Electron Emission Devices Using Carbon Nanocoils

Yoshikazu Nakayama, Lujun Pan and Taichi Hayashida
Department of Physics and Electronics, University of Osaka Prefecture
Sakai, Osaka, Japan

Abstract

We have found out that carbon nanocoils have a highly potential ability for an electron emission device. Carbon nanocoils were prepared in high yield by catalytic thermal chemical vapor deposition. The source gas and catalyst are acetylene and iron-coated indium tin oxide, respectively. The measurement of the field emission current from the nanocoils at a pressure of 1 x 10^{-6} Torr shows the turn-on voltage as low as 180 V at the electrode gap of 130 μm and the saturation current density more than 10 mA/cm^2, which is similar to or smaller than those of most carbon nanotube emitters. The fluorescence is more uniform compared with that of the nanotube emitters. The fluorescence experiment also indicates that the body as well as the tip of a coil work as an effective emission site. A lifetime test for 100 hours under the current density of 1 mA/cm^2 shows no large fluctuation. These results indicate that the nanocoils have a spatially uniform emission of electrons and a long stability.

Introduction

Development of electron emission devices being able to operate at a low voltage could be one of key issues in the field of imaging science. They will be used as charging devices in electrophotography and direct marking imaging, and also be applied to a flat panel display. It is well known that carbon nanotubes[1-7] are a good candidate for these devices, because of their unique shape of small tip radii and high aspect ratios and conductive properties. An array of nanotubes aligned perpendicular to the substrate, which is prepared by catalytic thermal chemical vapor deposition (CVD), has appeared as an ideal structure of electron emission devices.[4,5] However, these nanotubes are generally densely planted so that the advantage of high aspect ratios of nanotubes disappear in the array and the electric field is strongly concentrated at the edge of the array. This results in the nonuniformity and unstability of field emission in the whole area of the emitter.[6]

Recently, we have successfully synthesized the carbon coils of nanometer scale (called carbon nanocoils) using the catalytic thermal CVD method with iron and indium tin oxide (ITO) as catalyst.[8] We have also demonstrated that this carbon material has the similar advantage to field emission, because of their nanometer structure.[9] Furthermore, carbon nanocoils have exhibited a rather uniform field emission. This may be due to their peculiar helix morphology, which would greatly modify the distribution of the space electric fields in a field emitter. In this paper, we report the mechanism and long-term stability of the field emission from carbon nanocoils.

Fabrication of Nanocoil Arrays

We fabricated carbon nanocoil arrays by catalytic thermal decomposition of acetylene in a flow reactor at atmospheric pressure. The substrates used were ITO-coated glass. The substrates were patterned with 8 to 15 nm thick iron films by electron beam deposition through shadow masks or by a combination of electron beam deposition and photolithography. The flow rates of gases were 60 sccm for acetylene and 200 sccm for helium, respectively. The reaction temperature was maintained at 700°C for 30 to 60 min.

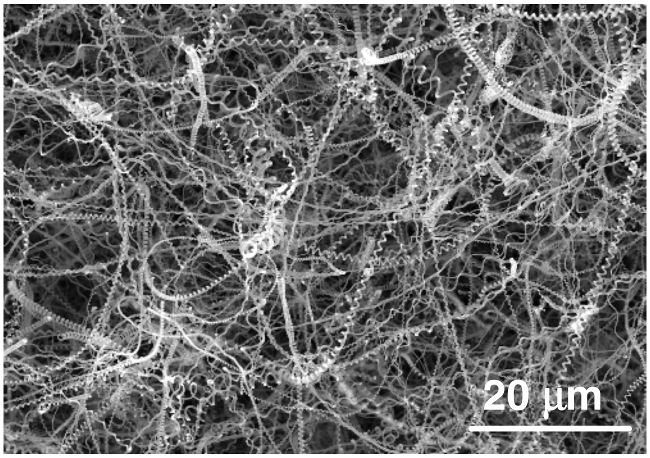

Figure 1. SEM image of carbon nanocoils prepared by catalytic thermal CVD. The coils grow out of the substrate with keeping self-organization during growth.

We have characterized the deposits using a scanning electron microscope (SEM) (S-4500, Hitachi) and a transmission electron microscope (TEM) (JEM-2000FXII). Figure 1 shows the SEM image of the deposits which were obtained only on iron-film patterned ITO. 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 grow out of the substrate with keeping self-organization well during growth, although they are not well aligned along the direction perpendicular to the surface. The length of the coils depends on the reaction time. The reaction time of 6o min provides ~ 300 μm long nanocoils.

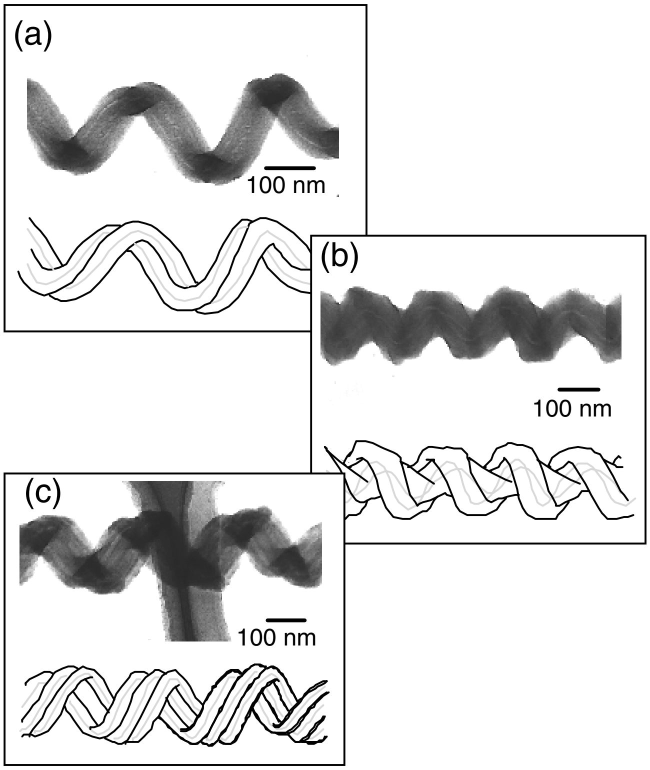

Figure 2. TEM images of carbon nanocoils and their schematic illustrations. (a) A coil formed by two tubules with almost the same coil diameter and pitch but a slight shift in phase. (b) A coil formed by two tubules with the same pitch but different coil diameters. (c) A coil formed by three tubules with almost the same coil diameter and pitch but a slight shift in phase.

TEM observation has revealed that the nanocoils consist of tubules. In most cases, two or more tubules form a coil as shown in Fig. 2. The shapes of the coils are determined by the correlation between the tubules. When two spiral tubes twine each other and have almost the same coil diameter and pitch (Fig. 2(a)), it appears as a normal coil with a circular cross section in the SEM observation. When two spiral tubules have different coil diameter and the same pitch (Fig. 2(b)), it appears as a drill bit in the SEM observation. When a coil contains more than two spiral tubules with the same coil diameter and pitch (Fig. 2(c), it has the appearance of a helix of ribbon in the SEM observation. More magnified TEM observation has crarified that the tubules partly consist of graphene sheets similar to those in carbon nanotubes.

Figure 3 shows the SEM images of the tips of coils. As seen in the images, every coil has a particle with a self-organized shape that contains tin, indium, ion, and/or oxygen. The particles act as catalyst in a tip growth. We have examined several kinds of catalysts to investigate the role of each component. Using the iron catalyst on glass or Si substrates, we obtain only the well-aligned carbon nanotubes arrays grown perpendicular to the substrate surface. However, no considerable product appears without iron on ITO and others such us In$_2$O$_3$, SnO$_2$, Si and glass. On iron- SnO$_2$ coated glass substrate, only carbon nanotubes appear. On iron-In$_2$O$_3$ coated glass substrate, we obtain coils but with a yield lower than that on iron-ITO. These results lead us to conclude on the role of each component in the iron-ITO catalyst that iron plays a role in the growth of carbon tubes, indium induces the helical growth, and tin enhances the growth of a coil.

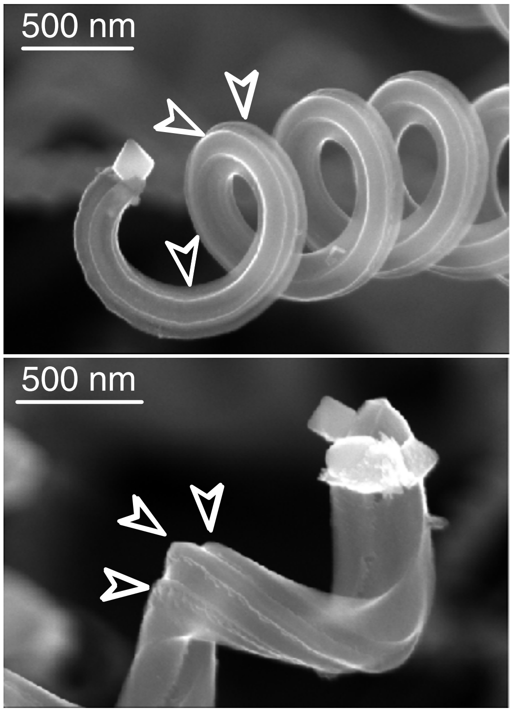

Figure 3. SEM images of the tips of carbon nanocoils. The catalyst particles are located at the tips, indicating a tip growth mechanism. The sharp rectangular parts at the bodies of the coils (arrowed) would be the electron emission sites.

It is also noted from Fig. 3 that the body of a coil takes an angular shape rather than a circular one, which is related to the structure of the catalyst particle, in most cases, a square one. These sharp edges or corner at the bodies of the nanocoils, which are arrowed in the figure, are possible to be the electron emission sites.

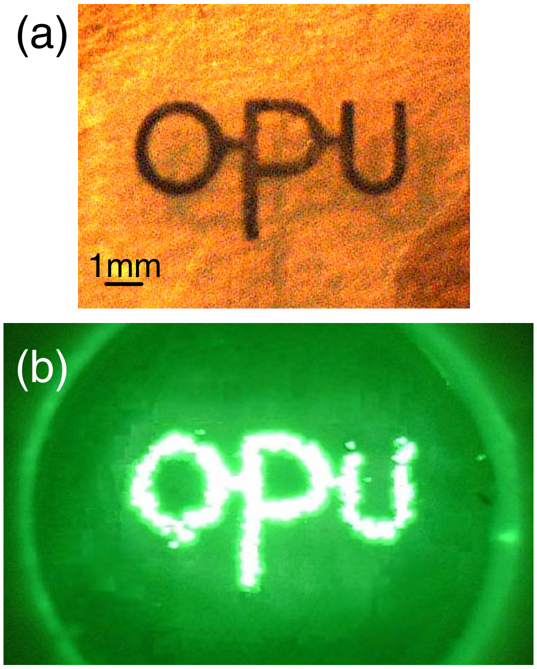

Figure 4. Photographs of (a) a patterned carbon nanocoils prepared on an ITO-coated glass substrate for a field emission experiment and (b) the fluorescence pattern from the emitter shown in (a) with an electrode gap of 130 μm.

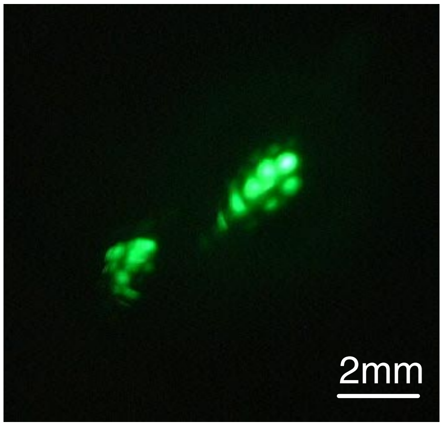

Figure 5. Fluorescence pattern from isolated carbon nanocoils. The electrode gap is 11 mm. The field emission occurs at the bodies as well as the tips of the coils.

Field Emission from Carbon Nanocoils

Figure 4(a) shows the photograph of a fabricated nanocoil field emission pattern on an ITO-coated glass substrate. For a field emission study, we used a phosphor-coated ITO glass plate as the anode. 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^{-6} Torr. The fluorescence pattern caused by the field emission is shown in Fig. 4(b). The electron emission form the carbon-nanocoil emitter is more uniform compared with that of the nanotube emitter. This is due to the more uniform distribution of the space potential in the nanocoil emitters.

The magnified fluorescence image from some isolated nanocoils is shown in Fig. 5. The magnification more than 10^4 is achieved by adjusting the electrode gap to 11 mm. This image clearly shows the emission sites in the coils and confirms that not only the tips but also the bodies of the nanocoils work as an effective electron emission site, as expected (see Fig. 2). It is reasonable to consider that these emission sites uniformly distribute in the nanocoil emitters because of the unique morphology of a coil. This is quite different form the case of the nanotube array grown densely and uniformly.

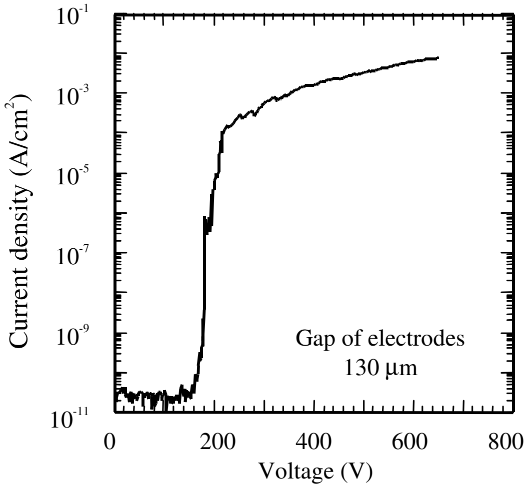

Figure 6. Emission current density plotted as a function of applied voltage for the nanocoil field emitter. The low turn-on voltage and high current density are obtained.

Figure 6 shows the current density versus the applied voltage curve. It is found that the turn-on voltage is as low as 180 V at an electrode gap of 130 μm, which is similar to or smaller than those of most CNT emitters.[3,5] A field emission current density of 1 mA/cm^2 required for practical field-emission-display devices is achieved at the voltage of 340 V and the current density as high as 10 mA/cm^2 can be achieved in the higher voltage.

We examined the temporal fluctuation of the emission current up to 100 h. The result is shown in Fig. 7. The current density of the level of 1 mA/cm^2 is kept without large fluctuation for whole of the examined period, exhibiting very stable field emission. The stability at the beginning is another advantage of the nanocoil emitters. This is quite different form the case of the nanotube emitters. The nanotube emitters usually show a considerable decay of the emission current at the beginning, because of the consumption of thin or protruded nanotubes. It is reasonable to consider that the sharp edges or corners on the body of the nanocoils (Fig. 2) working the electron emission sites are distributed rather uniformly and not too sharp to be consumed.

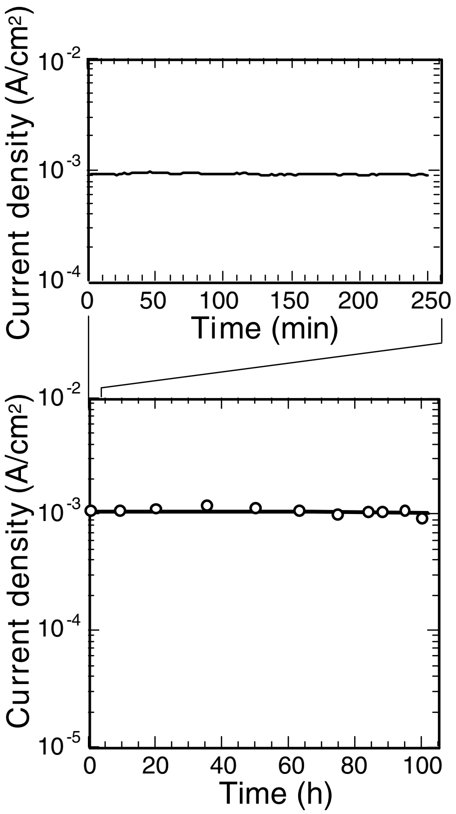

Figure 7. Temporal fluctuation of the emission current from the carbon nanocoils up to 100 h. No degradation of the current density appears at the beginning and for whole examined period.

Conclusion

We have prepared the carbon nanocoil field emitter by the catalytic thermal chemical vapor deposition. The nanocoils selectively grow at the patterned iron films on ITO to form the field emission array. The field emission experiments have exhibited the excellent properties such as the low turn-on voltage, high emission current density, high stability and uniformity. These characteristics of the nanocoil emitter are resulted from the unique morphology of the carbon nanocoils. The uniform distribution of the space potential over the nanocoil array and the large number of emission sites are considered to be the main contributors to the overall results. Carbon nanocoils show a promising application to the field emission devices in the field of imaging 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 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 is a member of the IS&T, the Material Research Society and the Japan Society of Applied Physics.