4. Conclusion

The MW-CNT or SW-CNT network-FET working in the buffer was fabricated easily using a simple method. We demonstrated that this method is useful to fabricate a nanotube-based FET device that has the potential to be a pH sensor. Fabrication can be accomplished within 20 min without coating a nanotube using materials such as a peptide and surfactant. Although the device is not applicable for use in memory devices in an electrical circuit because FET properties appear not in air but in the buffer, the device is applicable for use in pH sensors.

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