

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

We studied the density control of carbon nanotubes (CNTs) which were grown on the iron nanoparticles prepared from iron-acetate $[Fe(CH_3COO)_2]$ solution using freeze-dry method. The density of CNTs was controlled for the enhancement of field emission. The patterning process of iron-acetate catalyst-layer for the fabrication of electronic device was simply achieved by using alkaline solution, TMAH (tetramethylammonium hydroxide). We applied this patterning process of catalyst layer to formation of the electron emitter with under-gate type triode structure.

1. Introduction

The synthesis of catalyst nanoparticles has been intensively developed because of their important role as a seed for CNTs growth. The synthesis of well-dispersed nanoparticles with size ranging from 2 to 10 nm enables the growth of thinner CNTs at lower temperature. Newly, organometallic materials coated on a substrate for making catalyst layer have been used for CNT synthesis [1~6] to overcome disadvantage of PVD process and to easily control the catalyst characteristics. Organometallic materials containing transition metals used for CNT synthesis are solvated in organic solvents such as ethanol, and coated on 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 using nanoparticles instead of thin film, there are also problems about uniformity of particle distribution. When the particles are spread on the substrate, the particles tend to be agglomerated each other. So, in this study, we used liquid nitrogen to prevent agglomeration of catalyst particles on a substrate that happened during dry process. The iron acetate $[Fe(CH_3COO)_2]$ catalyst solution was coated onto a glass substrate by spin-

coating method and was frozen with liquid nitrogen. After formation the catalyst layer, we succeed in making pattern using by TMAH ($N(CH_3)_4OH$ tetramethylammonium hydroxide,) solution. Previous techniques to form patterned arrays relied on conventional photo or e-beam/ion beam lithography [7~10]. However, while this direct patterning method has successfully reduces the number of process, 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, it doesn't need any vacuum equipments to make patterned arrays. As the acid-base reactions are applied to the patterning process, even 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[11] where gate electrodes are located under the cathode electrodes.

2. Experimental

As the first preparation step of forming iron acetate solution, we intermingled iron acetate powder with ethanol. Ethanol has a good solubility for iron acetate. But ethanol has too high vapor pressure and viscosity. High vapor pressure and viscosity were cause of recrystallization of catalyst powder and non-uniform morphology after drying process. Therefore ethylene glycol was added to obtain the proper solution with low vapor pressure and viscosity. Ethylene glycol slightly dissolved iron acetate. Besides, to avoid agglomeration and recrystallization during drying or heating period, the substrate which was covered with liquid catalyst solution was quickly frozen in liquid nitrogen bath [12]. So we could obtain uniformly distributed catalyst particles on a substrate through this fast-freeze method. The molar concentration of iron acetate, and volume ratio of two solvents were experimental parameters to control the

concentration of catalyst.

To make a triode type device, as the first step, we pattern a metal line, molybdenum (200nm thickness, 150 μ m width), on a glass substrate as a gate electrode using photolithography process. And then, SiO₂ layer of thickness of 3 μ m was deposited by PECVD as a insulating layer. On the insulating layer, liquid catalyst was coated by spin coater and dipped immediately into liquid nitrogen for preventing particle agglomeration. After the drying process, the catalyst film was selectively patterned by TMAH to form a cathode line and emitter as well. Then, the iron acetate coated under-gate type triode substrate was loaded in vacuum oven, and annealed at 350-400 in air to burn organic compound. 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 process. But during decomposition step, cathode electrode was peeled easily from insulating layer because of electrode oxidation. So we decided to use catalyst solution of dense concentration (60mM, 400rpm) and make CNTs film as an emitter and cathode as well. Catalyst metal (Fe) coated triode structure was transferred into CNTs growth chamber and was consecutively heated up to 550 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 triode structure with CNT emitter were analyzed. The emission current was controlled by changing gate voltage at a constant anode voltage. The substrate and as-grown CNTs were analyzed by atomic force microscopy (AFM, LS, PSI) and field emission scanning electron microscopy (FE-SEM, A0344, Philips).

3. Results and Discussion

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

achieved in freeze-dried catalyst process. Besides, we know that it is essential step to achieve the patternability for the device applications. So we find out that the iron acetate catalyst layer can be selectively dissolved by TMAH (N(CH₃)₄OH tetramethylammonium hydroxide) solution. Namely, Fe²⁺ in iron acetate has a chemical reaction with the base OH⁻ in TMAH. So there is no catalyst layer under the photoresist (positive, AZ1512) which was illuminated by UV light. Because PR was first removed by TMAH (developer), and catalyst layer was also removed by the same TMAH later.

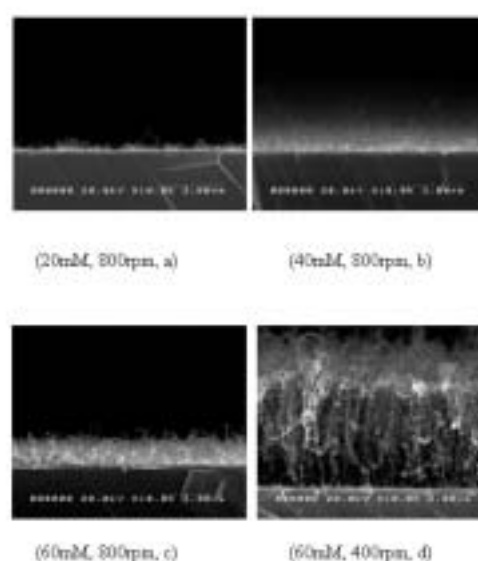


Figure 1. CNTs grown from 20 mM(800rpm), 40 mM(800rpm), 60 mM(800rpm) and 60 mM(400rpm) catalyst solution prepared by the freeze-dried method.

Figure 1 shows the SEM images of CNTs grown on catalyst solutions with different concentrations and coating speeds. The iron acetate concentrations (spin speed) were 20mM (800rpm), 40mM (800rpm), 60mM (800rpm), 60mM (400rpm) for sample a, b, c and d respectively, and coating time was 10 second. In this case, the monotonic distribution of CNT diameter was observed. Denser CNT film was obtained by decreasing coating speed from 800 to 400 rpm as shown in Figure 1(d). We measured the field emission characteristics from above 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 of CNT film was

decreased as iron acetate concentration increases from 20mM (800rpm) to 60mM (800rpm). But turn-on voltage of CNT increased as catalyst thickness increases by decreasing coating speed from 800 to 400 rpm. The turn-on voltage of the sample (a), (b), (c) and (d) were $5.76 \text{ V}/\mu\text{m}$, $4.48 \text{ V}/\mu\text{m}$, $3.56 \text{ V}/\mu\text{m}$ and $3.6 \text{ V}/\mu\text{m}$, respectively. By AFM analysis, the thickness of sample (a), (b), (c) and (d) were 70 \AA , 150 \AA , 330 \AA and 630 \AA . Field enhancement factor, β value were also changed 699, 2917, 4485 and 2862. These results imply that there exists the 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.

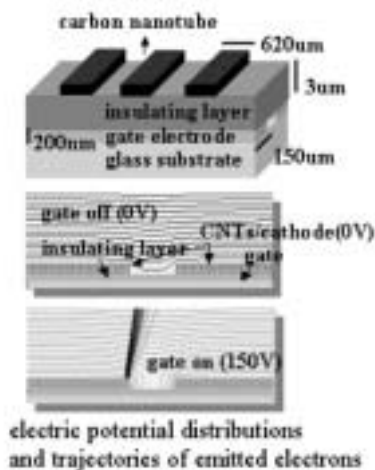


Figure 2. A schematic diagram of a triode structure with carbon nanotube emitters and electric potential distributions and trajectories of emitted electron near the cathode electrodes with and without gate voltage.

For full-scale imaging and a fast response for moving pictures, a triode structure is necessary. So, Figure 2 shows the schematic diagram of a triode structure with carbon nanotube emitters and electric potential distributions and trajectories near the cathode electrodes depending on gate voltages. This electric potential distributions and electron trajectories near the cathode electrodes were calculated using the commercial software SIMION. In triode structure, electrons are first field-emitted from the cathode by a gate voltage and then attracted to the anode. Gate electrodes in a normal triode structure are located

above the cathode electrode, which enables emission electrons to easily reach the anode electrode. But in our cases, the gate electrode is under the cathode, on the opposite side of the anode. Using this structure, we achieved the simplicity 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 cathode electrodes. So the electron emission turns on and off at depending on the gate voltages for a given anode voltage. And this under-gate triode structure has also the advantage of preventing broad electron emission.



Figure 3. An optical microscope image and SEM images of triode structure.

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

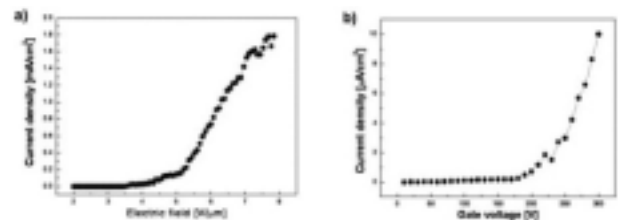


Figure 4. I-V characteristics of a triode structure in diode (a) and triode (b) modes, where the gate electrodes are electrically floated in the diode mode and the anode electrode is set to be 800 V in the triode mode.

In the triode mode, the current-voltage characteristics of triode were shown in figure 4. At first, Figure 4 (a) shows the emission characteristics of CNT emitters with diode configuration. The maximum current density was $2\text{mA}/\text{cm}^2$ and turn-on voltage was $3.6\text{V}/\mu\text{m}$. In figure 4 (b), the anode voltage was set at 800V, which was a little lower than the turn-on voltage of 900V for the anode voltage in the diode mode. At a cathode-anode gap of 1000 μm , we could get approximately 250V turn-on voltage in triode mode. But this measurement of turn-on voltage in the triode mode is much higher than expected. This result was due to the concentration or density of the CNT emitters. Although our structure has high turn-on voltage, our research is worthy of note. Triode structure in our experiment with liquid catalyst has assured advantages of its simple structure and fabrication process.

4. Conclusion

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

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7. References

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