

Effect of Morphology on Field Emission Properties of Carbon Nanocoils and Carbon Nanotubes

Lujun PAN^{1,2*}, Yasumoto KONISHI¹, Hiroyoshi TANAKA¹, Osamu SUEKANE³,
Toshikazu NOSAKA^{2,4} and Yoshikazu NAKAYAMA

¹Department of Physics and Electronics, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

²Innovation Plaza Osaka, Japan Science and Technology Agency, 3-1-10 Technostage, Izumi, Osaka 594-1144, Japan

³Handai Frontier Research Center, Graduate School of Engineering, Osaka University, 1-1 Yamadaoka, Suita, Osaka 565-0871, Japan

⁴Technology Research Institute of Osaka Prefecture, 2-7-1 Ayumino, Izumi, Osaka 594-1157, Japan

(Received October 12, 2004; accepted November 29, 2004; published April 8, 2005)

Helical carbon nanocoils exhibit excellent field emission properties, and are thus expected to be applicable as electron emitters in field emission displays. We have synthesized carbon nanocoils with different diameters by the catalytic thermal decomposition of acetylene using iron–indium–tin–oxide catalysts. It is found that the turn-on voltage is decreased by decreasing the average diameter of the grown carbon nanocoils. The turn-on voltage of as low as 30 V at the electrode gap of 130 μm was achieved when the coil diameter is decreased to 60 nm. The calculation for the concentration of the electric field on the coil surface has been performed using a finite element method. It is found that the strength of the electric field around the top ring of a coil is increased with the decrease of the tubular diameter of the coil and has a similar value as that at the tip of a carbon nanotube, suggesting that the efficiency of the field emission from nanocoils would be higher than that from nanotubes. These results can explain the high stability of field emission from carbon nanocoils.

[DOI: 10.1143/JJAP.44.1652]

KEYWORDS: carbon nanocoil, catalyst, field emission, carbon nanotube, finite element method

1. Introduction

The field emission properties of carbon nanomaterials^{1–4} have been widely investigated theoretically and experimentally, because these materials exhibit attractive properties for applications of such as field emission display (FED), electron gun and X-ray source. The well-known carbon nanotube (CNT) is a good candidate material for such devices because of its high aspect ratio, and small tip radii. In FED fabrication, CNT arrays are expected to be produced directly on the cathode substrate by means of chemical vapor deposition (CVD). However, it is found that the vertically aligned carbon nanotubes prepared by thermal CVD are densely packed and the electric field distribution on an array is not uniform and is strongly concentrated at the edge of the array.^{5,6} This results in the nonuniformity and instability of the field emissions from carbon nanotube arrays.

In recent years, we have succeeded in preparing helical carbon nanocoils with different diameters by means of CVD with Fe–In–Sn–O catalysts.^{7–10} We have also found that the carbon nanocoil is an alternative candidate for an effective field emission device material because it exhibits excellent field emission properties.^{11–13} Because of the specula helical morphologies of carbon nanocoils, the emission sites locate not only on the tip but also on the body of a nanocoil, although the structure of the nanocoils is not an ideal one and they have sharp edges (graphene edge) at the body. These sharp edges also function as effective emission sites. Furthermore, the spaces among carbon nanocoils are not as narrow as those among CNTs in an array, which allows modification of the concentration of the electric field. Thus the carbon nanocoil emitters show spatially uniform and temporally stable field emission. In the study of field emission from carbon nanocoils with different diameters, it

has been verified that the turn-on voltages of the field emission from carbon nanocoils are reduced by decreasing their average coil diameter.^{12,13} In this work, we demonstrate the simulation results for the electric field distribution on the surfaces of CNTs and carbon nanocoils with different diameters to explain the effect of morphology on the field emission properties of two kinds of carbon nanomaterials.

2. Experiments and Calculations

To synthesize carbon nanocoils with different average diameters by catalytic thermal CVD, two kinds of catalysts have been used. One was 10-nm-thick Fe evaporated indium–tin–oxide (ITO) film,^{7–9} by which the carbon nanocoils with average diameters of 500 nm and 200 nm were synthesized at the acetylene flow rates of 60 sccm and 30 sccm, respectively. The other catalyst is 200-nm-thick Fe–In–Sn–O film prepared by sputtering,¹⁰ by which the carbon nanocoils with the average diameters of 60 to 80 nm were synthesized. In addition, CNTs with average diameter of 20 nm were synthesized by the same method using the catalyst of 4 nm-thick Fe film. The carrier gas used was helium with a flow rate of 300 sccm. The reaction temperature was maintained at 700°C for 30 min. The deposits were characterized using a scanning electron microscope (SEM) and a transmission electron microscope (TEM).

The grown carbon nanocoils or CNT arrays were used as the cathode and the ITO-coated glass substrates as the anode for a field emitter. The gap between the two electrodes was set to be 130 μm . The field emission current was measured at room temperature as a function of applied voltage at a pressure of 1×10^{-5} Torr. The applied voltage was changed from 0 to 1000 V. The distribution of electric field in a standalone carbon nanocoil and a CNT field-emitter was calculated using a three-dimensional finite element method. The model used is shown in Fig. 1, for which the space between the two parallel electrodes was set to be 50 μm and

*E-mail address: pan@dd.pe.osakafu-u.ac.jp

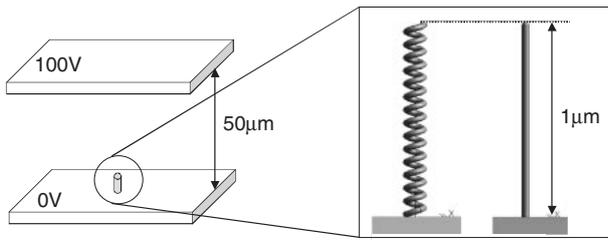


Fig. 1. Model of the simulation using finite element method.

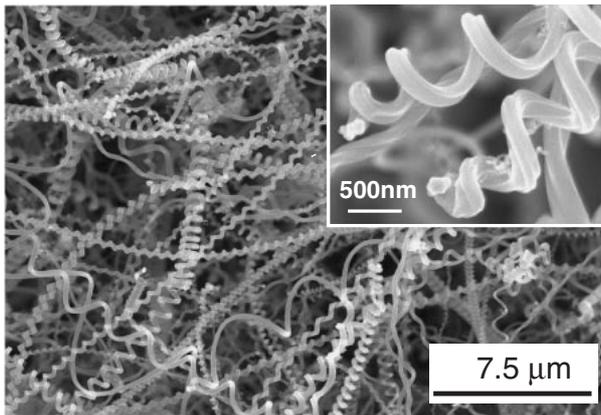


Fig. 2. SEM micrographs of carbon nanocoils synthesized at 700°C with the average diameter of 500 nm. The inserted SEM micrograph shows the tips of a number of coils.

the applied voltage was 100 V. The length of the carbon nanocoil or CNT is set to be 1 μm and the diameter of the carbon nanocoil is varied to be 12, 30, 60, 100, 200, and 500 nm, which correspond to the average diameters of the actually grown coils which range from 60 to 500 nm. For comparison, the CNT diameters are set to be 4, 10, 20 and 30 nm, respectively, which are the same as the average tubular diameters of the overall coils.

3. Results

Figure 2 shows SEM micrographs of carbon nanocoils grown at 700°C for 30 min with the acetylene flow rate of 60 sccm. More than 95% of the deposits are carbon coils with various diameters and pitches. The average diameter of these coils is 500 nm. The coils selectively grow out of the iron-deposited area although they are not well aligned along the direction perpendicular to the surface. The inserted SEM micrograph shows the tips of some coils. It is clearly observed that the catalyst particles are located at the tips of the coils, suggesting a tip growth mechanism. It is noted that the body of a coil takes an angular shape rather than a tubular 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 possibly form electron emission sites. The average diameter of the grown carbon nanocoils is decreased from 500 nm to 200 nm when the acetylene gas flow rate is decreased from 60 sccm to 30 sccm. The further decrease of the average diameter of the coils to 60 nm has been achieved by using the composite catalyst of Fe–In–Sn–O. This is because that the composition of the catalyst is spatially uniformly fabricated and

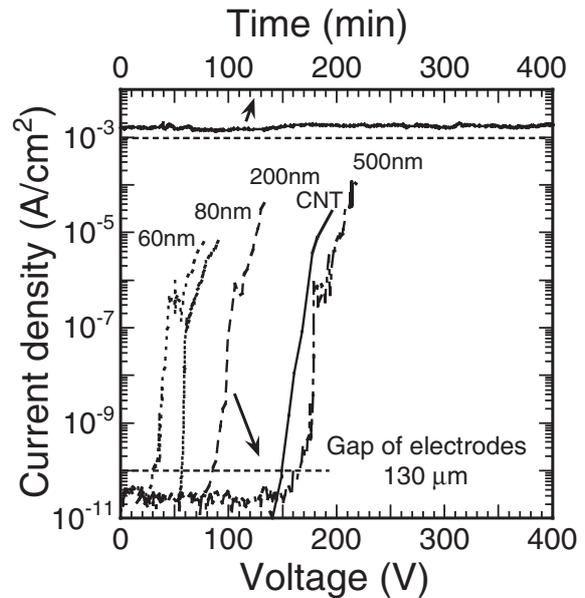


Fig. 3. I - V properties for carbon nanocoils with the average diameters of 500 nm, 200 nm, 80 nm and 60 nm, respectively, and the I - T property for the carbon nanocoils with the average diameter of 60 nm.

consequently the catalyst particles with uniform and small size are formed.

Figure 3 shows the current density–voltage curves of carbon nanocoil emitters with average coil diameters of 500 nm, 200 nm, 80 nm and 60 nm, respectively. For comparison, the curve for a CNT emitter with the average tubular diameter of 20 nm is also plotted. With the decrease of the coil diameter, the turn-on voltage (defined as the voltage where the emission current reaches 10^{-10} A) is decreased from 180 V to 90 V, and further to as low as 30 V when the nanocoil diameter is reduced to 60 nm. It is noted that this turn-on voltage is smaller than that of the array of nanotubes with the average diameter of 20 nm.⁴⁾ This is related to the consideration that many of the nanocoils are protruded from the array surface, which results in the high concentration of electric field on these protruded coils. The other important reason for this result is that the electric field concentration on the body surface of a nanocoil becomes stronger with decreasing the radius of the nanocoil tubule. The radius of the tubule is estimated to be 1/6 to 1/10 of the coil diameter. In the following discussion, we assume that the average radii of the tubules forming the nanocoils corresponding to Fig. 3 are (a) 75 nm, (b) 35 nm, (c) 15 nm and (d) 10 nm (approximately 1/6 of the average coil diameter of these nanocoils).

The current density–time properties for the coil emitter synthesized with the composite catalyst of Fe–In–Sn–O with the average coil diameter of 60 nm are also shown in Fig. 3. The current density of 1.0 mA/cm² required for conventional FEDs is held for 8 hours without large fluctuation, suggesting a stable field emission. This result is similar to that for the coil emitter synthesized using the catalyst of Fe evaporated indium tin oxide film.¹¹⁾

4. Discussion

The stability of the field emission from carbon nanocoils is considered to be related to the specula helix morphology.

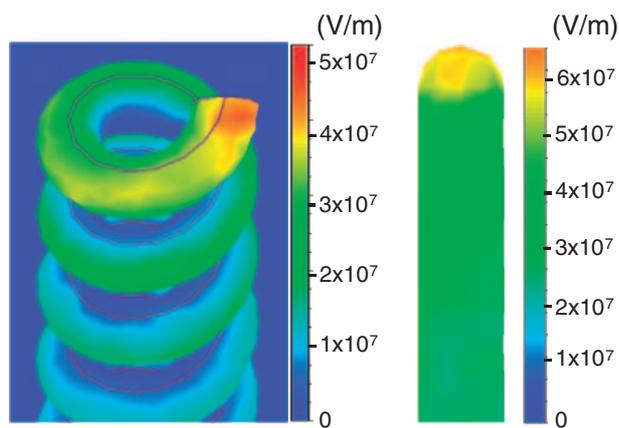


Fig. 4. Distributions of electric field on the surfaces of a carbon nanocoil and a CNT.

The electric field distributions on the carbon nanocoils with different diameters are calculated by means of a finite element method. Figure 4 shows images of the simulation result showing the distribution of electric field on the surface of a carbon nanocoil and a CNT with the same tubular radii of 15 nm. In the case of the CNT, the electric field is concentrated on its tip and decreases markedly along the side body away from its tip. It is reasonable that the emission from CNT mainly occurs at its tip. However, in the case of the carbon nanocoil, although the electric field is slightly larger at the tip, the decrease of the electric field is more moderate along the side body from its tip than that of the CNT. Therefore, the emission from a carbon nanocoil would occur not only at its tip, but also on its top surface where the electric field is concentrated. In addition, the sharp corners on the side bodies of actual nanocoils would produce higher concentrations of electric field on the bodies. These results suggest that a carbon nanocoil would have more emission sites and its emission efficiency is higher than that of a CNT.

Figure 5 shows the relationship between the calculated maximum electric field on a coil and its radii. The values of the CNTs with radii of 2, 5, 10 and 15 nm are plotted for reference. The electric field is increased by decreasing the diameter of the nanocoil, which is consistent with the experimental results. When the radii of a coil is reduced to

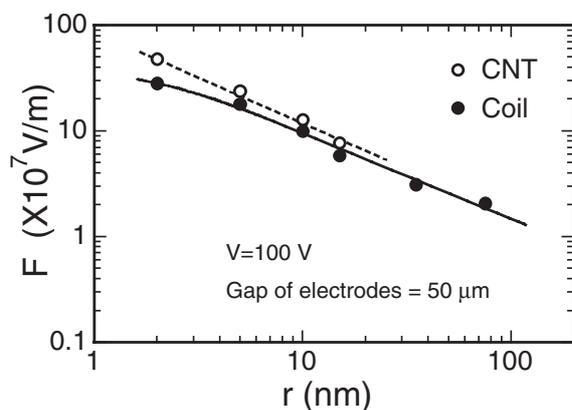


Fig. 5. Maximum values of the electric field at surfaces of coils with different diameters and CNTs as a function of their radius.

2 nm, the maximum electric field shows a lower value than that of a CNT. This is considered to result from the influences of the ring shape and the adjacent tubules of the coil, because the diameter and the pitch of the coil are proportionally decreased with the decrease of the tubular radii of the coil. It is noted that in the actual field emitters, the radii of the CNTs and coils used are almost all larger than 2 nm. When the radii is larger than 5 nm, the maximum electric field and its radii exhibit a reciprocal relation, which validates our theoretical prediction using a model of a ring instead of a coil.¹²⁾ The maximum electric field on a nanocoil has the same-level value as that on a CNT having the same tubule radii. It is speculated that a larger emission current could be obtained from the carbon coil than from the CNT because of the larger number of emission sites on the top surface of a carbon nanocoil.

5. Conclusion

Carbon nanocoils with different average diameters have been synthesized by means of catalytic CVD methods. Their field emission measurements and simulation of the electric concentration on a standalone coil and a CNT using a three-dimensional finite element method have been performed. The turn-on voltage is decreased by decreasing the coil diameter, which indicates a reciprocal relation between the maximum electric field on the carbon nanocoil and its radii. The electric field is concentrated on the tip of a CNT or a nanocoil having the same-level maximum electric field value. However, the electric field is also concentrated at the top surface of a coil. These results in addition to the sharp edges or corners on the side bodies of the coils suggest that the carbon nanocoils have a higher efficiency of field emission than the CNTs and would be a type of superior field-emitter material which can be used for FEDs.

This work was supported in part by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science.

- 1) W. A. de Heer, A. Chatelain and D. Ugarte: *Science* **270** (1995) 1179.
- 2) Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Buch, M. P. Siegal and P. N. Provencio: *Science* **283** (1998) 1105.
- 3) S. Akita, K. Yamamoto, Y. Yamaguchi and Y. Nakayama: *Proc. 4th IUMRS Int. Conf. in Asia, Symp. I, Chiba, 1997*, p. 81.
- 4) Y. Nakayama and S. Akita: *Proc. Pan-Pacific Imaging Conf./Japan Hardcopy 98, Tokyo, 1998*, p. 313.
- 5) L. Nilsson, O. Groening, C. Emmenegger, O. Kuettel, E. Schaller, L. Schlapbach, H. Kind, J. M. Bonard and K. Kern: *Appl. Phys. Lett.* **76** (2000) 2071.
- 6) O. Gröning, O. M. Kütel, Ch. Emmenegger, P. Gröning and L. Schlapbach: *J. Vac. Sci. & Technol. B* **18** (2000) 665.
- 7) M. Zhang, Y. Nakayama and L. Pan: *Jpn. J. Appl. Phys.* **39** (2000) L1242.
- 8) L. Pan, T. Hayashida and Y. Nakayama: *J. Mater. Res.* **17** (2002) 145.
- 9) Proc. IS&T's NIP17: *Int. Conf. on Digital Printing Technologies, Fort Lauderdale, 2001*, p. 542.
- 10) T. Nosaka, O. Suekane and Y. Nakayama: *Abstr. Int. Conf. on the Science and Application of Nanotubes 2003, Seoul, 2003*, p. 42.
- 11) L. Pan, T. Hayashida, M. Zhang and Y. Nakayama: *Jpn. J. Appl. Phys.* **40** (2001) L235.
- 12) Y. Nakayama, L. Pan and T. Hayashida: *Proc. IS&T's NIP 18, California, 2002*, p. 458.
- 13) Y. Nakayama, L. Pan and T. Hayashida: *Proc. IS&T's NIP 19: Int. Conf. on Digital Printing Technologies, New Orleans, 2003*, p. 727.