Field Emission from Carbon Nanocoils Synthesized by Using Fe-In-Sn-O Composite Catalyst

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Abstract

Carbon nanocoils, due to their specula helical morphology, have been proven to be excellent field emission cathodes, which can be applied to the charging devices in electrophotography and direct-marking systems and also to the flat panel display devices. Nanocoils synthesized by chemical vapor deposition using Fe and indium tin oxide show a large distribution of the diameters and pitches of the nanocoils, witch affects the uniformity of their field emission. An improved method has been adopted to synthesize nanocoils by using an Fe-In-Sn-O composite catalyst, where each component is controlled accurately. The synthesized nanocoils show small diameters with small distribution. The measurement of the field emission current from the nanocoils shows the turn-on voltage as low as 30 V at the electrode gap of 130 μm, which is smaller than those of most carbon nanotubes and the previous nanocoil emitters. This is due to the decrease of the curvature radius of the emission sites. A lifetime test under the current density of 1 mA/cm^2 shows that the nanocoil field emitter also has a good stability and long lifetime. These results indicate that the nanocoils are expected to be applied for the electron sources of high performance electron emission devices.

Introduction

Electron emission devices with a low-voltage operation could be one of the key issues in the field of imaging science. They will be applied for the charging devices in electrophotography and direct-marking systems as well as for flat panel display devices. Carbon nanotubes have attracted much attention for these devices because of their high aspect ratios causing a low driving voltage.[1-5] It has been reported that the electrons emit from pentagons of carbon atoms at the tip rather than the hexagons for nanotubes with end caps.[6]

This suggests that a helical coil of carbon nanotube (carbon nanocoil) is an alternative candidate for the effective field emission device because a large number of pentagons located on the outside of its body would be emission sites. Recently, we have succeeded to prepare carbon nanocoils with a high yield by thermal chemical vapor deposition (CVD) with iron and indium tin oxide (ITO) as the catalysts[7] and found out that they show excellent properties of field emission.[8] The emission sites are really located not only on the tip but also on the body, although the structure of the nanocoils is not an ideal and has sharp edges (edge of the graphene) at the body.[9] These sharp edges work as effective emission sites instead of the pentagon. Thus the array of the nanocoils shows spatially uniform and temporally stable field emission.

Very recently, we have demonstrated that decreasing the average coil diameter reduces the turn-on voltage of the field emission.[10] In this work, we have succeeded to prepare nanocoils with the average coil diameter of 60 nm and hence achieved the turn-on voltage as low as 30 V at the electrode gap of 130 μm. We have also investigated the concentration of the electric field at the body of nanocoils using a finite element method to compare it with that at the nanotube tip.

Synthesis of Carbon Nanocoils

The method of catalytic thermal CVD has been used to synthesize carbon nanocoils. We used catalysts of a 200 nm thick $Fe_1In_1Sn_xO_y$ film ($x<<1$) prepared by sputtering[11] and a Fe(10 nm)-coated ITO film. Si substrates with the catalyst films were placed on a quartz boat and 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 of helium with the flow rates of 200 to 230 sccm was mixed to make a total flow rate of 260 sccm. The reaction temperature was 700°C. The deposits were characterized by a scanning electron microscope (SEM) and a transmission electron microscope (TEM).

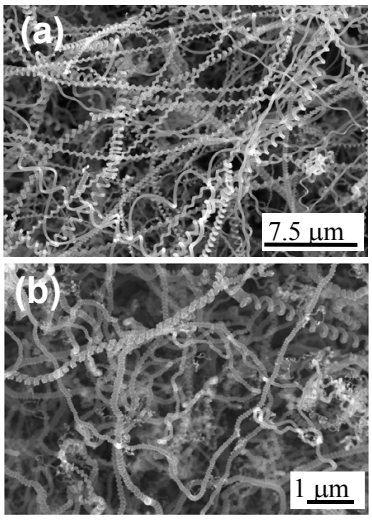

Figure 1. SEM micrographs of carbon nanocoils synthesized with the catalyst of Fe/ITO at 700℃ under the acetylene flow rates of (a) 60 sccm and (b) 30 sccm, respectively.

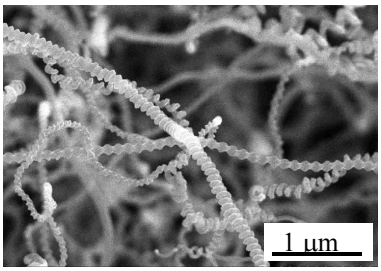

Figure 2. SEM micrographs of carbon nanocoils synthesized with the catalyst of Fe-In-Sn-O at 700℃ and the acetylene flow rate of 60 sccm.

Figures 1(a) and 1(b) show the SEM micrographs of nanocoils grown on the Fe-coated ITO films with the acetylene flow rates of 60 and 30 sccm, respectively. It is found that more than 95% deposits are nanocoils with various diameters and pitches. The coil diameters are different from each other, ranging from several tens to several hundreds of nanometers. The coils grow out although they are not well aligned along the direction perpendicular to the surface. Almost coils are not single but double stranded. Triple stranded ones are also seen. It is clearly observed that a catalyst particle is at the tip of every coil, suggesting a tip growth mechanism. The shape and the chemical composition of the catalyst determine the structure of the coil including its external diameter, pitch, number of tubules and the relative arrangement of the helix-shaped tubes.[7]

It is obvious from Fig. 1 that with the decrease of the flow rate of acetylene, the diameter and pitch of nanocoils are decreased. The average coil diameter is reduced from 500 nm for the acetylene flow rate of 60 sccm to 200 nm for that of 30 sccm. The diameter of a tube is related to the size of the catalyst particle at the tip. Thus it is reasonable to consider that the catalyst particles are formed when the source gas is fed and their size is affected by the concentration of the source gas.[10]

Figure 2 shows the SEM image of carbon nanocoils prepared using the catalyst of $Fe_1In_1Sn_xO_y$ with the acetylene flow rate of 60 sccm. As can be seen, nanocoils are grown with a high yield. The distribution of the coil diameters is quite narrow and their average value is as thin as 60 nm. This is because the composition of the catalyst is spatially uniform and consequently the catalyst particles with uniform size are formed.

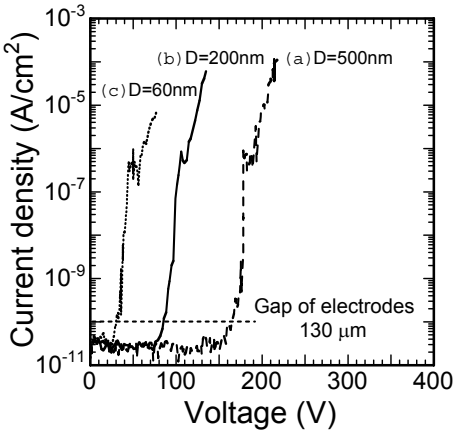

Figure 3. Emission current density plotted as a function of the applied voltage for carbon nanocoils with the average diameter of (a) 500 nm, (b) 200 nm and (c) 60 nm, respectively.

Field Emission Properties of Carbon Nanocoils

Figure 3 shows the current-voltage curves of nanocoil emitters with the average coil diameters of (a) 500 nm, (b) 200 nm and (c) 60 nm, respectively. The gap between the cathode and anode was set to be130 μm and the operation pressure was 1 x 10^{-5} Torr. Figures 3(a) and (b) are corresponding to the nanocoils shown in Figs. 1(a) and (b), respectively. Figure 3 (c) is corresponding to the nanocoils synthesized by the composite catalysts, which has the average diameter of 60 nm as shown in Fig. 2. It is found from Fig. 3 that the turn-on voltage of these nanocoil emitters is reduced to 30 V by decreasing the average diameter of the nanocoils to 60 nm. It is noted that this turn-on voltage is smaller than that of an array of nanotubes with the average diameter of 10 nm.[5] This is related to the consideration that the electric field concentration on the body surface of a nanocoil becomes stronger with decreasing the radius of the tube of the nanocoil. The radius of the tube is estimated to be 1/6 to 1/10 of the coil diameter. In the following section of discussion, we assume that the average radii of the tubes forming the nanocoils corresponding to the Fig. 3 are (a) 85 nm, (b) 35 nm and (c) 10 nm, respectively (approximately 1/6 of the average coil diameter of these nanocoils). It is also noted from Fig. 4 that the body of nanocoils has an angular shape rather than a

circular one. These sharp edges or corners at the bodies of the nanocoils resulted in the further concentration of electric field on them, which also causes the reduction of the turn-on voltage.

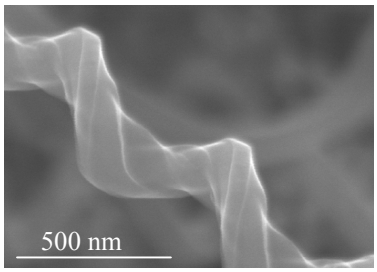

Figure 4. SEM micrograph of the surface of a synthesized carbon nanocoil.

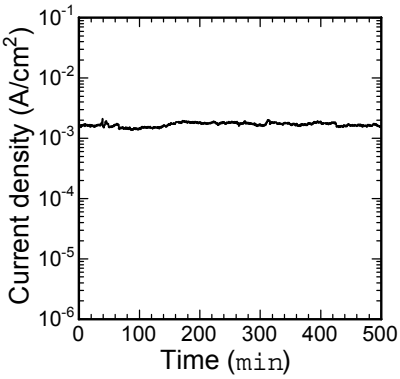

Figure 5. Stability of the emission current for the carbon nanocoil emitter. The current density is very stable near 1 mA/cm^2 for 500 min without large fluctuation.

The stability of the field emitter using the nanocoils synthesized by the composite catalyst has also been measured for the electrode distance of 300 μm, which is shown in Fig. 5. The current density of 1.0 mA/cm^2 is held on for 8 hours without a large fluctuation, suggesting a stable field emission. This result is similar to that for the emitter made by the nanocoils synthesized by the catalyst of Fe/ITO.[10]

Discussion

The field emission from carbon nanotubes is usually analyzed using the Fowler-Nordheim equation.[12] We have proposed a modified equation correctly applicable to nanotubes.[5] However, this analysis is not available for the field emission from a carbon nanocoil because the emission sites are not on the semisphere like a nanotube but on a curled tube. In the case that a nanocoil is vertically aligned to the electrode, the field emission occurs at the top surface of the coil end, which can be regarded as a ring, and in the case of that a coil axis is parallel to the electrode, the field emission occurs from the side body of the coil, which can be regarded as a wire. For an ideal wire located parallel to an anode plate, the electric field F at the body surface is given by

$$F=V/rln(L/r), \quad (1)$$

where L is the distance of the wire from the anode plate, r is the radius of the wire and V is the applied voltage. If L and V are constant, F is only a function of r. Furthermore, in the case of $L>>r$, F has a roughly reciprocal relation with r, i.e., decreasing the radius of the wire increases the electric field at the surface of the side body of the wire. However, this estimation dose not include the effect of the cathode plate on which the nanocoils are located.

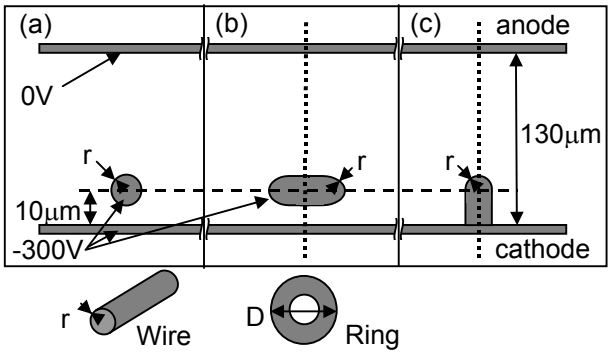

Figure 6. Schematic illustration of the configuration used for calculation of electric potential distribution in the two electrode plates for (a) a wire, (b) a ring and (c) a CNT, respectively.

In order to acquire an accurate estimation of the electric field concentrated on the nanocoils with two positions, the potential distribution between the two electrodes was calculated using the finite element method. The schematic illustration of the configuration used for the calculation is shown in Fig. 6, where (a) a wire and (b) a ring are placed 10 μm apart from the cathode plate. For a reference the case of a CNT standing on the cathode with a height of 10 μm denoted by (c) was also calculated. The distance between the two electrodes is 130 μm, which is the same as the experimental value. The potential is 0 V at the anode and –300 V at the cathode and the wire or the ring. The radius r is a parameter and set to be 10, 35 and 75 nm. In the calculation of the potential on the ring and CNT, the polar coordinate is introduced.

The results of the calculation are shown in Fig. 7. The solid circles are the maximum values of the electric field at the surface of the wire, and the open circles are those for the ring. The value for a CNT with a tip radius of 10 nm is also plotted by an open square for comparison. With the decrease of the r value, the maximum field increases for the wire and the ring, which shows a roughly reciprocal relation with r. This result is consistent with the theoretical estimation using Eq. (1). It is also found that the electric field for the ring is similar to that for the CNT, which is approximately three times larger than that for the wire. This means that the field emission effectively occurs at the top

surface of a nanocoil vertically aligned on the cathode. Considering that the edges and corners present on the body of a nanocoil cause the further concentration of the field, it is reasonable to believe that the turn-on voltage for the nanocoils is lower than that for nanotubes with the same diameter. It is also noted that the nanocoil has a larger number of the emission sites than the nanotube.

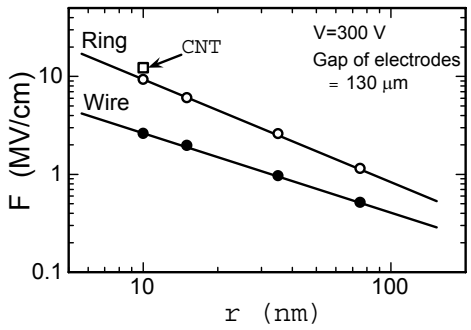

Figure 7. Maximum values of the electric field at the surface of wire, ring and CNT as a function of their radius.

Conclusion

The carbon nanocoils synthesized using the Fe-In-Sn-O catalysts have smaller diameters and their narrow distribution than those using the Fe/ITO catalyst. The turn-on voltage of the nanocoil field emitter is effectively decreased with the decrease of the average diameter of nanocoils. The finite element analysis has shown that a top surface of a nanocoil end has a similar concentration of the electric field to the nanotube tip. Taking into account of the existence of the sharp corners and edges on the nanocoils, the nanocoils can operate at a voltage lower than the value expected from the tube diameter. This is the reason that the turn-on voltage of 30 V has been achieved for the nanocoil with the coil diameter of 60 nm. This turn-on voltage is smaller than that of an array of nanotubes with the average diameter of 10 nm. These results confirm that the nanocoils are suitable for the high performance electron emission sources.

Acknowlegement

This work was supported in part by Grant-in-Aid for Encouragement of Young Scientists (B) from Japan Society for the Promotion of Science.

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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 was appointed to the position of professor in 1995. His work has primarily focused on nanoscience, including growth processes, nanophysics and nano-engineering of carbon nanomaterials. 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.