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Carbon nanofiber bundles grown by plasma enhanced chemical vapor deposition

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A bundle of carbon nanofibers (CNFs) was successfully obtained on a glass substrate through a plasma enhanced chemical vapor deposition (PECVD) process. CNFs having dimensions of 100 nm in diameter and 1 μm in length nucleated on the Ni-Cr catalysis and grew selectively in a circular area 3 μm in diameter with a number density of 50 in 1 μm^2. PECVD was used with mixed source gases of CH_4/H_2/He and a substrate temperature of less than 743 K which was lower than the transition temperature of glass substrate. Each CNF had a nanostructure of a stacked cup-cone shaped graphite shells with a Ni-Cr nanoparticle surmounted at the top. The field emission characteristics of the CNF bundle were also evaluated up to 3 μA at 130 V and the maximum in the current-voltage relation was converted to a Fowler-Nordheim (F-N) plot using a work function value of 5.0 eV for CNF which showed an explicit linear F-N relation. This means a CNF bundle is a candidate element for two dimensional field emitter devices.

Key words: Carbon nanofiber, CNF bundle, PECVD, Field emitter, F-N plot.

Introduction

Since a new type of fibrous carbon nanostructure was discovered, that is, the carbon nanotube (CNT) by Iijima [1], CNTs and carbon nanofibers (CNFs) as field emission (FE) sources have attracted considerable attention. CNTs or CNFs (CNT/CNF) have been synthesized by various methods, such as arc charging [2], thermal chemical vapor deposition [3] and plasma-enhanced chemical vapor deposition (PECVD) [4]. In particular, PECVD is efficient for the synthesis of CNT/CNFs at low temperatures and makes it possible to employ a glass substrate for the growth of CNT/CNFs. To fabricate CNT/CNFs by chemical vapor deposition methods, transition metal catalysts, such as iron group metals [5-9], nickel [10], cobalt [11] and palladium [12], have been widely employed for the growth of highly concentrated and vertically well-aligned CNFs in recent years.

The characteristics of field emission from CNT/CNF bundles depend on the morphology of CNT/CNF. CNT/CNFs on a uniform catalysis layer grow at a high density and are vertically well-aligned under optimized growth conditions, although uniformly well-aligned and high-density CNT/CNF structures show a low field emission efficiency because they do not concentrate and localize an electrical field at an electron emission site. To increase the field emission efficiency, it is necessary for CNT/CNF to concentrate an electric field for electron emission to its top. In particular, controlling the morphology, material quality and grade distribution of the catalysis is considered important for adjusting the interval and morphology of individual CNT/CNF structures.

In this study, to obtain a good field emission performance, we prepared a catalysis layer made of a nickel-based alloy and electrically conductive materials to synthesize CNFs of controlled bundle size and average inter-bundle distance. With the prepared catalysis layer, we evaluated the morphological and electrical characteristics of CNFs grown by plasma-enhanced chemical vapor deposition (PECVD) using a SEM, a TEM and field emission measurements. As a result, we obtained results on the low-temperature synthesis and the field emission (FE) characteristics of the optimized CNF bundles.

Experimental Procedure

To synthesize the CNF bundles at a temperature lower than the transition temperature of the glass substrate, CNFs were fabricated using a helicon wave PECVD system that enabled the growth of the CNF bundles with a catalyst at 700-800 K. By employing the helicon PECVD system, CNFs were synthesized at a low temperature. In the case of the industrial architecture, we used a soda-lime glass substrate with a higher transition temperature and a higher heat resistance to fabricate CNF emitters. A catalyst composed of a nickel (Ni)-chromium (Cr) alloy was employed to control the bundle size and distance between adjacent CNF bundles. The reason why Ni-Cr was employed was to separate each Ni catalyst region to synthesize bundle like CNFs. To increase the field emission efficiency, it was necessary to control the parameter localizing and enhancing the electrical field for electron emission. In this study, the parameter was bundle size and the space between bundles to enable the control of

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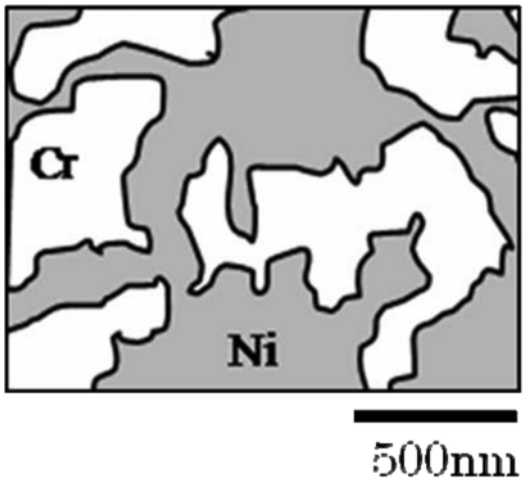

Fig. 1. Illustration of nickel and chromium grains in the Ni-Cr catalyst for the CNF growth. The nickel content in the catalysis film was 57 wt%.

the morphology of emitters artificially. Consequently, the effective emission of electrons from CNF bundles grown on Ni within a low electrical field was made possible. The Ni-Cr alloy catalyst layer was fabricated by sputtering nickel pellets on the chromium target. Figure 1 illustrates the morphology of the Ni-Cr alloy for the growth of CNFs in our research. Chromium grains separate a nickel catalyst layer for CNFs. The space between adjacent CNF bundles was controlled at 500-1,000 nm by the Cr grain size.

For reference, we also prepared a uniformly pure nickel catalyst for the growth of CNFs and compared the synthesized morphology and field emission characteristics of CNFs on the Ni-Cr catalyst with those on the pure nickel catalyst. In both catalyst specifications for the synthesis of CNFs, the deposition conditions in this PECVD system were $CH_4/H_2/He$ = 50/50/100 in the case of the pure Ni catalyst, 20/50/100 in the case of the Ni-Cr catalyst for inlet gases, gas pressure = 2 Pa, RF power = 300 W and substrate temperature = 743 K. The Ni concentration in the Ni-Cr catalyst layer was 57 wt%.

After helicon PECVD, a scanning electron microscope (SEM) and, a transmission electron microscope (TEM) were used to characterize CNF bundles. To evaluate the electrical characteristics, FE measurement was performed in a vacuum chamber with a diode structure.

Results and Discussion

Morphology of CNF bundles

Each part of Fig. 2 shows the morphology of CNF bundles on the Ni-Cr alloy catalyst and pure Ni catalyst grown at 743 K by $CH_4/H_2/He$ deposition. The CNF bundles grew on the Ni-Cr catalyst with a number density of 30-50 pieces per μm^2 having a diameter of 100 nm. The distance between elements in the CNF bundles was 800-1000 nm, which is of the same order of magnitude as the space between nickel catalysis films areas separated by chromium grains shown in Fig. 1. On the other hand,

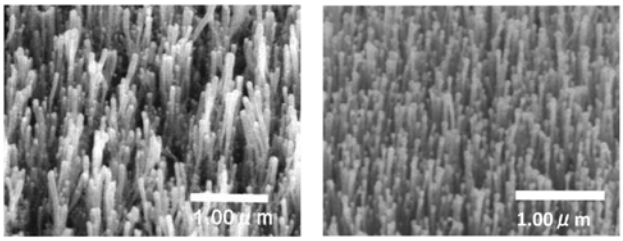

Fig. 2. SEM images of CNF bundles grown on the Ni-Cr catalyst (left) and pure Ni catalyst (right) film.

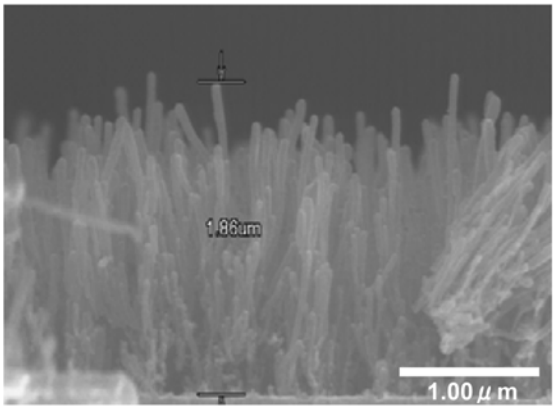

Fig. 3. Cross-sectional view of CNF bundles on the Ni-Cr catalyst taken by SEM. Ni nanoparticles surmount the top of each CNF.

the density of CNF bundles was over 50 pieces per μm^2 with good alignment and they grew with good uniformity. Fig. 3 shows a cross-sectional view of synthesized CNF bundles that are about 1-2 μm in length and well aligned vertically. CNFs on the pure nickel catalyst were also synthesized to compare the field emission characteristics with those in CNF bundles on the Ni-Cr alloy catalyst.

Differences in field emission characteristics

The field emission of electrons from CNF bundles was evaluated on the basis of current-voltage characteristic curves obtained using an apparatus with a diode structure. Figure 4 shows the FE measurement system in which the gap distance between cathode and anode was kept at 10 μm with glass spacers made by a printing process. The anode area was set smaller than the CNF cathode area (> 10 mm^2) to keep the field emission from the edge of the CNF bundle layer.

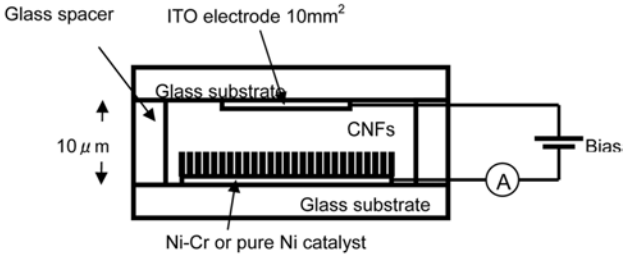

Fig. 4. Schematic diagram of the system used for field emission measurements having a diode structure.

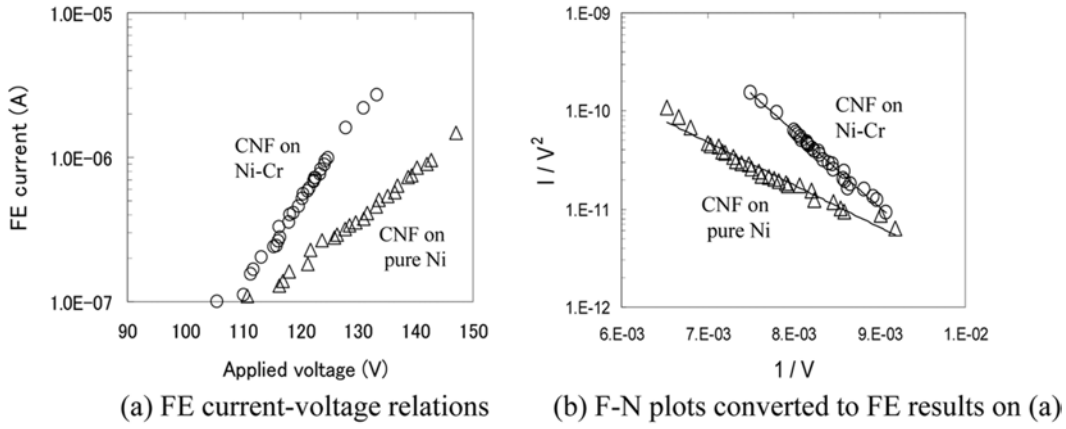

Fig. 5. (a) FE current-voltage characteristics obtained by diode measurements for the two cases. (b) F-N plot of FE current-applied voltage relation for the two types of CNF morphologies shown in Fig. 2. The solid linear line was fitted by calculation using a work function value of 4.7 eV. Open circles and triangles have the same meanings as in the left graph.

Figure 5(a) shows the current-voltage characteristics obtained by diode measurements for CNF cathodes grown under different conditions. In both Fig. 5(a) and (b), open circles and triangles denote the FE data of CNF bundles on the Ni-Cr catalyst and those of CNFs on pure nickel, respectively. The field emission characteristics of CNF bundles grown on the Ni-Cr alloy catalyst were as follows: the threshold voltage was 100 V, the same as that on the pure Ni catalyst, and the maximum current was 3 μA at 130 V, whereas the value for CNF on pure nickel was less than 2 μA at above 150 V. These current-voltage relations were converted to Fowler-Nordheim (F-N) plots as shown in Fig. 5(b). The slope of the F-N plot for the CNF bundles on the Ni-Cr catalyst was larger than that for CNF on pure nickel. This indicates that each sample, which was synthesized under a different catalyst condition, has different field emission efficiency. In the case of Fig. 5, the solid line shows calculated F-N plots obtained using a work function value of 4.7 eV for CNF showing an explicit linear F-N relationship.

These results indicated that the morphologies on the synthesis CNFs for FE were different from each catalyst condition. As a result, controlling the morphology of synthesized CNFs was shown to be an effective method of artificially producing CNFs with better FE performance characteristics.

In summary, to obtain excellent field emission performance with CNF bundles, it is important to control the composition ratio of the Ni-Cr alloy catalyst because this regulates the distance between adjacent CNF bundles in order to achieve effective CNF field emission.

Conclusions

Carbon nanofiber bundles were grown on a glass substrate at 743 K by helicon-wave PECVD. Nickel-chromium alloy layers were employed as catalysts to synthesize well-aligned CNF bundles selectively. In this case, a small CNF bundle was able to yield a higher field enhancement and a larger Fowler-Nordheim electron tunneling state. Once we are able to control the amount of nickel in the Ni-Cr catalyst and adjust the synthesis conditions for CNF bundles perfectly, it will be possible to achieve excellent field emission performance effectively.

Acknowledgment

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