The density control of carbon nanotubes using spin-coated nanoparticle and its application to the electron emitter with triode structure

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Abstract

The density-controlled carbon nanotubes (CNTs) were grown on the iron nanoparticles by using the freeze–dry method. The iron-acetate [Fe(II)(CH\textsubscript{3}COO)\textsubscript{2}] solution was used for the preparation of the catalytic iron nanoparticles. The density of CNTs was controlled in order to achieve the enhancement in the field emission process. Furthermore, the patterning of the iron nanoparticle catalyst layer for the fabrication of electronic devices was simply achieved by using an alkaline solution, TMAH (tetramethylammonium hydroxide). We applied this patterning process of catalyst layer to the formation of the electron emitter with under-gate type triode structure.

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1. Introduction

There has been momentous development in both the production and the application of carbon nanotubes (CNTs) since their discovery in 1991 [1], and CNTs have received considerable amount of attention during the last decade due to their unique physical and chemical properties [2,3]. So far, a number of methods such as laser ablation, arc discharge and catalytic pyrolysis have been established for the synthesis of CNTs [4–7]. Among them, the method of chemical vapor deposition (CVD) has been extensively employed for the synthesis CNTs using the catalytic nanoparticle substrate. Furthermore, the CVD process has allowed the selective growth of individual CNTs and simplified the process for making CNT-based devices [8]. When CVD process is applied to the synthesis of CNTs, the most important factor which determines properties of CNTs such as the length and diameter is catalyst control [9]. Besides, the field emission characteristics are affected by the length, diameter and density of CNTs. Properties of CNTs grown on controlled catalyst and their diversity were the dominant factor of FE characteristics.

The synthesis of catalyst nanoparticles has been extensively developed because of their important role as a seed for the CNTs growth. The synthesis of well-dispersed nanoparticles with sizes ranging from 2 to 10 nm enables the growth of thinner CNTs at a lower temperature. Generally, iron, nickel, and cobalt metals and their alloys were typically used as a catalyst material to synthesize CNTs. These materials usually have been used in the form of thin films. Thin film catalyst is the most common and better form of catalyst to achieve selective deposition of CNTs on a desired position. There are several ways to deposit thin-film catalyst on a substrate. The physical vapor deposition (PVD) method is a commonly used method and the properties of CNTs are controlled by changing the deposition rate, temperature, thickness and the way of combing multi-layers [10]. However, it requires a vacuum system and relatively complex equipment. Moreover, the step coverage is not good when a very thin catalyst layer is used in order to decrease the CNT diameter so that a precise control of thin-film deposition process is required to control the diameter of CNTs. Newly organometallic materials coated on a substrate for making a catalyst layer have been used for CNT synthesis [11–16] to overcome the disadvantage of the PVD process and to easily control the catalyst characteristics. Furthermore, organometallic materials containing transition metals used for...
CNT synthesis are dissolved in organic solvents such as ethanol and coated on the substrate by dip-coat or spin-coating method. A solution containing catalyst particles is easy to handle and does not require complex systems to coat it. However, in case of nanoparticles application instead of thin film, there are several problems about the uniformity of particle distribution. When the particles are spread on the substrate, these particles have a tendency of agglomeration. In the present study, we have used liquid nitrogen to prevent the agglomeration of catalyst particles on a substrate that takes place during the dry process. The iron acetate [Fe(II)(CH₃COO)₂] catalyst solution was coated onto a glass substrate by spin-coating method and was frozen with liquid nitrogen.

After the formation of the catalyst layer, we succeeded in making a pattern using TMAH (tetramethylammonium hydroxide, N(CH₃)₄OH) solution. Other techniques to form patterned arrays relied on conventional photo or e-beam/ion beam lithography [17–20]. However, while this direct patterning method has successfully reduced the number of processes, the required vacuum for the e-beam exposure is still costly and could potentially limit the throughput of such a technology. In our experiments, however, we do not need any vacuum equipment to make patterned arrays. As the acid–base reactions are applied to the patterning process, even a simpler patterning methodology could be achieved. Using this phenomenon of catalyst layer in our experiment, we suggest a triode structure for FEDs with CNT emitters, designed as an under-gate triode [21] where gate electrodes are located under the cathode electrodes.

2. Experimental

In the first preparation step which was the formulation of iron acetate solution, we mixed iron acetate powder with ethanol. Iron acetate has a good solubility in ethanol. In contrast, the ethanol has too high vapor pressure and low viscosity, which may cause the recrystallization of the catalyst powder and the non-uniform morphology after the drying process. Therefore, ethylene glycol was added to obtain the proper solution with low vapor pressure and high viscosity. The ethylene glycol slightly dissolved iron acetate, in order to avoid agglomeration and recrystallization during the drying or heating period, the substrate which was covered with liquid catalyst solution was quickly frozen in a liquid-nitrogen bath, so we could obtain uniformly distributed catalyst particles on a substrate through this fast-freeze method. The molar concentration of the iron acetate and the volume ratio of the two solvents were experimental parameters to control the concentration of the catalyst.

To make a triode-type device, as the first step, we pattern a metal line, molybdenum (200 nm thickness, 150 μm width), on a glass substrate as a gate electrode using the photolithography process. After that, a SiO₂ layer of thickness 3 μm was deposited by PECVD for insulation. On the insulating layer, the liquid catalyst was coated by a spin coater and dipped immediately into liquid nitrogen to prevent particle agglomeration. After the drying process, the catalyst film was selectively patterned by TMAH to form a cathode line as well as an emitter. The photo-resist (PR) was coated on the iron acetate layer by spin-coating method. After UV exposure through a quartz mask on the iron acetate/PR double layer, the substrate was immersed in the developer (TMAH). The developer was an alkali-based solution that dissolves UV-exposed PR. The UV-exposed PR and the underlying iron acetate was dissolved in the developer. Iron acetate reacted with the development solution in an acid–base reaction form and it was dissolved into solution. Fe²⁺ in iron acetate produces a chemical process by the action of the base OH⁻ in TMAH. As a result, there is no catalyst layer under the part of the PR which is illuminated by UV light. Because PR was first removed by TMAH (developer), the catalyst layer was removed next by the same TMAH. Furthermore, the iron acetate-coated under-gate type triode substrate was loaded in a vacuum oven and annealed at 350–400 °C in air to burn the organic compound. The 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. For reference, the cathode electrode (molybdenum) on the insulating layer was used at the early stage of the process. However, during the decomposition step, the cathode electrode was peeled easily from the insulating layer because of electrode oxidation. So we decided to use a catalyst solution of dense concentration (60 mM, 400 rpm) and make CNT film as an emitter and cathode as well.

The catalyst metal (Fe)-coated triode structure was transferred into CNTs growth chamber and was consecutively heated up to 550 °C and sustained for 40 min in CO (0.5 slm) and H₂ (1.0 slm) ambient. After the growth of CNTs, the field emission characteristics of the triode structure with the CNT emitter were analyzed. The emission current was controlled by...
3. Results and discussion

The iron acetate was uniformly dispersed on the glass substrate by freeze-drying process. Particles treated by the liquid nitrogen were very effective for the density control in CNTs growth. In the case of the freeze-dried catalyst compared with the conventional drying process, the catalyst was immobilized by liquid nitrogen freezing, resulting in the prevention of agglomeration. Therefore, the more uniform dispersion of catalyst particles and the distribution of particle size were achieved in the freeze-dried catalyst process.

In addition, it is an essential step to achieve the patterning for the device applications. So we found out that the iron acetate catalyst layer can be selectively dissolved by the TMAH solution. Specifically, due to the chemical reaction of Fe\(^{2+}\) ions in iron acetate and OH\(^{-}\) ions in TMAH, the catalyst layer was removed. Hence, the first exposed PR layer was removed by TMAH, and then the catalyst layer was removed by the same TMAH solutions.

Fig. 1 shows the SEM images of the CNTs grown on catalyst solutions with different concentrations and coating speeds. The iron acetate concentrations (spin speed) were 20 mM (800 rpm), 40 mM (800 rpm), 60 mM (800 rpm), 60 mM (400 rpm) for a, b, c and d samples, respectively, and coating time was kept at ~ 10 s. In this case, the monotonic distribution of CNT diameter was observed. The denser CNT film was obtained by decreasing the coating speed from 800 to 400 rpm as shown in Fig. 1(d). We measured the field emission characteristics for the above prepared samples. It shows the effect of CNT density resulting from the catalyst concentration and coating speed on the field emission characteristics. The turn-on voltage (the applied electric field that produces the emission current of 10 \(\mu\text{A/cm}^2\)) of CNT film was decreased as the iron acetate concentration increases from 20 mM (800 rpm) to 60 mM (800 rpm). However, the turn-on voltage of CNT was found to be increased as the thickness of the catalyst increases by decreasing the coating speed from 800 to 400 rpm. The turn-on voltage of samples a, b, c and d were 5.76 V/\(\mu\text{m}\), 4.48 V/\(\mu\text{m}\), 3.56 V/\(\mu\text{m}\) and 3.68 V/\(\mu\text{m}\), respectively. The AFM analysis shows that the thickness of the catalyst layer for samples a, b, c and d were 70, 150, 330 and 630 Å. The field enhancement factor, \(\beta\), values were also changed as 699, 2917, 4485 and 2862. These results indicate that there exists an optimum density of CNTs, and it can be controlled by iron acetate concentration and the coating conditions. It may be concluded that lower turn-on voltage can be obtained by the precise control of the iron acetate concentration on the substrate surface.

For a full-scale imaging and a fast response for moving pictures, a triode structure is necessary. Fig. 2 shows the schematic diagram of a triode structure with carbon nanotube emitters and electric potential distributions and trajectories near the cathode electrodes. This electric potential distributions and electron trajectories near the cathode electrodes were calculated using the commercial software SIMION. In the triode structure, electrons are first field emitted from the cathode by a gate voltage and then attracted to the anode. The gate electrodes in a normal triode structure are located above the cathode electrode, which enables the emission electrons to easily reach the anode electrode. But in our case, the gate electrode is under the cathode on the opposite side of the anode. Using this structure, we achieved the simple form of the structure and the fabrication process which seems...
to enable the under-gate type triode to possess high potential for practical applications.

In this under-gate triode structure, it is well known that the electric field strength is concentrated at the edges of a cathode electrode. So, the electron emission turns on and off depending on the gate voltages for a given anode voltage. Thus, this under-gate triode structure has also an advantage of preventing the broad electron emission.

Fig. 3 shows the optical microscope image and the SEM images of a triode structure. Fig. 3(a) shows two lines crossing at right angles. Horizontal lines are gate electrodes and perpendicular lines represent a cathode electrodes and a catalyst layer. There are insulating layers between two electrodes. Fig. 3(b) and (c) shows a cross-sectional SEM image of the triode structure with a CNT emitter. The catalyst layers were coated on the substrate by spin coating of 60 mM iron-acetate solution of 400 rpm.

In the triode mode, the current–voltage characteristics of the triode were shown in Fig. 4. At first, Fig. 4(a) shows the emission characteristics of CNT emitters with a diode configuration. The maximum current density was ~2 mA/cm² and the turn-on voltage was ~3.6 V/µm. In Fig. 4(b), the anode voltage was set at 800 V, which was a little lower than

the turn-on voltage of ~900 V for the anode voltage in the diode mode. At a cathode–anode gap of ~1000 µm, we could get approximately 250 V turn-on voltage in a triode mode. However, this measurement of turn-on voltage in the triode mode is much higher than expected. This result was due to the concentration or the density of the CNT emitters. Although our structure has high turn-on voltage, our research work is worthy to make a note. The triode structure in our experiment with liquid catalyst has assured advantages of its simple structure and fabrication process.

4. Conclusion

We have fabricated the under-gate-type triode structure using carbon nanotubes grown from the iron nanoparticles as electron emission sources and characterized their field emission properties. The freeze-drying process for uniform distribution of catalyst particles was also applied to the triode structure to form a catalyst layer. In our results, it was verified that electron emission was operated by a modulation of gate voltages. Although there are some technical problems to be solved, the formation of a catalyst layer using by the fast-freeze method and a trial for its device application were worthy of being researched more.

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References


