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단 신

수직으로 배향된 탄소 나노 튜브 다발의 형성

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Formation of Vertically Well-Aligned Carbon Nanotubes Bundles

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For the practical application of carbon nanotubes to electron emitter, especially for field emission displays (FEDs), the achievement of vertically well-aligned carbon nanotubes is preferential.[1-4] Due to the vertical stability of a geometrical dimension, multi-wall, instead of single-wall, could give the facility for the formation of vertically well-aligned carbon nanotubes. Consequently, multi-walled carbon nanotubes would be regarded as the promising candidates for the nanotubes field emitter in FED.[1] However, even in multi-walled case, the alignment of carbon nanotubes as a vertical-type directly onto the substrate surface would be a difficult barrier to overcome.

To practically achieve the vertical alignment of carbon nanotubes onto the substrate surface, the carbon nanotubes should be produced and simultaneously vertically aligned onto the substrate surface. The manipulation of as-formed carbon nanotubes as a vertical-type onto the substrate surface might not be a good choice for the practical application, because it needs an accurate skillful technique. Recently, the plasma technique has been chosen as an adequate method to provide a simultaneous reaction process for carbon nanotubes formation with vertical alignment.[5] In detail, the application of the negative bias voltage during the plasma reaction has been reported to align carbon nanotubes as a vertical direction to the substrate surface.[6]

This work presents one of the possible methods to achieve a well-alignment of carbon nanotubes as a vertical direction to the substrate. We applied negative high bias voltage during microwave plasma enhanced chemical vapor deposition reaction. Finally, we achieved the vertically well-aligned carbon nanotubes bundles directly onto the substrate surface. Based on these results, we discussed the causes for carbon nanotubes formation according to the reaction process.

EXPERIMENTAL SECTION

We deposited carbon nanotubes films on the nickel coated 1.0×1.0 mm^2 Si substrate in a horizontal-type MPECVD system. Nickel coating could be achieved by radio frequency (RF) sputtering system. In RF-sputtering experiment, we used Ar gas with 30 mTorr total pressure under 500 W RF power condition. The thickness of nickel on Si substrate is about 100 nm after 10 min sputtering.

Before the carbon nanotubes deposition reaction, we cleaned the substrate with H_2 plasma for a few minutes. CH_4 and H_2 were used as source gases. To elucidate the effect of the bias voltage on the forma-

Table 1. Experimental conditions of carbon nanotubes formation

Exp. Conditions / Kinds of samples	Microwave power	Source gases	Flow rates of source gases	Substrate Temp.	Total Pressure	Reaction time
Sample without bias voltage	500 W	CH_4, H_2	CH_4: 30 sccm H_2: 170 sccm	700 °C	10 Torr	10 min
Sample with bias voltage (-400 V)	600 W	CH_4, H_2	CH_4: 2.5 sccm H_2: 57.5 sccm	900 °C	80 Torr	5 min

tion of the vertical alignment of carbon nanotubes, we deposited carbon nanotubes via two different ways, namely, either the presence of bias voltage or without bias voltage. *Table* 1 shows the experimental conditions of carbon nanotubes formation according to the different reaction process.

The detailed morphologies of carbon nanotubes were investigated by using field emission scanning electron microscopy (FESEM).

RESULTS AND DISCUSSION

After 10 min deposition reaction, we first investigated the surface images of as-deposited carbon nanotubes films onto the substrate. *Fig*. 1 shows SEM image of carbon nanotubes on nickel coated Si substrate without applied bias voltage. The cracked image in *Fig*. 1 would be due to the damaged nickel layer by the plasma. As previous report, the cracked surface of nickel layer is indispensable to initiate the growth of carbon nanotubes.[5] The injection of carbon species into the crack of nickel layer could

Fig. 1. SEM image of carbon nanotubes on nickel coated Si substrate without applied bias voltage.

initiate the formation of the carbon nanotubes on Si substrate by the catalytic effect of nickel. And then, carbon nanotubes could grow on the Si substrate surface with the nickel capped on the end position of carbon nanotubes.[7]

In this case, we could only observe the formation of the relatively large size (diameter = ~100 nm) carbon nanotubes on the substrate. The large size diameter indicates that it must be a multi-walled nanotubes. Unfortunately, we could not obtain the vertical-type carbon nanotubes alignment onto the substrate surface under this condition. On the other hand, carbon nanotubes places horizontally. The number density of carbon nanotubes under this condition is not so high.

We consider that the cause for the large size diameter and the low density of carbon nanotubes on the substrate may be attributed to the amount of nickel. It was reported that the diameter of carbon nanotubes increased with increase the thickness of the metal layer on the substrate.[1,8] After deposition reaction, we could obviously observe a thick nickel layer with cracks. These results obviously reveal that a large amount of nickel would be existed during carbon nanotubes formation reaction. So, a relatively large size nickel cluster, instead of small size nickel clusters, can be formed and it tends to participate in the formation of carbon nanotubes. Consequently, a large size diameter of carbon nanotubes can be produced. Furthermore, due to the lack of optimal size nickel clusters for carbon nanotubes formation, the number density of carbon nanotubes on the substrate would be a low.

Fig. 2 shows SEM image of carbon nanotubes on nickel coated Si substrate under the condition of the presence of applied bias voltage. The high-magnified image was also shown in the inset of *Fig*. 2. In

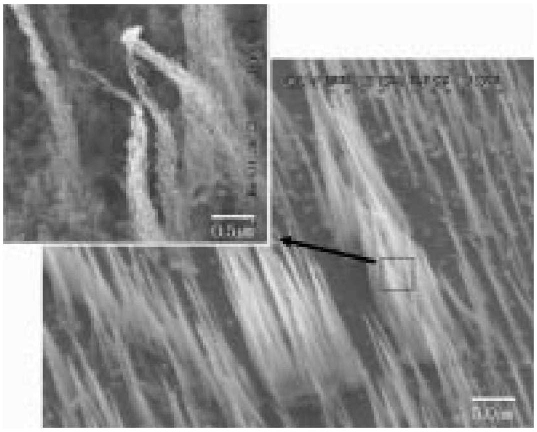

Fig. 2. SEM image of carbon nanotubes on nickel coated Si substrate with applied negative bias voltage (−400 V). The high-magnified image was also shown in the inset.

this case, we applied negative high bias voltage (−400 V) during carbon nanotubes formation reaction. Detailed experimental conditions were shown in *Table* 1. As shown in *Fig*. 2, we could readily observe the high density of carbon nanotubes formation. Noticeably, carbon nanotubes unites in groups and forms bundles. Furthermore, these bundles well align as a vertical direction to the substrate surface. Actually, these bundles were composed numerous carbon nanotubes as shown in the inset of *Fig*. 2. Although the exact mechanism of carbon nanotubes bundles formation cannot be well identified, we are sure that these kinds of morphologies would be suitable for the electron emitter application. For example, the cone-type shape like this one seems to be suitable for the fabrication of electron emitter gun. In addition, this shape can be applicable to use as a tip of scanning probe microscope,

The number density of carbon nanotubes is much more enhanced than that under no bias voltage condition. On the other hand, the diameter (~ 20 nm) of carbon nanotubes is reduced, as compared with that under no bias voltage condition. In addition, as shown in *Fig*. 2, we did not observe any cracked surface image like that of *Fig*. 1.

The causes for these results may be attributed to the effect of negative high bias voltage. Negative high bias voltage application to the substrate can induce high plasma density on the surface of the substrate. So, during plasma reaction, the surface temperature of the substrate might be high enough for melting nickel layer. And then, the melted nickel would be etched away by the plasma or it can participate as a catalyst to form carbon nanotubes. No image concerning the cracked surface of *Fig*. 2 confirms that the amount of nickel would be decreased during nanotubes formation. Indeed, it was reported that a few amounts of nickel nanograins on the substrate was sufficient to form the high density of carbon nanotubes.[5] Therefore, due to the decrease of nickel density and the high surface temperature of the substrate, relatively small size nickel clusters can be readily formed. Consequently, the possibility for the formation of a relatively small size (~ 20 nm) carbon nanotubes during plasma reaction can be increased. Furthermore, the facility for forming small size nickel cluster would be enhanced by the application of negative high bias voltage. Therefore, the number density of carbon nanotubes would be enhanced, Vertically well alignment and the formation of carbon nanotubes bundles were also considered to be due to negative high bias voltage application during carbon nanotubes formation.

CONCLUSIONS

Without bias application, we could merely observe the relative large size (~100 nm) carbon nanotubes onto the substrate surface. They merely place onto the substrate surface as a horizontal-type. On the other hand, vertically well-aligned carbon nanotubes bundles on nickel coated Si substrate could be obtained in MPECVD system by the application of the high negative bias voltage. Negative bias voltage application was considered to enhance the number density of carbon nanotubes with the reduction of the diameter size. In addition, vertically well alignment and the formation of carbon nanotubes bundles were also considered to be due to negative high bias voltage application during carbon nanotubes formation.

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