Electron Emission Properties of Carbon Nanocoils

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Abstract

We have fabricated carbon tubule coils in nanometer scale (called nanocoils) and found that they are a good candidate for the electron emission devices rather than carbon nanotubes. This is attributed to their specula helical morphology and the larger number of emission sites uniformly dispersed in the carbon nanocoil field emitter arrays. The field emission from carbon nanocoils with different diameters and lengths shows that the turn-on voltages of carbon nanocoil field emitters are dependent on the diameters of the coiled tubules. Decreasing the thickness of iron film and the flow rate of acetylene gas can decrease the average diameter of grown carbon nanocoils. Decreasing the growth time can proportionally decrease the average length of the coils. Furthermore, increasing the growth temperature increases the density and length of the carbon nanocoils. It is expected to use carbon nanocoils with small diameter and short length to fabricate high performance flat panel display, which can be driven at low voltage and has high resolution and brightness.

Introduction

Development of electron emission devices being able to operate at a low voltage could be one of the key issues in the field of imaging science. Field emission device using carbon nanomaterials[1-5] have attracted much attention in this field because of their low driving voltage, which can be applied for such as the charging devices in electrophotograph, direct making imaging, and flat panel display. The well-known carbon nanotube is a good candidate for these devices. However, carbon nanotubes grown in an array prepared by chemical vapor deposition (CVD) are generally densely planted and the electric field is strongly concentrated at the edge of the array.[6-8] This results in the nonuniformity and instability of field emission from carbon nanotube arrays.

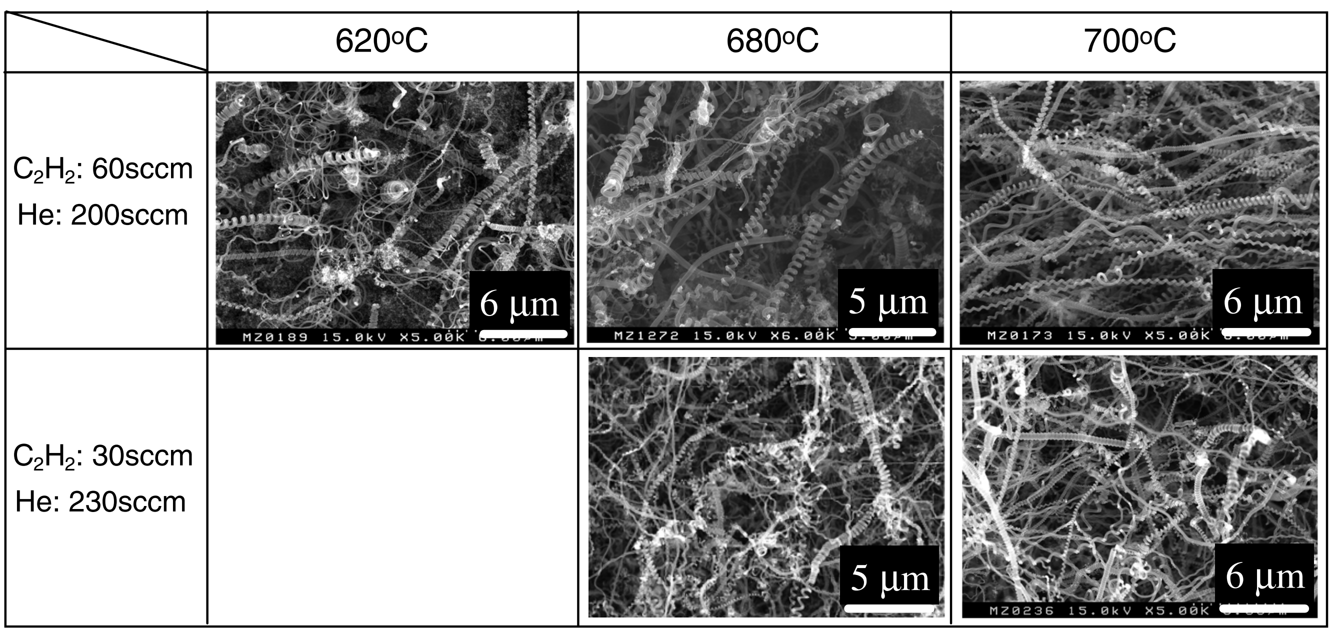

Figure 1. SEM micrographs of carbon nanocoils synthesized at different temperatures with the iron film thickness of 10 nm and the acetylene flow rate of 30 and 60 sccm, respectively.

In our previous work, we have reported that carbon nanocoils prepared by thermal CVD[9-11] with iron and indium tin oxide (ITO) as the catalysts have the similar excellent properties of field emission because of their nanostructure and specula helical morphology.[12-14] It is inferred that the field emission from carbon nanocoils would also be affected by their geometric sizes which are directly related to their radii of curvature, nanostructures and the number of field emission sites, etc. In this paper, we report the effective methods to control the average coil diameter and the coil length so as to improve the properties of their field emissions.

Synthesis of Carbon Nanocoils

The method of catalytic thermal CVD has been used to synthesize carbon nanocoil. We used ITO-coated glasses as the substrates. The substrates were patterned with iron films by electron beam deposition through shadow masks or by resist process. The film thickness was changed from 8 to 20 nm. The samples were placed on a quartz boat inserted into the center of a tubular electric furnace. The reaction gas used was acetylene with the flow rates of 30 to 60 sccm and the carrier gas was helium with the flow rates of 200 to 230 sccm. The reaction temperature was changed from 620 to 700•C for 3 to 30 min. The deposits were characterized by a scanning electron microscope (SEM) and a transmission electron microscope (TEM).

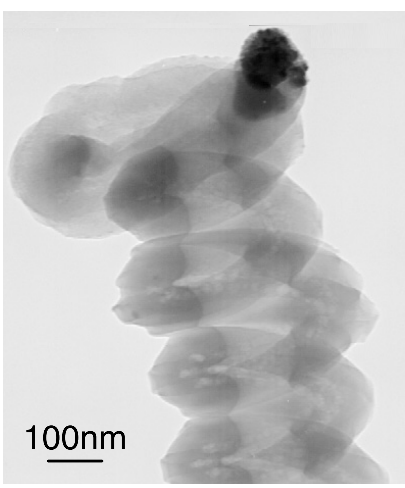

Figure 2. TEM micrograph of a carbon nanocoil. The carbon coil consists of three helical tubules with a same pitch. A catalyst particle is at the tip of the coil.

Figure 1 shows the SEM micrographs of carbon nanocoils grown at the temperature of 620, 680 and 700°C for 30 min with the acetylene flow rate of 30 and 60 sccm, respectively. The Fe film thickness is 10 nm. It is found that more than 95% deposits are carbon coils with various diameters and pitches. The coil diameters are different from each other, ranging from several tens to several hundreds of nanometers. The coils selectively grow out at the iron-deposited area although they are not well aligned along the direction perpendicular to the surface. Figure 2 shows the TEM micrograph of the tip of a carbon nanocoil. It is observed that a carbon coil usually consists of two or more carbon tubules (three tubules in this image) and each of them grows with the same pitch but is different in diameter. The enlarged TEM micrograph shows that the coiled tubules partly consist of graphene sheets similar to that in carbon nanotubes.[8] We have also measured the electric conductivity of carbon nanocoils with different diameters and pitches, which is ranged from 90 to 200 S/cm and shows no obviously dependence on these parameters.[15] It is also clearly observed that a catalyst particle is at the tips of the coil suggesting a tip growth mechanism. The shape and the chemical composition of the catalyst determines the structure of the coil including its external diameter, pitch, number of tubules and the relative arrangement of the helix-shaped tubules.[13]

It is observed from Fig. 1 that increasing the reaction temperature increases the density and the length of the carbon nanocoils. This is resulted from the increase of the reactivity of the catalyst particles and the density of hydrocarbon in the gas phase created from the pyrolysis of acetylene. With the decrease of the flow rate of acetylene, the diameters and pitches of carbon nanocoils are decreased. In the case of growth temperature of 700°C, the average diameters are reduced from 500 nm for the acetylene flow rate of 60 sccm to 200 nm for that of 30 sccm. The diameter of a tubule is considered to be determined by the size of the catalyst particle at its tip. This indicates that either the formation of catalyst particles is affected by the concentration of the reactive gas or the coils are grown mainly under the catalyst particles with smaller sizes at a lower acetylene flow rate.

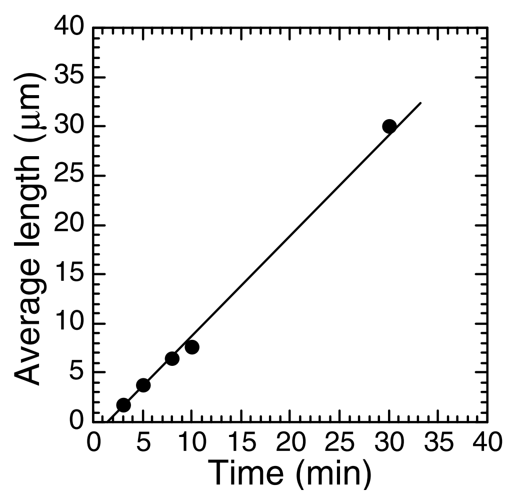

Figure 3. Dependence of the average length of carbon nanocoils on the growth time.

Figure 3 shows the dependence of the average length of carbon nanocoils on the growth time in the reaction conditions of acetylene flow rate of 60 sccm and the growth temperature of 700°C. It is clear that the length of carbon nanocoils is proportional to the growth time. The offset time of near 1 min is correspondent to the time needed for the transport of the acetylene in gas line until it reaches the sample surface. The growth rate of carbon nanocoils in this case is about 1 μm/min. This value would be different from the conditions of sample, such as the Fe thickness and the kind of ITO substrate used.

Field Emission Properties

Field emitters were fabricated using the grown carbon nanocoil arrays as the cathode and the ITO-coated glass substrates as the anode. The gap between the two electrodes was set to be 130 μm. In order to observe the field emission directly, we also used some phosphor-coated ITO glass plates as the anode. The field emission current was measured at room temperature as a function of applied voltage at a pressure of $1x10^{-6}$ Torr. The applied voltage was changed from 0 to 1000 V.

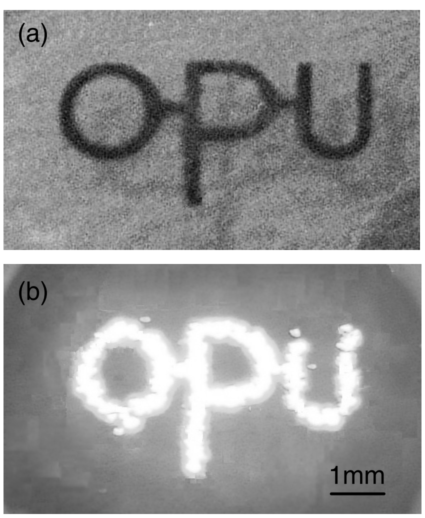

Figure 4. Optical micrographs of (a) carbon nanocoil field emission array prepared on an "OPU" patterned Fe film by CVD method and (b) the fluorescence pattern from the same carbon nanocoil field emission display.

Figure 4(a) shows the optical micrograph of a fabricated nanocoil field emission array on an ITO-coated glass substrate. The black parts are carbon nanocoils synthesized on the patterned iron films by CVD method. The coils selectively grow out at the iron-patterned area. There is no coil grown on the substrates without the iron film, suggesting that the iron is essential catalyst to grow carbon nanotubules. The bright fluorescence pattern from the FED is shown in Fig. 4(b). The electron emission form the carbon nanocoil field emitter is more uniform compared with that of the CNT emitter. It is observed from Fig. 2 that the body of a coil takes an angular shape rather than a circular one, which is believed to be determined by the structure of the catalyst particles at its tip. These sharp edges or corners at the bodies of the carbon nanocoils are possible to form the electron emission sites. Because of the unique morphologies of the coils, a large number of edges or corners exist and are uniformly dispersed. These characteristics of the nanocoils indicate that the space potential in a nanocoil field emitter is uniform from the center to the edge of the coil array, which is quite different form the case of the CNT array grown densely and uniformly. The long-term test was performed and shows that carbon nanocoil field emitter is very stable up to 100 h. The stability of the field emission would be attributed to the large number of emission sites formed by the sharp tips, edges or corners on the bodies of nanocoils.[12,14]

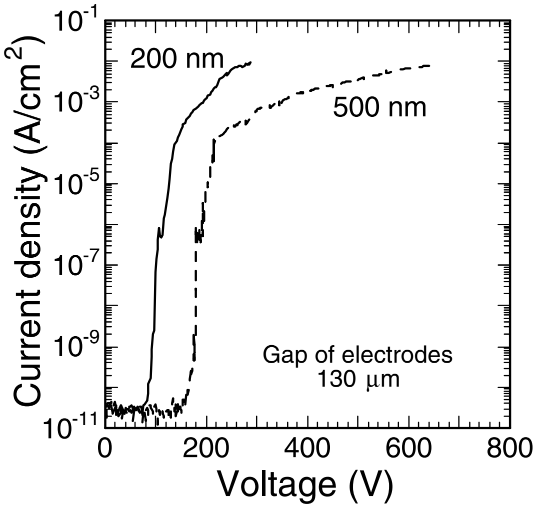

Figure 5. Curve of the emission current density vs applied voltage for the nanocoil field emitters with the average coil diameters of 200 and 500 nm, respectively.

It is known that the field emission properties can be improved by decreasing the radii of curvature of emission sites. So decreasing the diameters of the carbon nanocoils is desired to get better performance. As mentioned above, the diameter of carbon nanocoils can be effectively reduced by decreasing the acetylene flow rate in CVD process. We take this method to fabricate carbon nanocoil field emitter under the conditions of acetylene flow rate of 60 and 30 sccm, respectively with the Fe film thickness of 8 nm. Figure 5 shows the I-V properties of the corresponding carbon nanocoil filed emitters. The dotted and solid curves are for the average diameters of 500 nm and 200 nm, respectively. With the decrease of the coil diameter, the turn-on voltage is decreased from 180 to 90 V. This is attributed to the reduction of the radii of emission sites.

It is noted that the carbon nanocoils used in the above experiments are as long as several tens of micrometers. In these cases, the circuit short would happen when reducing the electrode gap to decrease the operation voltage and reduce the dot gap to improve the resolution of FED. It is necessary to decrease the coil lengths. We take the method of reducing the growth time in CVD process. In comparison, we fabricated the carbon nanocoil field emitter array under the condition of growth temperature of 700°C and growth times of 3 and 8 min, respectively on the substrates with the Fe film thickness of 20 nm. In the case of 3 min growth, carbon nanocoils are grown together with a great number of carbon nanofibers. With the increase of growth time, the length and the density of carbon nanocoils are all increased as shown in Fig. 3. It is also found that the diameters of the grown coiled tubules are larger than those synthesized in the condition of Fe film thickness of 10 nm as shown in Fig. 1. This behavior is similar to the growth of carbon nanotubes using the iron or nickel film as the catalyst.[16]

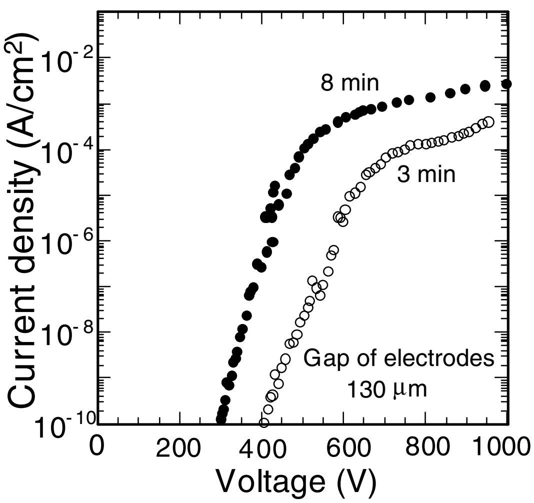

Figure 6. I-V properties in the field emission from the samples with the growth time of 3min and 8 min.

Figure 6 shows the I-V properties in the field emission from the samples with the growth times of 3 min and 8 min. For the 3 min growth (open circles), only a few coils grow, the emission is mainly from the carbon fibers, while for the 8 min growth (closed circles), the emission is mainly from the carbon coils. However, as mentioned above, the larger the diameter of tubules is, the higher the turn-on voltage is. In order to obtain short and slender coils, it would be an effective method to decease the iron thickness, gas flow rate and growth time in the CVD process and this is also a subject for our further study.

Conclusion

Due to the uniform distribution of the electric field and the large number of emission sites, the carbon nanocoils exhibit excellent field-emission properties. The growth of the carbon coils can be controlled. Decreasing the growth time decreases the length of carbon nanocoils. Reducing the gas flow rate reduces the average diameter of coiled carbon tubules and consequently reduces the turn-on voltage of the field emission. Decreasing of the growth time, gas flow rate and iron film thickness is advisable to fabricate the high-performance carbon nanocoil field emitters.

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Biography

Yoshikazu Nakayama received his B.S. degree in Electric Engineering from Osaka Prefecture University in 1972, and a Ph.D. in Applied Physics from Osaka University in 1985. In 1972, he joined Matsushita Electric Industry Co., Ltd. where he worked on research in optical memory using holograms. In 1979, he moved to Osaka Prefecture University and has worked on applied physics, especially photoconductive materials, and plasma processing for semiconductor materials. He was appointed to the position of professor in 1995. He currently leads a large-scale nanotechnology project supported by Japan Science and Technology Corporation. He is a member of the IS&T, the ISJ, the Imaging Society of Japan, the Material Research Society and the Japan Society of Applied Physics.