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To cite this article: Takashi Ikuno et al 2005 Jpn. J. Appl. Phys. 44 1655

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Correlation between Field Electron Emission and Structural Properties in Randomly and Vertically Oriented Carbon Nanotube Films

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(Received October 12, 2004; revised December 2, 2004; accepted December 8, 2004; published April 8, 2005)

We investigated the influence of the structural properties of randomly oriented carbon nanotube (R-CNT) and vertically oriented carbon nanotube (V-CNT) films on their field electron emission properties. The R-CNT and V-CNT films were synthesized using FeNi catalysts by means of thermal and dual-RF plasma-enhanced chemical vapor depositions, respectively. The structural properties of the R-CNT and V-CNT films were dependent on the initial thickness of the FeNi catalyst. As the FeNi film thickness decreased, the diameters of both types of CNTs decreased. Although the field emission property of the V-CNT film improved with increasing the aspect ratio of V-CNT, the field enhancement factor, β, obtained from the Fowler–Nordheim plot was found to be 100 times larger than that obtained from the geometric properties. R-CNTs exhibited a lower threshold field than V-CNTs. These results suggest that the field emission property is markedly influenced by the surface state rather than by the geometric factors of CNTs. [DOI: 10.1143/JJAP.44.1655]

KEYWORDS: carbon nanotube, randomly and vertically oriented carbon nanotube, structural property, field electron emission, field enhancement factor

1. Introduction

Carbon nanotubes (CNTs) are attracting considerable interest due to their extraordinary mechanical, chemical, and electronic properties and many versatile potential applications.1) One of these is as a field electron emission source for field emission displays (FEDs). CNTs have unique advantages in terms of their use as field electron emitters because of their unique properties such as high aspect ratio, small curvature, and chemical inertness. There are two methods for the fabrication of CNT emitters: an arc discharge or laser evaporation method in which the fabricated CNTs are adhered to the substrate by mixing them with metal particles2) or by applying them by means of electrophoresis deposition,3) and chemical vapor deposition (CVD).4,5) Since CNTs are grown directly on a substrate by CVD, the CNT emitter can be fabricated simply. Thermal CVD (T-CVD) and plasma-enhanced CVD have been utilized in the synthesis of randomly oriented CNTs (R-CNTs) and vertically oriented CNTs (V-CNTs), respectively.6) In particular, many researchers have devoted efforts to the artificial control of alignment, number density, and aspect ratio of V-CNTs.5,7-9) Recent studies have shown that the field electron emission property of R-CNTs compares favorably with that of V-CNTs.10) However, although it is essential for FED application to elucidate the correlation between the structural properties and field electron emission properties of both R-CNTs and V-CNTs, systematic experiments for this purpose have not been carried out.

In this study, using both R-CNTs and V-CNTs, the correlation between the field electron emission properties and the structural properties was investigated as a function of the film thickness of the FeNi catalyst. As the FeNi film thickness was decreased, the diameter of both CNTs decreased. Although the field electron emission properties of the V-CNT film were improved with increasing the aspect ratio of V-CNT, the field enhancement factor obtained from the Fowler–Nordheim plot was found to be much larger than that obtained from the geometric factors. Furthermore, R-CNTs exhibited a lower threshold field than V-CNTs. These results suggest that the field electron emission from both R-CNTs and V-CNTs is strongly influenced by the local electronic states induced by surface defects in the graphite lattice, rather than by their geometric factors.

2. Experimental

T-CVD and dual-RF plasma-enhanced CVD (RF-CVD) were used to synthesize R-CNTs and V-CNTs, respectively. FeNi thin films deposited on Si wafers with thicknesses ranging from 5 to 100 nm were used as substrates. On the basis of X-ray photoemission spectroscopy analysis, the composition ratio of FeNi was estimated to be 3 : 2. The FeNi thin films were transformed to nanoparticles upon annealing at 600°C for 30 min. The diameter of the nanoparticles decreased markedly with decreasing the film thickness of the FeNi catalyst. Our T-CVD apparatus consisted of a quartz reactor and an electric furnace. C2H2 gas diluted with He gas (C2H2/He = 3/12 sccm) was introduced into the quartz reactor held at 600°C and 1 kPa. Our RF-CVD apparatus is a simple capacitively coupled system. Since the apparatus has been described elsewhere,11) only an outline is given here. RF power was applied to the two electrodes (anode and substrate) independently, and the applied power at the anode and that at the substrate were 300 and 100 W, respectively. Pure CH4 gas was used as a source gas for RF-CVD at 600°C and 10 Pa.

The surface morphology and internal structure of the
resultant CNT films were characterized by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Field electron emission properties were measured using a diode-type configuration in ultrahigh vacuum.\(^{12}\) The distance between the anode plate and sample was 800 \(\mu\text{m}\).

3. Results and Discussion

The FeNi film thickness dependences of the morphologies of both the R-CNTs and V-CNTs were investigated in the thickness range from 5 to 100 nm. Figure 1 shows SEM images of FeNi nanoparticles after annealing the FeNi thin film in vacuum at 600 \(^{\circ}\)C for 30 min. The diameter of the nanoparticles increases with increasing the film thickness in the range from 5 to 10 nm. Above the film thickness of 50 nm, nanoparticles were scarcely formed. Figure 2(a) shows an SEM image of the R-CNT films grown by T-CVD using a FeNi catalyst with an initial thickness of 5 nm. R-CNTs were grown with a high number density throughout the substrate. Figure 2(d) shows a TEM image of the R-CNTs shown in Fig. 2(a). The R-CNTs exhibit a bamboo-like structure, which consists of stacked hollow compartments and a metal nanoparticle at the tip, whose shape reflects those of the compartments. As can be seen in Fig. 2(b) (10-nm-thick FeNi film), the diameter of the R-CNTs increases with FeNi film thickness. However, at a film thickness of 50 nm, no CNTs were observed as shown in Fig. 2(c).

Figure 3(a) shows a typical SEM image of the V-CNTs grown by RF-CVD using an FeNi film of 5 nm thickness. CNTs are found to grow perpendicularly to the substrate with a high number density. Figure 3(d) shows a TEM image of the V-CNT shown in Fig. 3(a). Since a metal nanoparticle is observed at the top of the V-CNT, V-CNT formation, as well as R-CNT formation, is considered to occur in the tip growth mode.\(^{13}\) The V-CNT has a hollow structure and well-crystallized graphite sheets. Figures 2(b) and 2(c) show SEM images of the V-CNTs grown for FeNi thicknesses of 10 and 50 nm, respectively. In contrast to the case of the R-CNTs, V-CNTs were obtained in the entire thickness range of 5–100 nm, in which the diameter of V-CNTs increased with FeNi film thickness. This result is in agreement with the previous report showing that the diameter of CNT depends on the size of catalyst nanoparticles.\(^{5}\) Figure 4 shows the average diameter and number density of V-CNTs as functions of FeNi film thickness. Although the diameter increases with the FeNi film thickness in the range from 5 to 100 nm, the number density does not change markedly with the film thickness, maintaining an order of \(10^{9}/\text{cm}^2\).

The FeNi film thickness dependences of the field electron emission properties of both CNT films were investigated. Figure 5(a) shows emission current density as a function of applied electric field for the R-CNT and V-CNT films. The emission area of these films is \(8 \times 10^{-3} \text{cm}^2\). It is evident that R-CNT films exhibit a better field emission property than that for V-CNT films. In the case of the V-CNT films, the emission property is improved with decreasing FeNi film thickness. Here, we define the applied electric field at an emission current density of 1 \(\mu\text{A/cm}^2\) as the threshold electric field, \(E_{\text{th}}\). Figure 5(b) shows \(E_{\text{th}}\) as a function of the film thickness of the FeNi catalyst. The V-CNT films exhibit an increase in \(E_{\text{th}}\) with FeNi film thickness. Since the diameter of V-CNT is reduced with thinning of the FeNi film as shown in Fig. 4, it is likely that a V-CNT with a small diameter induces electric field concentration at the tip, yielding an excellent field electron emission characteristic. On the other hand, in the case of the R-CNT films, it is found that \(E_{\text{th}}\) remains almost constant, ranging from 2.4 to 2.9 \(\text{V/}\mu\text{m}\) for all thicknesses of the FeNi catalyst. These values compare favorably with those reported thus far.\(^{10,14,15}\)

Next, we estimated the field enhancement factor for both V-CNT and R-CNT films. The Fowler–Nordheim (F–N) equation can be described as\(^{16}\)

\[
J = \frac{1.56 \times 10^{-6}(\beta E)^2}{\phi} \exp\left(-\frac{6.83 \times 10^9 \phi^{3/2}}{\beta E}\right),
\]

where \(J \text{ (A/cm}^2\) is the emission current density, \(E \text{ (V/}\mu\text{m}\) is the applied electric field, \(\beta \) is the field enhancement factor, and \(\phi \) is the work function of the emitter. Figure 6(a) shows an F–N plot on the basis of the results shown in Fig. 5(a). The linear relationships indicate that the measured current stems from field emission for both the V-CNT and R-CNT films. Considering that the work function of CNTs is 5 eV,\(^{17}\) the experimental value \(\beta \) in Fig. 6(a) was estimated on the basis of the slope of the F–N plot, for which geometric factors such as diameter and length estimated on the basis of the SEM images were not used. The obtained
value of $\beta$ for the V-CNT films ranged from 1550 to 3300. On the other hand, $\beta$ for the R-CNT films, which was independent of their morphology, was approximately 7600, although this value indicates an apparent field enhancement factor. In the present study, the field electron emission property of the V-CNT whose number density is optimized to suppress the field-screening effect has not been measured. It has been reported that by changing the number density from $10^9$ to $10^8$/cm$^2$, $\beta$ was increased from 770 to 1081 (namely, approximately 1.4 times).

Since the values of $\beta$ for our R-CNT films are more than two times larger than those for V-CNT films, it is likely that the field emission property for the V-CNT film is not better than that for R-CNT films, even when their number densities

![Fig. 2. SEM images of R-CNT films and carbon nanostructure films formed by thermal chemical vapor deposition for FeNi film thicknesses of (a) 5, (b) 10, and (c) 50 nm. (d) TEM image of the R-CNTs shown in Fig. 1(a) for FeNi thickness of 5 nm.](image1)

![Fig. 3. SEM images of V-CNT films formed by dual-RF plasma-enhanced chemical vapor deposition for FeNi film thicknesses of (a) 5, (b) 10, and (c) 50 nm. (d) TEM image of the V-CNT shown in Fig. 2(a) for FeNi thickness of 5 nm.](image2)

![Fig. 4. Average diameter and number density of V-CNTs as functions of FeNi film thickness.](image3)
are optimized. These results suggest that another factor in addition to the geometric factor strongly affects the field electron emission from the R-CNT films. Moreover, since $\beta$ for R-CNT films exhibited approximately the same value, the field enhancement due to the standing-up of the R-CNTs out of the films can be considered to be negligible.

Figure 6(b) shows the values of $\beta$ estimated on the basis of the slope of the F–N plot [Fig. 6(a)] for V-CNT films as a function of V-CNT diameter estimated by means of SEM observation. $\beta$ increases with decreasing V-CNT diameter. On the other hand, $\beta$ is simply estimated on the basis of the height, $h$, and the diameter, $d$, of a cylinder terminated by a half-sphere, as:

$$\beta = 1.2[2h/d + 2.15]^{0.90}, \tag{2}$$

in which the field-screening effect on $\beta$ is negligible. When the aspect ratio, $h/d$, is sufficiently large, $\beta$ is proportional to $(1/d)^{0.9}$. The solid curve in Fig. 6(b) shows the result of best fitting using $\beta \sim (1/d)^{0.9}$. The fitting curve indicates that a geometric factor, diameter, seems to affect the field electron emission. However, a comparison between the $\beta$ obtained from the F–N plot and that obtained from the morphology of V-CNTs reveals the existence of another factor affecting field electron emission. Figure 6(c) shows the $\beta$ obtained from eq. (2), where $h$ and $d$ were estimated by means of SEM observation, as a function of V-CNT diameter. It is found that the obtained $\beta$ is low compared with that in Fig. 6(b), as it ranges from 14 to 28. In other words, the $\beta$ obtained from the F–N plot does not directly imply that it is a field enhancement factor, but that it includes another factor for the improvement of field electron emission.

Another factor affecting field electron emission from both R-CNT and V-CNT can be correlated with the surface electronic state of the CNTs. To investigate the surface structure in detail, a close inspection by means of TEM observation was performed. Figure 7 shows a high-resolution TEM image of the straight wall of a R-CNT. At the edge of the wall (upper region of the wall), there are many nanoprotusions, which are seen in the form of graphite caps. These protrusions are likely to act as emission sites. To form protrusions in a graphite sheet, $n$ ($n \neq 6$)-membered rings are needed in a graphite lattice. It has been theoretically predicted that a sharp peak of the local density of state (LDOS) exists near the Fermi level in the 4- and 7-membered ring systems, promoting an increase in tunneling probability. Experimentally, LDOS near the Fermi level for surface defects of graphite has been identified by means of a scanning tunneling microscopy (STM) study. Moreover, very recently Oshima and co-workers demonstrated that a carbon nanoprotusion of CNTs acts as an electron emission site. In this study, since the value of $\beta$ obtained from the F–N plot is more than 100 times larger than that obtained from the SEM image, the effect of the geometric factor on field electron emission property is concluded to be small in comparison with that of the surface electronic state.
It is reasonable to consider that the number density of the emission site originating from the local electronic structure at the tip of our V-CNT dominantly effects field electron emission, rather than the concentration of the local electric field on the specific protuberant V-CNT. In the case of R-CNTs, it is likely that only the surface electronic state influences field electron emission. It seems that the number of defects in R-CNTs does not have a direct correlation with the morphology of these nanotubes, which explains why the threshold field of R-CNT films is independent of the film thickness of the FeNi catalyst. It is also understandable that the threshold electric field of R-CNTs is smaller than that of V-CNTs because of the existence of numerous defects in the R-CNT bodies.

4. Conclusions

We investigated the correlation between the field electron emissions and structural properties of R-CNT and V-CNT films. R-CNT and V-CNT films were formed by T-CVD and RF-CVD, respectively. The structural properties of R-CNT and V-CNT films were dependent on the initial thickness of the FeNi catalyst. The diameters of both CNTs decreased with decreasing FeNi film thickness. From the field electron emission measurements, the threshold electric field of the R-CNT films was found to be lower than that of the V-CNTs and independent of the FeNi film thickness. Regarding the V-CNT films, the threshold electric field was improved with the aspect ratio, partly due to the increase in the geometric factors. A comparison between the field enhancement factor derived from the F–N plot and that from the geometric property indicates that there is another factor in addition to the geometric factor that effects the improvement of the emission property, which can be correlated with the local electronic states induced by surface defects in the graphite lattice. For both R-CNT and V-CNT, the number of surface defects on the CNT rather than the geometric factors is more likely to influence their field electron emission properties.

Acknowledgements

This work was supported by the Frontier Carbon Technology (FCT) project of the Ministry of Economy, Trade, and Industry (METI) of Japan through the New Energy and Industrial Technology Development Organization (NEDO) and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan. One of the authors (T. I.) acknowledges the support of the Japan Society for the Promotion of Science.

13) A. V. Melechko, V. I. Merkulov, D. H. Lowndes, M. A. Guillorn and