Field emission characteristics of self-assembled carbon nanotubes on the gold surface

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A method was studied to fabricate carbon nanotube (CNT) field emitters through self-assembly of thiol-modified CNTs onto a gold-coated substrate. By adsorption through simple immersion of the gold-coated substrate into thiol-modified CNT solution overnight, deposition of CNTs was accomplished. It was found that CNTs were deposited on the substrate as random aggregates of CNT bundles. The population density of CNTs on the gold-coated substrate was varied by controlled CNT concentration in ethanol. The $I–V$ measurement of the self-assembled CNTs shows relatively good field emission characteristics with a low turn-on field ($2.5 \text{ V/\mu m}$) and a high current density ($40 \text{ mA/cm}^2$ at $3 \text{ V/\mu m}$). In addition, more-populated CNTs on the substrate produce a higher current density. Therefore, the technique of self-assembly of CNTs on a selected area is expected to be a reliable way to prepare large-size panels with easy process and low cost. These advantages recommend further investigation of the self-assembly of CNTs. © 2003 American Vacuum Society.

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I. INTRODUCTION

Recently, great attention has been focused on the application of carbon nanotubes (CNTs) as field emitters to realize full-color field emission displays (FEDs).1 Due to their high-aspect ratio, allowing low-emission fields as well as their high chemical and mechanical stabilities, there are some advantages to using CNTs as field emitters. The fabrication of CNT FEDs has been tried by various techniques such as chemical vapor deposition (CVD) (Ref. 2) and the screen-printing method.3 Strong efforts have been made to develop a highly efficient CNT FED with a triode-type geometry for the generation of high-quality moving images to overcome some difficulties in large-size vacuum display. One attempt was the incorporation of CNTs into a triode-type structure by electrophoresis.4 In this article, we introduce another attempt to fabricate CNT field emitters through self-assembly using Ni-capped CNTs and a gold-coated substrate. Through this method, we expect that difficulties, such as large-size panel preparation and the outgassing problem during vacuum operation, may be avoided easily.

Chemists have performed extensive research in the area of self-assembly of several chemical functional groups on specific metal surfaces.5 For examples, self-assembly of alkylsilane on hydroxylated surfaces,6 carboxylic acids on aluminum oxide,7 and alkanethiols on gold,8 silver, and copper surfaces, all utilize thermodynamic advantages through exothermic spontaneous reactions and relatively strong bond formations. Several research groups have accomplished the self-assembly of CNTs on gold surfaces9,10 or chemically modified patterned surfaces11–14 through chemical modification of the open end or the surface area of the CNTs. According to those results, the self-assembly of CNTs shows great potential to apply the techniques to diverse fields ranging from fabrication of nanoelectronic devices to molecular-level probes.14 The application of the self-assembly of CNTs to FED systems has strong appeal. However, the field emission characteristics of self-assembled CNTs on an electrode have not been reported yet. The emission characteristics of CNTs are important to determine whether this self-assembly technique is applicable to the FED fabrication process. If the emission performance is stable within an acceptable limit, the preparation of FED panels might be easily achieved through the self-assembly of CNTs on a patterned triode-type structure with no size limitation and with low cost.

We argue in this article the possibility to use self-assembled CNTs as field emitters in CNT FEDs. We base ours argument on comparison of the current density observed with the film obtained by the plasma enhanced (PE) CVD process. The article includes (i) the preparation of the thiol-modified CNT solution, which allows the self-assembly of CNTs on a gold-coated substrate; (ii) the adsorption of CNTs

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on a gold-coated substrate, together with density control of CNT deposition on the substrates; and finally, (iii) the field emission characteristics shown by $I-V$ measurement that produce the higher-emission current density from the substrate where more CNTs are deposited.

II. EXPERIMENTS

Nickel-capped CNT films were prepared by the PECVD process by dc plasma using C$_2$H$_2$ and NH$_3$ as the carbon source and etching gases, respectively, on a Ni/Cr/glass substrate.$^{15}$ The CNTs were separated from the substrate and were found to be a multiwalled structure with average dimensions of 1–3 $\mu$m long and 30 nm diam. The CNTs were dispersed in ethanol with the aid of ultrasonification. The thiol-modified (i.e., surface treated by the functional group of thiol) CNT solution was prepared by the addition of 50 $\mu$L of 1.8-octanedithiol into 10 mL of CNT-dispersed ethanol solution, where the number of CNTs is roughly $10^9$. After the overnight reaction at room temperature, filtration of the solution through a membrane filter having 100-nm-diam holes and successive washing with ethanol removed the excess unreacted 1.8-octanedithiol from the thiol-modified CNTs. Next, the filtrate containing the thiol-modified CNTs was re-dispersed in 20 mL ethanol. The relative concentration of the latter CNT solution will be described in this article as 100% (its absolute concentration is about $10^8$ CNTs/mL). Dilution of the latter CNT solution with ethanol produced 50% and 25% concentrated solutions. Next, these concentration-varying thiol-modified CNT solutions were used for density control of CNT deposition on a gold-coated substrate. The gold-coated substrate was prepared by electron-beam evaporation of gold on the Si(100) wafer with a titanium adhesion layer, producing Au(1000 Å)/Ti(100 Å)/Si. Immersion of the gold-coated substrates into the three different solutions having 100%, 50%, and 25% concentrations of the thiol-modified CNT caused the adsorption of the CNT on the substrates. For each concentration, the immersion time was varied, with durations of 1 min, 1 h, and 1 day. After each immersion time, the substrate of the adsorbed CNTs was taken out from the solution, washed with ethanol and water three times, and then blown dry using nitrogen gas flow.

The deposition image of the self-assembled CNTs on the gold-coated substrates was recorded by field-emission scanning-electron microscopy (FESEM). The adsorption of 1.8-octanedithiol on CNTs was confirmed by Fourier transform infrared (FTIR) spectroscopy. This spectroscopy identified the existence of alkyl chain groups of 1.8-octanedithiol. The field emission characteristics of the self-assembled CNTs were detected by diode-type field emission (FE) measurement. A series of positive voltages ranging from 0 to 2000 V was applied to an anode plate (a stainless metal mesh or an indium–tin–oxide glass) with a spacer separation of 430 $\mu$m to the cathodic self-assembled CNT substrate, which was electrically grounded. The current of the FE from the self-assembled CNTs was collected on the anode, where the open area exposed to the anode was 8.5 $\times$ 8.5 mm$^2$.

III. RESULTS AND DISCUSSION

The SEM images shown in Fig. 1 indicate that adsorption of the CNTs is successful. The deposition of CNTs is identified as random aggregates composed of CNT bundles together with particles suspected to be nickel [Fig. 1(a)]. Therefore, a uniform layer of CNTs on the surface was not observed. The density of the CNT bundles is approximately $10^7$/cm$^2$, exhibiting a low-populated distribution. Almost no amount of CNTs was observed from the 1 min and the 1 h immersed substrates, and the variation of CNT concentration did not influence the tendency of CNT deposition. For the case of 1 day immersion, however, the variation of CNT concentration leads to a difference of CNT deposition density on the gold-coated substrate. This is clearly presented in Figs. 1(b)–1(d). The immersion time, being at least overnight, is critical to allow CNT deposition, where overnight immersion is applied to both of the thiol-modification process on CNTs and the adsorption process of CNTs on the substrate.

The fabrication of nanoparticles such as cadmium sulfide on a gold substrate employing a modified gold surface by alkanedithiol self-assembled monolayers was well studied by several research groups.$^{16-18}$ Our approach for CNT attachment on a gold substrate is similar in materials. One small difference is that the 1.8-octanedithiol treatment was carried on the CNTs, not on the gold substrate. This helps to reduce organic contamination on the gold surface, which may reduce the outgassing effect during vacuum operation. The following is the proposed adsorption process in our approach. During the process of of 1.8-octanedithiol attachment to the CNTs, one terminal thiol group of 1.8-octanedithiol adsorbs to the nickel or CNT surfaces of the Ni-capped CNT, where the nickel cap exists in most of the PECVD-grown CNTs.$^{15}$ Next, the other unbound terminal thiol group adsorbs to the gold-coated substrate during the adhesion process of the
CNT to the substrate. In the real process, however, adsorption of thiol to nickel or CNT surfaces might be very complex due to sulfur–sulfur bond formation. These complex bond formations would lead to aggregates of the CNTs, as we observed in this experiment (see Fig. 1). The adhesion of CNT aggregates to the gold substrate is understood as chemisorption of unbound thiol of the thiol-treated CNTs to the gold substrate, although the bond between CNT and 1.8-octanedithiol in thiol-treated CNTs is not clearly defined as chemisorption. The characteristics of self-assembly between the thiol group to the CNT are under investigation in our laboratory with the aid of theoretical simulation. According to early findings, the bond between sulfur to the carbon in the CNT is found to be chemisorption if we crudely define the chemisorption as the stronger bond strength than physisorption, in which the adsorbent is separated from the adsorbate under high vacuum condition.

The adsorption of 1.8-octanedithiol on CNTs was confirmed by FTIR spectroscopy. First, the powder of thiol-modified CNTs was prepared by filtration of thiol-modified CNT solution through a membrane filter, and subsequently thorough washing with ethanol to remove excess 1.8-octanedithiol unbound to the CNTs. Next, the powder of the thiol-modified CNTs was redissolved in ethanol. The spectra of the FTIR absorbance of the filtrates with duration time difference are shown in Fig. 2. The spectrum of Fig. 2(a) was obtained from the filtrate of the solution that had been filtrated immediately after redistribution of thiol-modified CNTs in ethanol and (b) was from the solution that had been left overnight before filtration.

The adsorption of 1.8-octanedithiol exists in both CNTs, indicating that 1.8-octanedithiol was not desorbed from the CNTs in ethanol even after the overnight duration. From the existence of 1.8-octanedithiol in the filtrate of the overnight duration, the deactivation process concerning CNT adhesion on the gold surface may be understood as the termination of active free-unbound terminal thiol groups. The possible termination process could be adsorption of the free-terminal thiol onto the adjacent surface area of the originally adsorbed sites or sulfur–sulfur bond formation between adjacent thiol groups. Therefore, the FTIR spectra support that 1.8-octanedithiol is adsorbed to the CNT, although the site of adsorption, whether it sticks to the nickel cap or to the surface of the CNT, and the state of activity for adhesion are not clear.

The FE measurement (Fig. 3) exhibits relatively good FE characteristics with a low turn-on field (2.5 V/μm) and a high current density (40 μA/cm² at 3 V/μm). In this article, we defined the turn-on field as the electric field applied for FE current density to produce 1 μA/cm². The knocking off of the deposited CNTs does not seem to occur under our applied field range, since serious reduction in emission current was not found after several FE measurements. For comparison, the FE measurement of a PECVD-grown CNT film is also shown in Fig. 3, where the turn-on field is 2.0 V/μm and the current density is 20 μA/cm² at 3 V/μm. The relatively good emission property of the self-assembled CNTs occurred due to the intensity increase of the electric field that arises from an adequate population of CNTs with little field screening effect. The density of the CNTs is predicted to be important for tuning the best-field emission performance to realize high-quality moving images in FEDs. The density control of the CNTs on the patterned film was introduced by the microcontact printing of the catalyst and subsequent growth of CNTs by CVD. They show the possibility to tune the FE properties of CNT film emitters with the density of CNTs deposited. Moreover, they show that films with medium density have the lowest emission field and the highest current density. From our result, the density of CNTs on the substrate seems to be quite low. However, the emission cur-

Fig. 2. FTIR spectra of the filtrates for two duration times, where (a) was obtained from the filtrate of the solution that had been filtrated immediately after redistribution of thiol-modified CNTs in ethanol and (b) was from the solution that had been left overnight before filtration.

Fig. 3. FE characteristics of the self-assembled CNTs on the gold-coated substrates and as-grown CNTs. Inset is their log scale plot.
rent density from the self-assembled CNTs is comparable to the PECVD-grown CNTs. It suggests that this method may be reliable to be applied to the FED system with advantages of easiness of deposition process as well as scaling up to a large-sized panel. In order to improve the poor reliability of FE characteristics for a FED, a uniformity issue, such as size, shape, and position of deposited CNTs, is required. In addition, the deposition sites of CNTs might be selectively controlled by patterning the gold or other selected metals that allow self-assembled adsorption, since thiol-modified CNTs adsorb onto selected metal surfaces with more probability. As an example, in Ref. 20 CNTs were selectively deposited on a nickel cathode surface, which was located inside the triode hole of the CNT FEDs.

Figure 4 shows the FE characteristics of the CNT’s density-controlled substrate. Figure 4 clearly shows that the FE current density tends to decrease as the deposition density of CNT aggregates is reduced. The FE measurements from Figs. 3 and 4 indicate that the proper density of CNT deposition may be close to the case of the 100% concentration solutions. Figs. 3 and 4 indicate that the proper density of CNT deposition is reduced. The FE measurements from Figs. 3 and 4 clearly show that the FE current density tends to decrease as the deposition density of CNT aggregates is reduced. The FE measurements from Figs. 3 and 4 clearly show that the FE current density tends to decrease as the deposition density of CNT aggregates is reduced. The FE measurements from Figs. 3 and 4 clearly show that the FE current density tends to decrease as the deposition density of CNT aggregates is reduced. The FE measurements from Figs. 3 and 4 clearly show that the FE current density tends to decrease as the deposition density of CNT aggregates is reduced.

**IV. CONCLUSION**

We introduced a new method of fabricating CNT field emitters by self-assembly of thiol-modified CNTs onto a gold surface. The FE measurement of the self-assembled CNTs shows relatively good FE characteristics with a low turn-on field and a high current density. Adjusting the concentration of the thiol-modified CNT solution performed the density control of CNT deposition on the gold-coated substrate although the highest concentration used in this experiment showed the best performance in emission current density. We expect that the self-assembly of CNTs is a promising way to prepare large-size FED panels with easy processing. Therefore, we strongly recommend further research in this field.

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