Preparation of uniformly dispersed iron-acetate nanoparticles using freeze-drying method for the growth of carbon nanotubes

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Abstract

We studied the growth characteristics of carbon nanotubes which were grown from the uniformly dispersed iron nanoparticles prepared from iron acetate \([\text{Fe(II)(CH}_3\text{COO)}_2]\). The density of CNT was controlled from precursor concentrations. We also investigated the field emission properties of CNTs. We found that the optimization of CNT density is an important factor for field emission properties. Patterning process of iron acetate was achieved simply by alkaline solution.

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1. Introduction

Carbon nanotubes (CNTs) have received considerable attention during the last decade due to their unique physical and chemical properties [1–3], as one of the promising materials for electronic devices such as field-effect transistors, field-emitter arrays, sensors, and actuators [4–8]. To date, many methods have been developed for synthesizing CNTs [9–13]. Compared with arc discharge, laser ablation, and catalytic pyrolysis, chemical vapor deposition (CVD) method has been intensively researched for several years to synthesis CNTs directly on substrate so far. The CVD process has allowed selective growth of individual CNTs and simplified the process for making CNT-based devices [14]. When CVD method is applied to synthesis CNTs, catalyst control is the most important factor that determines the CNT properties such as length, diameter, crystallinity, and density [15]. Thin-film catalyst is the most common and a better form of catalyst to achieve selective deposition of CNTs on a desired position. There are several ways to coat thin-film catalyst on a substrate. Physical vapor deposition (PVD) method is the commonly used and the properties of CNTs are controlled by changing deposition rate, temperature, thickness, and the way of combing multi-layers [16]. However, it requires vacuum system, and relatively complex machines. Moreover, the step coverage is not good when very thin catalyst layer is used to decrease the CNT diameter and a precise control of thin-film deposition process is required to control the density of CNTs. Recently, organometallic materials coated on substrate have been used as catalyst for CNT synthesis [17–24]. Organometallic materials containing transition metals used for CNT synthesis are solvated in organic solvents, and coated on substrate. Solution is easy to handle and does not require complex systems to coat it. Most results have reported that solutions containing organometallic catalyst are contained in nanometer dimension template like Zeolite to prevent agglomeration or recrystallization during drying or heating period, resulting in the increases in catalyst domain size [25,26]. Yoichi Murakami [17] and co-workers demonstrated the synthesis of CNTs from cobalt acetate solutions without using Zeolite. They precisely controlled the coating...
conditions of cobalt acetate solution and got a quite lower density of CNTs from it. It is considered that a very low concentration of solution is required to get a small diameter of CNTs by avoiding agglomerization or recrystallization during drying or heating period. Here, we developed quick freeze-dry method avoiding recrystallization of catalyst solution during the dry process. It was possible to easily control the density of CNTs from $3 \times 10^7$ to $1.31 \times 10^{10}$ cm$^{-2}$ from iron acetate solvated in ethanol and ethylene glycol. Catalyst solution was coated by spin-coating method, frozen with liquid nitrogen, dried in vacuum, decomposed in air, and finally used as CNT growth catalyst. The increase in CNTs density was observed by increasing iron-acetate concentration and by decreasing spin-coating speed. Field emission properties were compared as a function of CNT density. Moreover, the photolithography patterning of catalyst was achieved by a simple process with alkali solution.

In this work, multi-walled CNTs were grown by thermal CVD using CO and H$_2$ gases (50 Torr) at 550 °C from diluted iron acetate. The change of catalyst form and their pattern formation were demonstrated. The field emission properties from different catalyst concentrations and coating conditions were compared and they were interpreted as a combination of field enhancement factors and field screening effect due to CNT density.

2. Experimental

Iron-acetate solution was prepared as follows. Iron-acetate powder (Aldrich; 95%) was weighed and dissolved in ethanol (Fisher Scientific; 99.9%). Ethanol has a good solubility for the metal acetate. However, it was not easy to use ethanol only as a solvent due to its high vapor pressure and viscosity at room temperature. High vapor pressure and high viscosity made it difficult to make a uniform thin film due to the agglomeration of catalyst particles during drying process. Therefore, ethylene glycol was added to obtain the proper solution with low vapor pressure and viscosity. Ethylene glycol slightly dissolved iron acetate. The molar concentration of iron acetate, and volume ratio of two solvents were experimental parameters to control the surface concentration of catalyst.

After preparing catalyst solution, it was spin coated on a glass substrate. Here, we used two spin speed, 400 and 800 rpm for 10 s. The glass substrate was quickly frozen in liquid nitrogen bath as soon as possible and moved into vacuum chamber. The chamber was evacuated to $1 \times 10^{-2}$ Torr and substrate was heated to 100 °C for 20 min. The substrate was taken out and atomic force microscope (AFM) observation was done. The iron-acetate-coated substrate was loaded in vacuum oven, and heated at 300 °C for 20 min for decomposition. Decomposition conditions were investigated with thermal gravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). It was found that iron acetate changed into iron oxide in air, or into iron carbide in nitrogen ambient by thermal decomposition. Decomposed iron acetate was moved into growth chamber and was consecutively heated up to 550 °C and sustained for 40 min in CO(0.5 slm) and H$_2$(1.0 slm) ambient. After the growth of CNTs, scanning electron microscope (SEM) and field emission (FE) measurement were used for the CNT film characterization.

3. Results and discussion

Fig. 1 shows the SEM image of the catalyst after drying. The substrate which is coated with 20 mM solution is obtained and it shows the 10 to 12 nm size nanoparticles as shown in Fig. 1(a). Fig. 1(b) (60 mM, 400 rpm) shows an increase of particle size as compared with the spin-coating speed and solution concentration. It shows well-dispersed particles which have 20 to 26 nm diameter. As concentration of catalyst solution and thickness of coated layer increase, the diameter of catalyst particle becomes larger.

Fig. 2 shows the representative SEM images of CNTs grown from 60 mM of iron acetate in ethanol and ethylene glycol solvent. It shows the comparison of SEM image of CNTs grown on the freeze-dried with that of CNTs grown on conventionally dried catalyst solutions. More uniform

![Fig. 1. SEM image of the catalyst after drying. (a) 20 mM solution (b) 3 times coating with 60 mM solution (10 nm inset scale bars).]
and denser CNTs were grown from the freeze-dried catalyst film. This was due to the fact that the catalyst particles were agglomerated during drying process in a conventional way. However, in the case of freeze-dried catalyst, the catalyst was immobilized by liquid nitrogen freezing, resulting in preventing from agglomeration. Therefore, more uniform dispersion of catalyst particles and fine particle size distribution was achievable in freeze-dried catalyst process.

Fig. 3 shows the SEM images of CNTs grown from catalyst solutions with different catalyst concentrations and coating speeds. The iron-acetate concentrations were 20 mM, 40 mM, and 60 mM for samples a, b, and c, respectively, and coating speed was 800 rpm for 10 s. In this case, the monotonic distribution of CNT diameter was observed. Denser CNT film was obtained by decreasing coating speed to 400 rpm as shown in Fig. 3(d). We tried to increase the CNT density by coating iron acetate 3 times. Coating-freeze-drying steps were repeated 3 times to make a thicker iron-acetate film. As a result, a much more denser CNT film was obtained as shown in Fig. 3(e). When thicker iron acetate was coated on glass, bimodal distribution of CNT diameter was observed in Fig. 3(d) and (e). It was thought that the agglomeration of iron-acetate particles resulted in bimodal distribution of diameter from thick catalyst film. This is the general case when thin-film catalyst coated by physical vapor deposition (PVD) method is used.

As shown in Fig. 4, the field emission measurement shows the effect of CNT density resulting from the catalyst concentration and coating process on the field emission characteristics. The turn-on voltage of CNT film was decreased as increasing iron-acetate concentration to 60 mM. However, turn-on voltage was increased as increasing iron-acetate thickness by decreasing spin-coating speed and by increasing number of coating steps. This means that there exists an optimum density of
CNTs, and it can be controlled by iron-acetate concentration and coating conditions. It may be concluded that lower turn-on voltage can be obtained by precise control of the iron-acetate concentration on substrate surface.

Now, we tried to fabricate electronic device based on CNTs with iron-acetate catalyst. The first step of fabrication of device is the patterning of CNTs through the patterning of iron-acetate catalyst. We did the patterning of iron acetate as follows. Iron-acetate solution was coated on glass substrate and freeze-dried. The photo-resist (PR) was over-coated on iron acetate by spin-coating method. After the UV exposure through quartz mask on iron acetate/PR double layer, substrate was dipped in developer. Developer was alkali-based solution that dissolves UV-exposed PR. The UV-exposed PR and underlying iron acetate was dissolved in developer. Iron acetate reacted with developer in the acid–base reaction form and it was dissolved into solution. When UV-exposed PR was removed by PR stripper, there was no damage on iron acetate resulting in catalyst pattern formation. CNTs were grown on this line-patterned catalyst. Fig. 5 is an optical microscope and SEM image of substrate having the line pattern and CNTs. Line patterns after development, PR strip, and after CNT growth is shown in Fig. 5(a), (b), and (c), respectively. CNT growth was selectively performed on patterned lines. No CNTs were observed on the spacing between lines, and the line edge was very sharp as shown in Fig. 5(d). There were several reports on the selective line patterning of organometallic catalyst or CNT. Nilsson [24] and colleagues used stamping method to fabricate catalyst line patterning and Lustig [27] group spin-coated CNT–polymer composite followed by PR patterning and reactive ion etching (RIE) of CNT–polymer composite. However, previous reports could not report high precision or process simplicity. In our process, we can easily fabricate line pattern of catalyst for selective growth of CNTs without any other complex post treatment except for simple exposure-develop-strip process.

4. Conclusion

Iron acetate was uniformly dispersed onto glass substrate by freeze-drying process. It was demonstrated that freeze-drying process for catalyst control was very effective. Density of CNTs was controlled by changing iron-acetate solution concentration and spin-coating speed and coating times. The effect of CNT density on the field emission property was observed and there existed the optimum concentration of iron acetate in our experimental condition. Simple patterning process of iron-acetate catalyst was demonstrated, and line-patterned CNT films were selectively deposited on the patterned catalyst.

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References