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Field emission characteristics of carbon nanfiber bundles

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Abstract Carbon nanofiber bundles were formed on silicon substrate using microwave plasma-enhanced chemical vapor deposition system. These bundles were vertically well-grown under the high negative bias voltage condition. The bundles were composed of the individual carbon nanofiber having less than 100 nm diameters. Turn-on voltage of the field emission was measured around 0.8 V/μm. Fowler-Nordheim plot of the measured values confirmed the field emission characteristic of the measured current.

Key words Carbon nanofiber bundles, Field emission, Microwave plasma, Vertical alignment

1. Introductoin

Recently, the carbon nanofilaments have been regarded as promising material candidates for cold electron emission sources, due to their unique tip shape which plausibly produces high electric field properties [1-4]. For practical application of carbon nanofilaments to electron emitters, the achievement of vertically well-aligned carbon nanofilaments is preferential [5-8]. In addition, to enlarge the application area of vertically well-aligned carbon nanofilaments to various shapes, such as convex and concave [9], the enhancement of the vertical stability of carbon nanofilaments would be required. The vertical stability of carbon nanofilaments may be enhanced by increase the diameter of carbon nanofilaments [1]. This is the reason why multi-walled carbon nanotubes, instead of single-walled carbon nanotubes, are regarded as good candidates for electron emitters [1]. In this respect, the bundle formation of carbon nanofilaments could be one of the best choices to use in the specific area requiring vertical stability.

This work presents the bundle formation of carbon nanofibers grown in a vertical direction to the substrate. We applied a negative bias voltage of −350 V during microwave plasma-enhanced chemical vapor deposition reaction. Finally, we could achieve the growth of vertically well-aligned carbon nanofiber bundles (CNFBs) directly onto the substrate surface. Field emission characteristics of these bundles were investigated.

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2. Experimental

We deposited CNFBs films on nickel layer-coated 10.0× 10.0 mm^2 Si substrate in a horizontal-type microwave plasma-enhanced chemical vapor deposition (MPECVD) system. Nickel coating was be achieved by radio frequency (RF) sputtering. In RF-sputtering, we used Ar gas with 30 mTorr total pressure under 500 W RF power. We obtained around 50 nm film thicknesses after 5 min sputtering reaction.

Before the CNFBs deposition reaction, we cleaned the substrate with H_2 plasma for a few minutes. CH_4 and H_2 were used as source gases. The bias voltage value was constantly maintained at −350 V. The detailed experimental conditions of the CNFBs formation under MPECVD were shown in Table 1.

The morphologies of CNFBs were investigated by using field emission scanning electron microscopy (FESEM). The nanostructures of carbon nanofibers were examined by transmission electron microscopy (TEM). The samples for TEM were prepared by dispersing the carbon nanofibers using acetone in an ultrasonic bath. A drop of suspension was placed onto a carbon film supported by a Cu grid. Then, the Cu grid was placed into the TEM chamber and the detailed morphologies of carbon nanofibers were investigated.

The field emission measurement was carried out in a diode type field emission measuring system under ultra high vacuum condition. The emission current at the anode was measured as a function of the applied bias voltage between the anode and the cathode. Quartz having around 500 μm thickness was used as a spacer between the anode and the cathode.

Table 1
Experimental conditions of carbon nanofiber bundles formation

Microwave power	Source gases	Flow rates of source gases	Sub. temp.	Total pressure	Reaction time	Bias voltage
600 W	CH_4, H_2	CH_4 : 2.5 sccm, H_2 : 57.5 sccm	950°C	85 Torr	5 min	–350 V

3. Results and Discussion

After 5 min Ni catalyst deposition on a Si substrate, we observed the surface morphology of the substrate. Figure 1a shows the FESEM images of the Ni catalyst layer-deposited substrate surface. The inset of Fig. 1a shows the magnified FESEM image at the specific area of Fig. 1a. We could observe the smooth plane surface (Fig. 1a) with grain-like morphology (the inset of Fig. 1a). The existence of nickel was found as a result of detecting nickel using electron probe micro analysis (EPMA). After cleaning the substrate with hydrogen plasma for 10 minutes in the reaction chamber, we found a development of a grain-like morphology as shown in Fig. 1b. Previously, this kind of grain-like morphology was reported to be transformed into the small grains during the initial carbon nanofilaments plasma reaction [9]. So, we deduced that the nickel layer seemed to be transformed into the small grains during the carbon nanofilaments formation reaction.

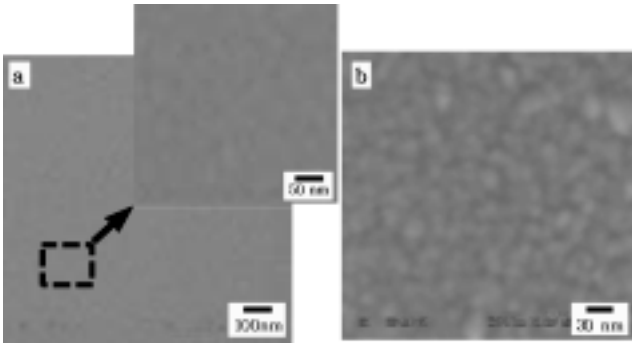

Fig. 1. (a) FESEM image of the Ni catalyst layer-deposited substrate surface. The inset of Fig. 1a shows the magnified FESEM image at the specific area of Fig. 1a. (b) FESEM image of the Ni catalyst layer-deposited substrate surface after cleaning the substrate by the hydrogen plasma for 10 minutes.

After 5 min $CH_4 + H_2$ plasma reaction under the –350 V bias voltage condition (see Table 1 for the detailed experimental condition), we investigated the surface FESEM images of the substrate. Figure 2 shows the vertical growth of the carbon nanofilaments on the substrate surface. The magnified image clearly shows the bundles formation of these carbon nanofilaments (see Fig. 2a). As shown in Fig. 2a, these bundles were composed of the individual carbon nanofilaments.

Figure 3 shows the surface image of the substrate after the carbon nanofilaments formation reaction without applied bias voltage condition. We couldn't observe the vertical growth of the carbon nanofilaments bundles. Based on these results, we suggest that the negative bias voltage application during the plasma reaction seemed to play a significant role for the vertical growth of the carbon nanofilaments formation, as the previous report [10].

To identify whether these bundles are carbon nanotubes or carbon nanofibers, we carried out a TEM study. Figures 4a and b show the detailed structure of the

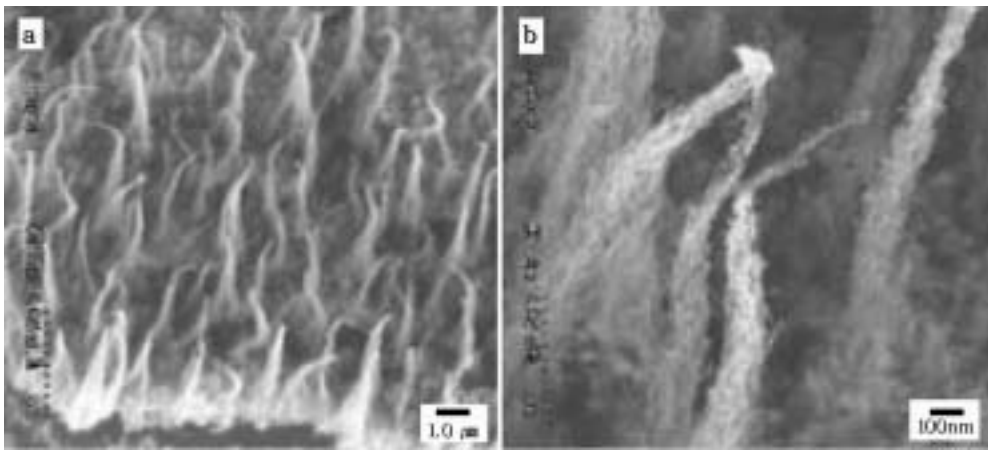

Fig. 2. (a) FESEM image of the vertical growth of the carbon nanofilaments on the substrate surface. (b) High magnified FESEM images of Fig. 2a.

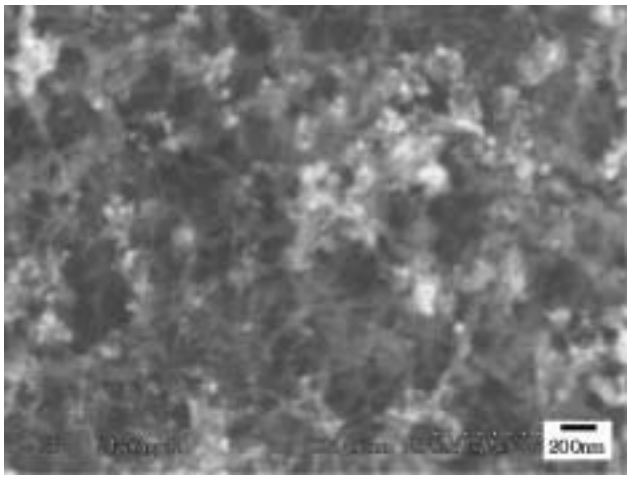

Fig. 3. FESEM image of the substrate surface after the carbon nanofilaments bundles formation reaction without the applied bias voltage.

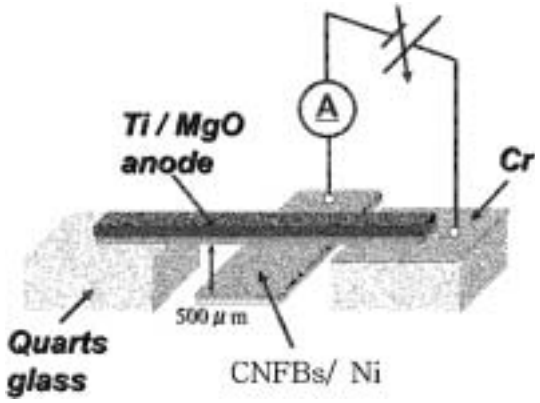

Fig. 5. The schematic diagram of the field emission measurement system.

carbon nanofilaments. From the well-developed stacking lattices across the principal axis of the filaments and the filled image at the inside of the filaments, we confirmed that these filaments were carbon nanofibers. The diamenters of the carbon nanofibers in this work were measured in the range of between 30 and 100 nm.

Figure 5 shows the schematic diagram of the field emission measurement system. The vertically well-aligned CNFBs were separated from titanium/MgO anode using a quartz spacer. We measured the variation of the anode current as a function of anode to cathode voltages as shown in Fig. 6. Turn-on voltage of the field emission current was measured around 0.8 V/μm. This value is one of the lowest values among the reported turn-on voltage using carbon nanotubes or nanofibers [3]. The geometry of CNFBs seems to be the cause for the lowest turn-on voltage value. Namely, the circular cone shape of CNFBs might have an advantage for the electron emission, as a straight line, from the tip area of CNF to the anode of Ti/MgO (see Fig 5). We defined J_{max} as the maximal current obtained without the destruction of the emitter. As shown in Fig. 6, J_{max} was measured around 0.1 A/cm^2 at 1.0 V/μm voltage. These values indicate that CNFBs is the promising material for the field emitters.

Figure 7 shows the corresponding Fowler-Nordheim plot for Fig. 6. The straight line in Fig. 7 confirms that the emission current principally comes from field emission characteristics.

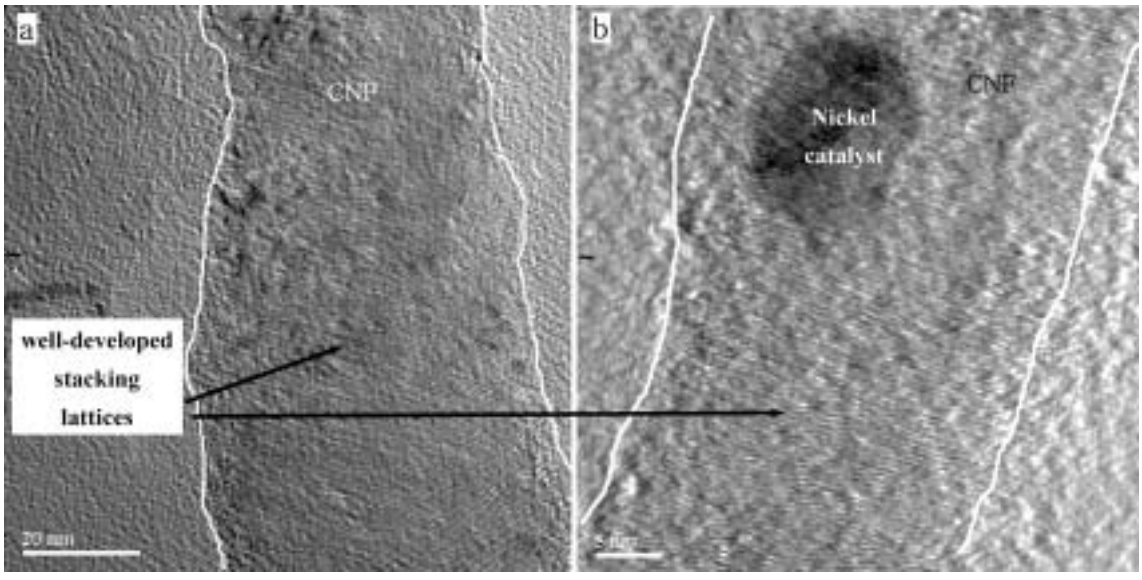

Fig. 4. TEM image showing the morphology of carbon nanofibers and the detailed TEM images indicating the stacking nanostructure (a) at the middle position of carbon nanofiber and (b) at the end position of carbon nanofiber with the nickel catalyst grain.

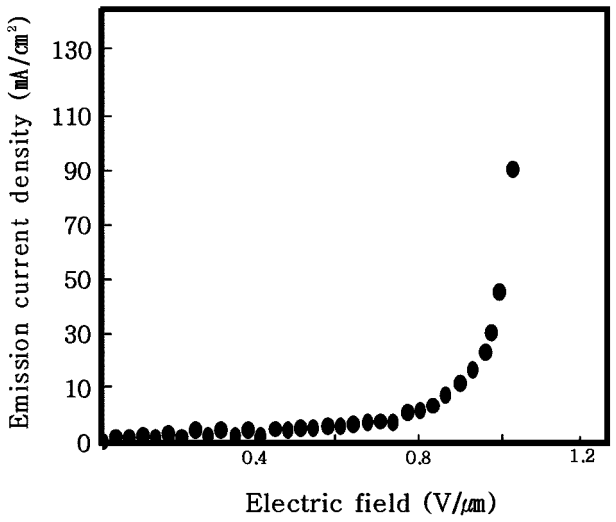

Fig. 6. The measured field emission current as a function of anode to cathode voltage.

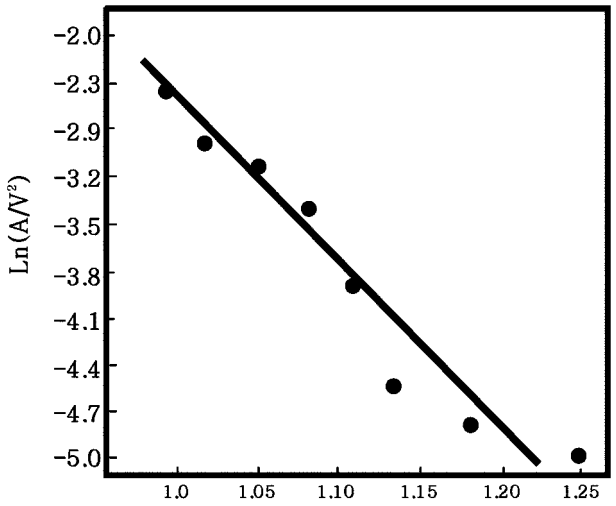

Fig. 7. Fowler-Nordheim plot for Fig. 6.

4. Conclusions

Carbon nanofiber bundles were vertically grown on a silicon substrate using negative bias voltage-applied microwave plasma-enhanced chemical vapor deposition. The bundles were composed of individual carbon nanofibers having less than 100 nm diameters. And, individual carbon nanofiber incorporates Ni at the top position of the nanofiber. The carbon nanfiber bundles show a 0.8 V/μm for turn-on voltage of field emission and around 0.1 A/cm^2 for the maximal field emission current density at 1.0 V/μm bias voltage.

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