Increased Sensitivity of Carbon Nanotube Sensors by Forming Stable and Low Resistance CNT/Metal Electrode

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ABSTRACT

Although the bottom-contact process is easier in view of the carbon nanotube (CNT) device fabrication, the bottom-contact is weak and high in resistance because CNT bonds to the electrode via van der waals force. By utilizing low-temperature melting eutectic alloy as an electrode for CNT wire, we could achieve rigid and low resistance contact while we could take advantage of the bottom-contact process. After patterning the electrode which consisted of Au and Al layer, we laid the carbon nanotube on the electrode by dielectric electrophoresis. The sample was then annealed at 250 °C in air briefly to form Au-Al alloy grains and to embed the CNT into the electrode. The resistance of the resulting contact decreased by more than a factor of 4. Finally, we could conclude that the eutectic electrode valid for fabrication of CNT cross-junctions and CNT sensors.

Keywords: carbon nanotube, contact, contact resistance, eutectic alloy

1 INTRODUCTION

An intensive effort is given to utilize carbon nanotube (CNT) for ultra-small scale electronic devices with novel functions. CNT field effect transistors [1] and sensors [2] use CNT as a current channel, of which the resistance varies with the gate voltage or upon molecule adsorption. The performance, however, greatly depends on the CNT/metal contact resistance. Therefore, for these devices to function properly, the CNT/electrode contact must be stable and the contact resistance must be small. Depending on the geometry of CNT/electrode contact, it can be categorized into the end-contact, embedded-contact (top-contact), and side-contact (bottom-contact) [3, 4]. Because of difficulties in the sample preparation, the end-contact CNT device is seldom practiced [5]. The embedded-contact in which CNT is embedded inside the electrode is desirable due to its rigidness and the low contact resistance. Fabrication of this structure is complicated, however, because each CNT has to be located under a high-resolution microscope and then the electrode is patterned by electron beam lithography [5, 6]. The side-contact is done by depositing CNT electrophoretically or by precipitating on the patterned electrode. Although this contact is fragile and the contact resistance is relatively high, the side-contact by far has been widely practiced because of its simple fabrication process [7, 8].

Here we introduce a simple method to embed CNT inside the electrode while taking advantage of the bottom-contact process. The idea is to utilize as an electrode a eutectic material which melts at low temperature so that CNT is not damaged while annealing to melt the electrode to embed CNT. In our experiment, we used a eutectic Au/Al film which melts at 250 °C [9-11]. After depositing CNT on the electrode made of an Au/Al thin film, we annealed the sample at 250 °C in air to induce eutectic melting. As a result, Au-Al alloy grains formed under which the CNT was embedded to produce a rigid and low resistance contact.

2 EXPERIMENTAL

The 2 μm gap Au/Al electrode was formed on the SiO_2/Si substrate by using a standard photolithography, thermal evaporation, and lift-off process. We deposited a 30 nm thick Al layer first and a 20 nm thick Au layer next to induce eutectic melting at the boundary between Au and Al when the sample is exposed at 250 °C (Fig. 1).

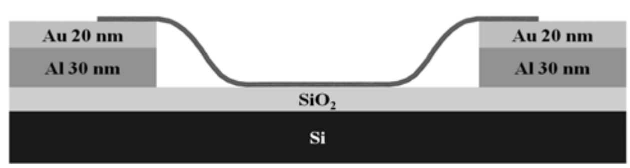

Figure 1: Schematic of the electrodes and MWNT before eutectic melting. SiO_2 layer is 500 nm thick.

Alternating current dielectrophoresis (AC DEP) method was used to deposit a single metallic multi-walled CNT (MWNT) connecting the electrodes [7, 12, 13]. We dropped about 1 μl of MWNTs suspension (2 μg/ml) on the electrode pattern, and applied a 10 V_{pp}, 1 kHz voltage between the electrodes. The average diameter of the MWNTs estimated from atomic force microscopy (AFM) images was about 6 nm. After depositing a MWNT, we annealed the entire sample at 250 °C in air by putting it on a hot plate to melt the Au/Al electrode eutectically. The

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melting was verified by the electrode color change and AFM images of the electrode morphology.

3 RESULTS AND DISCUSSIONS

When the Au/Al bilayer film electrodes were annealed at 250 °C for a while, its color changed to purple which is a typical color of Au-Al alloy. Although this temperature is much lower than the eutectic melting temperature of bulk Au and Al mixture [11], the diffusion of Au and Al atoms at the interface starts at temperature as low as 200 °C and can form a Au-Al binary alloy of all different stoichiometries [10]. Since our Au/Al bilayer film is very thin, the eutectic melting could occur at 250 °C.

AFM image of two Au-terminated electrodes and a single MWNT bridging them is shown in Fig. 2a (hereafter this sample will be designated as MWNT/Au-terminated). Both of the MWNT end parts laid on the electrode surface is also visible. We annealed this sample to induce the Au-Al eutectic melting and form Au-Al alloy at 250 °C for 3 min in air. The initial Au-terminated electrodes were yellow but after annealing they changed their color to purple, which is the color of Au-Al alloy known as purple gold, thus this confirms that the Au-Al electrodes melted and turned into Au-Al alloy by annealing. Fig. 2b is an AFM image obtained after annealing the sample shown in Fig. 2a (hereafter this sample will be designated as MWNT/Au-Al alloy). One can recognize that the morphology of Au-Al electrodes has changed because of Au-Al alloy grains formation, but the mid part of MWNT between the electrodes depicted in Fig. 2b looks exactly the same as in Fig 2a. The end parts of MWNT on the electrodes are not seen in Fig. 2b because it is buried under and between Au-Al alloy grains. For comparison, we also prepared MWNT/pure-Au-electrode samples and annealed them at 250 °C, but MWNT in these samples stayed on the Au surface after annealing.

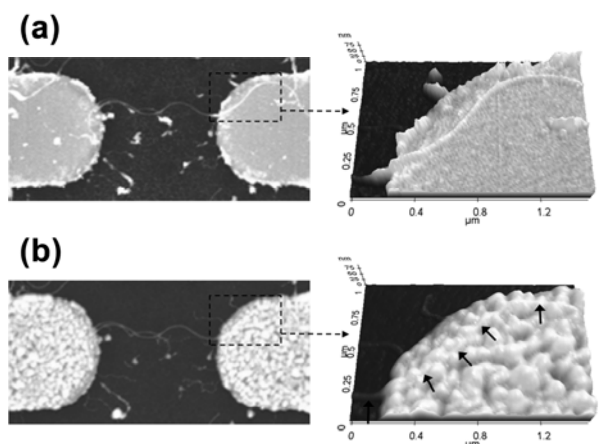

Figure 2: AFM images of (a) MWNT/Au-terminated electrode and (b) MWNT/Au-Al alloy electrode.

MWNT is not heavy enough to submerge when Au-Al melts. We instead suggest that the stress and the morphology change created by the Au and Al atom diffusion and Au-Al alloy formation when the Au/Al binary film melted caused mixing of MWNT and Au-Al grains. The average roughness of the initial Au-terminated surface is 1.7 nm, but that of the Au-Al alloy surface is 7.2 nm, which is larger than the diameter of the MWNT used in this study (6 nm).

The contact resistance of MWNT/Au-terminated and MWNT/Au-Al alloy was examined by measuring the current while applying bias voltage between electrodes connected by MWNT. The result displayed in Fig. 3 shows that the average current of 30 samples increased by more than a factor of four when MWNT/Au-Al alloy was formed. This was possible because of the rigid contact and the contact area increase as a result of MWNT embedment into the Au-Al alloy electrode. The sample dependence of current-voltage relation revealed in Fig. 3b is somewhat large. This was because the degree of MWNT embedment and the diameter of MWNT in each sample were not steady.

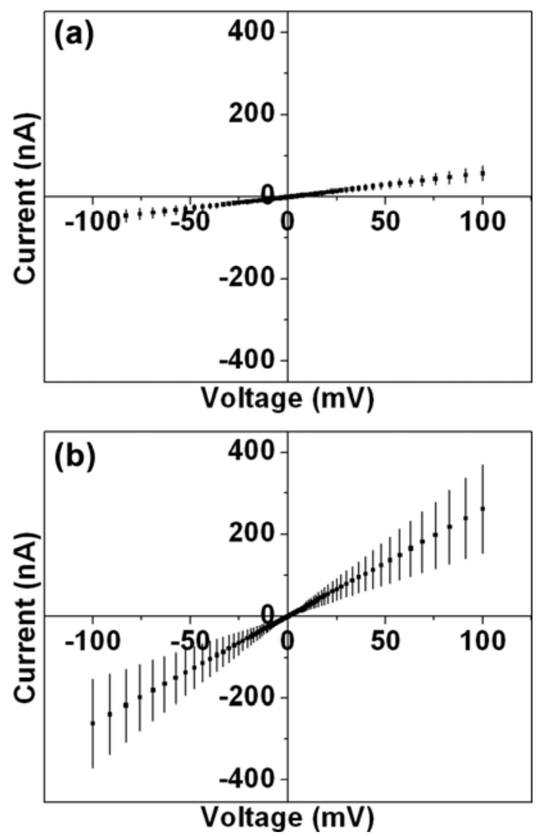

Figure 3: (a) Current-voltage curve with error bars averaged over 30 samples before annealing and (b) after annealing.

CNT cross-junctions are promising device for various electronics and sensing devices, but their fabrication process is complicated [14, 15]. Within the side-contact structure, AC DEP method is not desirable to deposit two CNTs in cross direction because the electric field applied for depositing the second CNT affect the first CNT out of its position. Our CNT/Au-Al alloy structure can be available to make CNT cross-junctions with ease because the first CNT is gripped strongly by the electrode. To prove this, we added two electrodes in cross direction on the MWNT/Au-Al alloy sample by going through the standard semiconductor processes of photoresistive film coating, photolithography, Au/Al metal film deposition and lift-off. After this, the second MWNT was deposited by AC DEP method to connect the second electrode pair to form a cross junction. We then annealed the sample again to induce eutectic melting of the second electrode pair. The second annealing does not affect the previously transformed first Au-Al alloy electrodes because once an Au-Al alloy forms much higher temperature is needed to melt it. According to Au-Al phase diagram, melting point of Au-Al alloys is higher than 500 °C [11]. Fig. 4a is an AFM image showing the first Au-Al alloy electrode pair bridged by MWNT. The second electrode pair formed on this sample by the standard semiconductor process and the second MWNT was deposited by AC DEP and annealed at 250 °C, so we could achieve the MWNT cross-junction (Fig. 4b).

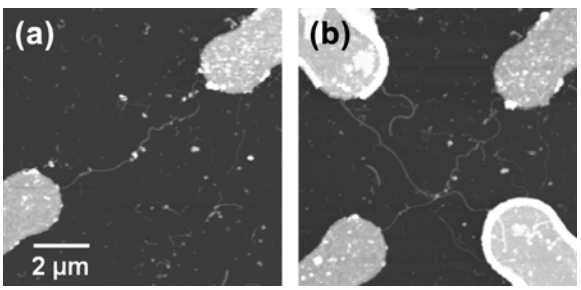

Figure 4: AFM image showing (a) MWNT on electrode pair and (b) MWNT cross junction fabricated by adding a second electrode pair bridged by CNT to the substrate shown in (a).

It is important that sensors should maintain their detection ability even after washing process. CNT/Au-Al alloy structure is also available for CNT sensors because it can sustain the strong washing process. We examined Au ion detection ability of samples like shown in Fig. 2 by immersing in $HAuCl_4$ solution and measuring channel current before and after washing process (Fig. 4). Au ion is spontaneously reduced to CNT surface and increases current across CNT [16]. Fig. 4a shows that MWNT/Au-terminated sample lost its detection ability after washing in dichlorobenzene with 40 kHz, 150 W ultrasonic agitation. MWNT/Au-Al alloy sample, however, maintained Au ion detection ability after washing process (Fig. 4b).

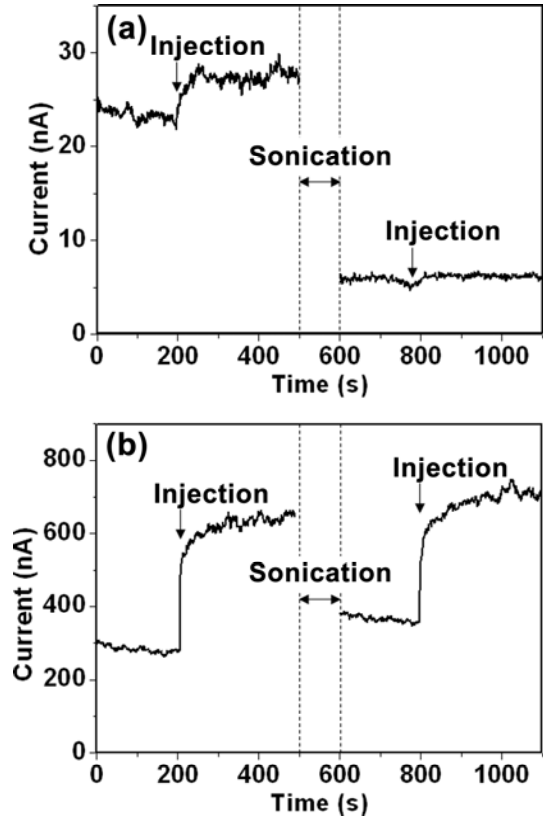

Figure 4: Au ion detection of (a) MWNT/Au-terminated electrode sensor and (b) MWNT/Au-Al alloy electrode sensor. Sonication time was 3 min and bias voltage was 10 mV.

4 CONCLUSION

We presented a simple method to make embedded-contact by taking advantage of the low melting temperature of a eutectic material. We utilized as an electrode with Au/Al film which transforms to Au-Al alloy at 250 °C. After bridging the two Au/Al electrodes by a CNT, the sample was annealed at 250 °C for 3 min in air. AFM images obtained after annealing confirmed that the CNT was embedded between the Au-Al alloy grains. The current-voltage measurement exhibited the resistance of the CNT/Au-Al alloy structure decreased by a factor of four. Our embedded CNT contact was strong enough to sustain the semiconductor fabrication process and ultrasonic agitation, so we could apply it to CNT cross-junctions and CNT sensors.

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