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탄소 나노 튜브의 수직 배향에 대한 바이어스 인가 전압의 효과

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Effect of the Applied Bias Voltage on the Formation of Vertically Well-Aligned Carbon Nanotubes

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Abstract Carbon nanotubes were formed on silicon substrate using microwave plasma-enhanced chemical vapor deposition method. The possibility of carbon nanotubes formation was related to the thickness of nickel catalyst. The growth behavior of carbon nanotubes under the identical thickness of nickel catalyst was strongly dependent on the magnitude of the applied bias voltage. High negative bias voltage (- 400 V) gave the vertically well-aligned carbon nanotubes. The vertically well-aligned carbon nanotubes have the multi-walled structure with nickel catalyst at the end position of the nanotubes.

Key words carbon nanotubes, microwave plasma, vertical alignment, bias effect, nickel catalyst.

1. Introduction

Due to the fascinating shape suitable for connecting with nanometer diameters and micrometer lengths and the high electron emitting properties applicable to the electron field emitter, carbon nanotubes (CNTs) have been regarded as the promising material for the nanowiring of the nanoelectronic device[1,2] and the field emission display.[3-5]

For the nanowiring application, the electrical properties of CNTs should show the metallic characteristics. Unfortunately, the electrical properties of CNTs were known to be varied as metallic, insulating, or semiconductor characteristics according to their diameter, wrapping angle, or post-growth treatment.[6,7] Therefore the formation of CNTs having entirely metallic characteristics is preferential for the nanowiring application. However, the formation of CNTs having completely single electrical properties is too difficult to achieve. From the practical point of views, therefore, the nanowiring application of CNTs has been excluded.

On the other hand, the electron emitter, especially for the field emission display (FED), has been noted for the practical application of CNTs. Because the vertical stability of CNTs is required For FED application, multi-wall type CNTs instead of single-wall type, are regarded as the optimal geometrical dimension.[8] The manipulation of as-formed CNTs as a vertical-type onto the substrate surface might not be a good choice, because it needs a time-consuming unpractical manipulation technique. Therefore the CNTs should be formed and simultaneously vertical-aligned onto the substrate surface. Recently, the plasma technique has been chosen as an adequate method to provide a simultaneous reaction process for CNTs formation with vertical alignment.[9] The application of the bias voltage during the plasma reaction was also considered to be one of the choices for the enhancement of the vertical alignment of CNTs.[10]

This work presents the applied bias voltage effect on the formation of vertically well-aligned CNTs. In this work, we increased the bias voltage up to - 400 V. This value is about two times higher than the previously reported ones.[10] The possibility of CNTs formation was investigated in connection with the thickness of nickel catalyst.

2. Experimental Section

We deposited CNTs films on the nickel layer-coated 1.0 $\times$ 1.0 mm^2 Si substrate in a horizontal-type microwave plasma enhanced chemical vapor deposition (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

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under 500 W RF power condition. We obtained the various thicknesses, such as 100, 200 and 300 nm, of nickel on Si substrate after 10, 20 and 30 min sputtering reaction.

Before the CNTs 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 formation of the vertical alignment of CNTs, we deposited CNTs via two different ways, namely, either the presence of bias voltage or without bias voltage. Bias voltage value was varied in the range of - 200 V~- 400 V. The detailed experimental conditions of the CNTs formation under MPECVD were shown in Table 1.

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

3. Results and Discussion

After CNTs deposition using - 200 V bias voltage, we investigated the surface images of the substrate as a function of the thickness of the nickel catalyst. Figs. 1a~c show FESEM images of the 100 (Fig. 1a), 200 (Fig. 1b) or 300 nm (Fig. 1c) nickel layer-coated Si substrates which were carried out the CNTs deposition reaction under the experimental condition I (see Table 1). At 100 nm nickel layer, we could find the formation of CNTs on the substrate surface. However, we could not observe any CNTs formation at 200 or 300 nm nickel layer (see Figs. 1b and c). This result reveals that the CNTs formation favors thin nickel layer. CNTs formation was known to be initiated by the injection of carbon species into the cracks of nickel layer.[11,12] Consequently, nickel layer should be thin in order to readily crack its layer and initiate the growth of CNTs. At thick layer, we could merely observe the peculiar morphologies on the surface of the substrate as shown in Figs. 1b and c.

The presence of CNT in this work was confirmed using TEM (see Figs. 2a and b). As shown in Fig. 2b, the pattern of the nanostructure at TEM image clearly confirms the formation of CNT in this work.

Fig. 3 shows the high-magnified FESEM images of Fig. 1a. In this image, we could find the nickel on the end position of CNTs. It indicates that the CNTs growth would follow the tip growth mode,[12] instead of base growth mode. The average diameters of CNTs were measured in the range of 10 to 50 nm, revealing the multi-wall type CNTs.

To elucidate the effect of the applied bias voltage, we investigated the surface morphologies of the 100 nm nickel layer-coated substrate which had been carried out the deposition reaction without applied bias voltage under the experimental condition I. Indeed, we couldn't obtain the

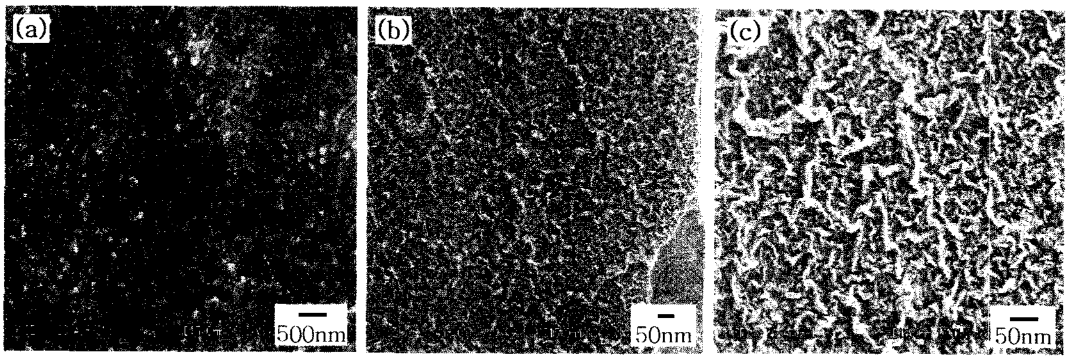

Fig. 1. FESEM images of the (a) 100, (b) 200 and (c) 300 nm nickel layer-coated Si substrates which were carried out the CNTs deposition reaction with -200 V applied bias voltage under the experimental condition I.

Table 1. Experimental conditions of carbon nanotubes formation.

	Microwave power	Source gases	Flow rates of source gases	Sub. Temp.	Total Pressure	Reaction time	Bias Voltage (V)
Experimental condition I	600 W	CH_4, H_2	CH_4: 2.5 sccm H_2: 57.5 sccm	900 °C	80 Torr	5 min	0, -200 -300, -400
Experimental condition II	500 W	CH_4, H_2	CH_4: 30 sccm H_2: 170 sccm	700 °C	10 Torr	10 min	0

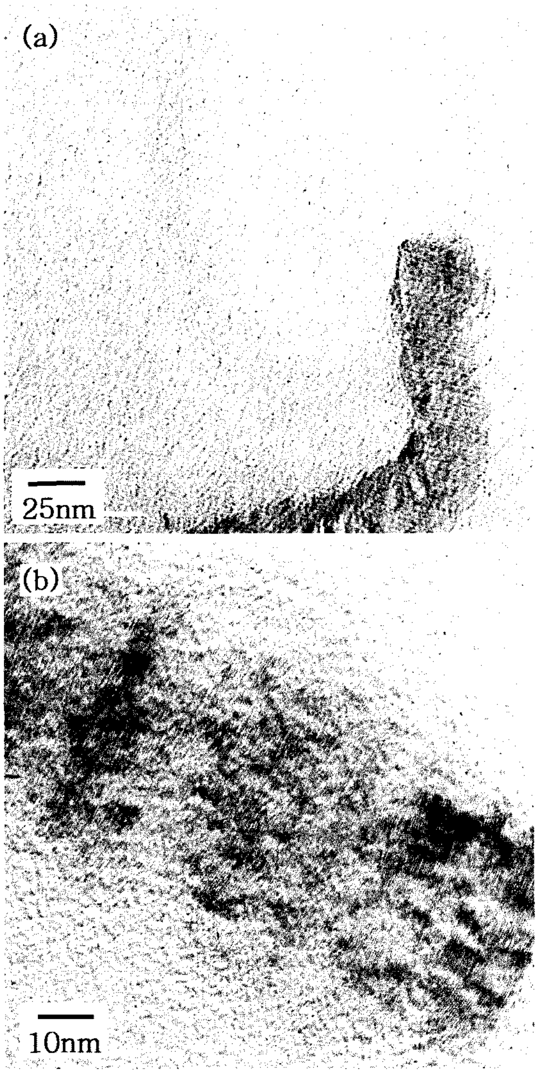

Fig. 2. TEM images for (a) one of CNTs morphologies and (b) CNTs nanostructure.

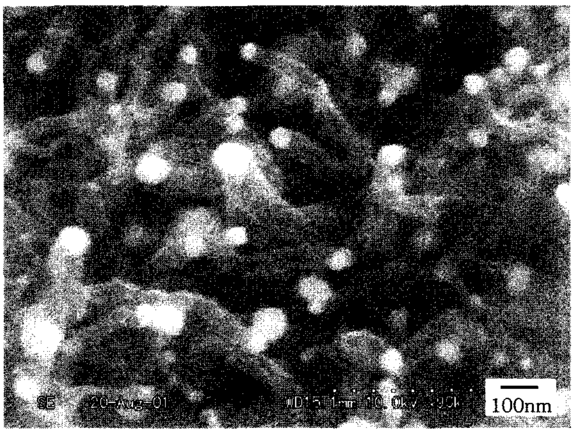

Fig. 3. The high-magnified FESEM images of Fig. 1a.

CNTs formation without the bias voltage application (see Fig. 4a). However, by increasing the CH_4 flow rate and decreasing microwave power (see the experimental condition II of Table 1), we could observe the CNTs formation as shown in Fig. 4c. In this case, we could only observe the formation of the relatively large size (diameter = ~100 nm) CNTs on the substrate. The number density of CNTs at this condition is low, compared with those of with applied bias voltages (compare Fig. 4 with 5). The large size diameter indicates that it must be a multi-wall type CNTs. In this case, we could not obtain the vertical-type CNTs alignment onto the substrate surface. On the other hand, most of CNTs horizontally places to the substrate. It was reported that the diameter of CNTs increased with increase the thickness of the metal layer on the substrate.[8,13] After deposition reaction, we could obviously observe nickel layer with cracks as shown in Fig. 4d. It obviously indicates that a large amount of nickel would be still existed during CNTs formation reaction. So, a relatively large size nickel clusters tend to be formed. And then, they can participate in the formation of large-size multi-wall type CNTs. We consider that the cause for the relatively large size diameter of CNTs on the substrate may be attributed to the amount of nickel.

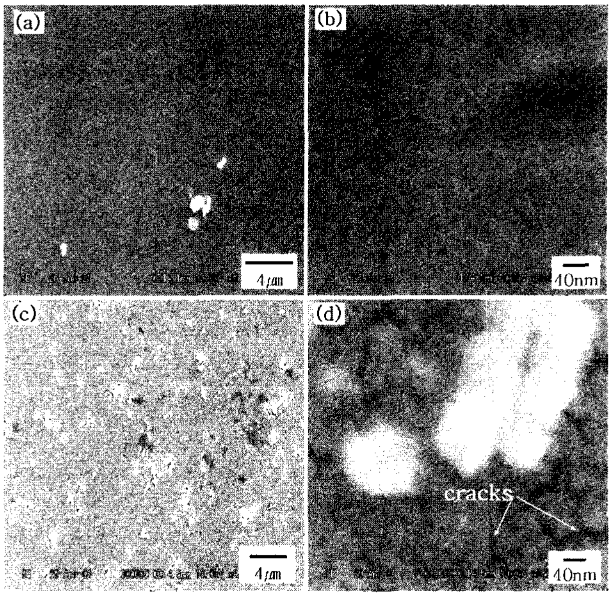

Fig. 4. (a) FESEM image for the sample without the applied bias voltage under the experimental condition I and (b) the high magnified image of Fig. 4a. (c) FESEM image for the sample without the applied bias voltage under the experimental condition II and (d) the high magnified image of Fig. 4c.

Figs. 5a~c shows the surface morphologies of the 100 nm nickel layer-coated substrate which had been carried out the deposition reaction with - 200 (Fig. 5a), - 300 (Fig. 5b) or - 400 (Fig. 5c) applied bias voltages. As shown in Fig. 5, we could readily observe the high density of CNTs formation. Noticeably, the vertical alignments of CNTs to the substrate were enhanced with increase the applied bias voltages from - 200 to - 400 V. At - 200 V, we could find

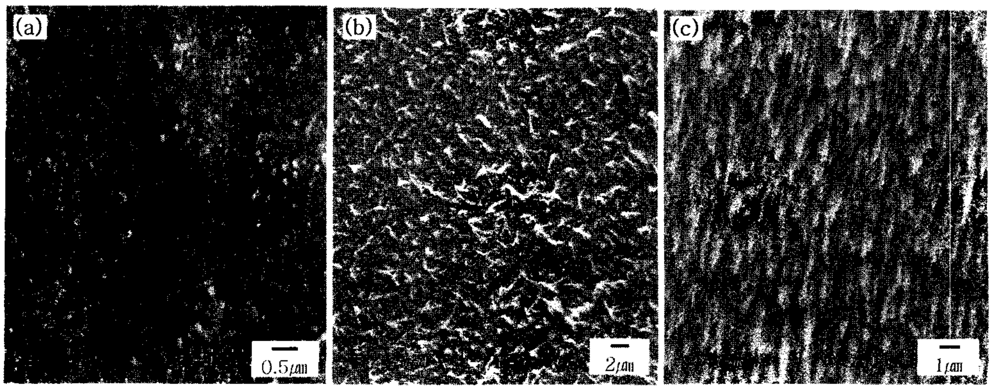

Fig. 5. The surface morphologies of the 100 nm nickel layer-coated substrate which were carried out the deposition reaction with (a) -200, (b) -300 or (c) -400 applied bias voltages under the experimental condition I.

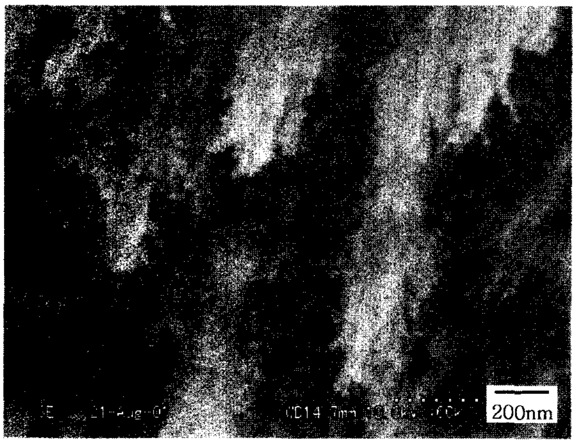

Fig. 6. The high-magnified image of Fig. 5c.

merely vertical growth of CNTs without well alignment as shown in Fig. 5a. At - 300 V, however, we can see the initiation of the vertically well-aligned growth of CNTs (see Fig. 5b). At highest applied bias voltage (- 400 V) in this work, the CNTs unite in groups and forms bundles. Furthermore, these bundles well aligned as a vertical direction to the substrate surface (see Fig. 5c).

Actually, these bundles were composed with numerous CNTs, as shown in Fig. 6. These results clearly reveal that the increase of the applied bias voltage would enhance the alignment of the vertical growth of CNTs. Although the exact mechanism of the vertical alignment of CNTs bundles by increasing the applied bias voltage can't be well identified, we suggest that the tip growth mode of CNTs seems to be associated with the alignment at high applied bias voltage. The vertical alignment of the CNTs bundles might 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.

4. Conclusions

The thick (200 and 300 nm) nickel catalyst layer gave no CNTs formation under - 200 V biased microwave plasma reaction. On the other hand 100 nm nickel catalyst layer produced the vertically grown CNTs formation on the substrate. The vertical alignment was enhanced by increasing the bias voltages from - 200 to - 400 V. Without applied bias voltage, a few number of multi-wall type CNTs horizontally placed to the substrate. Consequently, the formation of the vertically well-aligned CNTs seems to favor the high applied bias voltage during the microwave plasma reaction.

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