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Different Growth Position of Iridium-catalyzed Carbon Nanofibers on the Substrate According to the Value of the Applied Bias Voltage

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Abstract Vertical growth of iridium-catalyzed carbon nanofibers could be selectively grown on the MgO substrate using microwave plasma-enhanced chemical vapor deposition method. Growth positions of the iridium-catalyzed carbon nanofibers on the MgO substrate could be manipulated according to the applied bias voltage. At –150 V, the carbon nanofibers growth was confined only at the corner area of the substrate. Based on these results, we discussed the cause for the confinement of the vertically grown carbon nanofibers on the specific area of the MgO substrate as a function of the applied bias voltage.

Key words carbon nanofibers, iridium catalyst, confinement of the carbon nanofibers, microwave plasma, applied bias voltage.

1. Introduction

Due to their unique geometries, carbon nanofilaments, called carbon nanotubes if hollow and carbon nanofibers if filled, have regarded as the promising material candidate for the elements of nano-electronic devices, especially for the interconnection lines and the electron emitters.[1-4]

For an application of carbon nanofilaments to the interconnection lines, lateral growth is required because this direction makes connection plausible.[3,4] To apply carbon nanofilaments to the electron emitter, however, an achievement of a vertical alignment are preferential.[5,6] For aligning the carbon nanofilaments, Jang et al. reported that multi-walled carbon nanotubes (MWCNTs) were laterally aligned by an electric field.[7] They selectively grew MWCNTs between lateral sides of the catalytic metals on predefined electrodes. Then, they found that the electric field direction at the vicinity of catalyst and nanotubes-substrates interactions were principal factor in aligning MWCNTs laterally. Zhu et al. reported the different growth direction of carbon nanotubes on the substrate according to the gravity factor.[8]

In addition, the patterning of the carbon nanofilaments would be required to enlarge the application area of the aligned carbon nanofilaments to various shapes. For patterning the carbon nanofilaments, the selective deposition technique using the metal catalyst has been reported.[9-11] The enhancement of the vertical stability would be also required for the carbon nanofilaments formation especially on the specific area such as convex and concave.[12]

Despite these efforts, the manipulation of the carbon nanofilaments growth positions are still required to maximize their applicable purpose. In this work, we observed the different growth positions of the carbon nanofibers on the substrate according to the different applied bias voltage. Finally, we could achieve the confinement of vertically grown carbon nanofibers dominantly at the protruded area of the substrate corner.

2. Experimental Section

Iridium coated $1.0 \times 1.0\ cm^2$ MgO substrate was prepared by iridium coating on a MgO substrate using a radio frequency (RF) sputtering. In RF-sputtering experiment, we used Ar gas with 30 mTorr total pressure under 500 W RF power condition. Detailed experimental condition for the iridium catalyst coating was shown in Table 1.

Before the carbon nanofilaments deposition reaction, we pre-cleaned the substrate with H_2 plasma for a few minutes. For carbon nanofilaments deposition, 5% CH_4 and 95% H_2 were introduced to the deposition system after pre-cleaning the substrate. Negative bias voltage applied microwave plasma-enhanced chemical vapor deposition (MPECVD) system was employed for the formation of the carbon nanofilaments as shown in Fig. 1. Table 2 shows

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Table 1. Experimental condition for the iridium catalyst layer deposition

Radio Frequency power	Injection gas	Flow rate of injection gas	Substrate Temperature	Total Pressure	Reaction time
20 W	Ar	10 sccm	25°C	30 mTorr	5 min

Table 2. Experimental condition of carbon nanofibers formation

Microwave power	Source gases	Flow rates of source gases	Sub. Temp.	Total Pressure	Reaction time	Bias Voltage (V)
600 W	CH_4, H_2	CH_4: 2.5 sccm H_2: 47.5 sccm	900°C	80 Torr	5 min	-50~-350 V

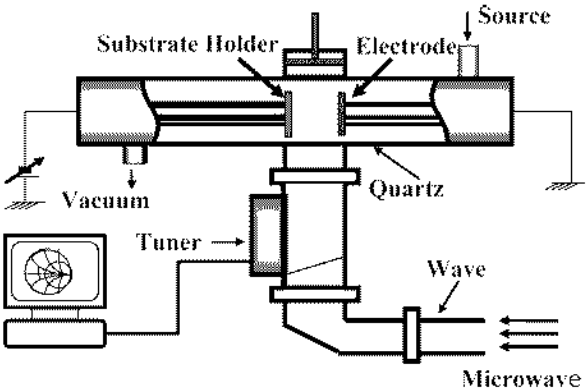

Fig. 1. Systematic diagram of a horizontal-type microwave plasma-enhanced chemical vapor deposition (MPECVD) system.

the detailed experimental condition for carbon nanofilaments deposition.

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

3. Results and Discussion

After 5 min carbon nanofilaments deposition as a function of the applied bias voltage, we investigated the surface morphology of the substrate. As shown in Fig. 2, the formation of the carbon nanofilaments couldn't be observed at any place of the substrate under -50 V bias voltage application condition.

Under -150 V bias voltage condition, however, we could observe the confinement of the carbon nanofilaments growth within a protruded area of the substrate corner (see Fig. 3). Indeed, any carbon nanofilaments couldn't be observed at any other area except the protruded area of the substrate corner. To identify whether these carbon nanofilaments are carbon nanotubes or carbon nanofibers,

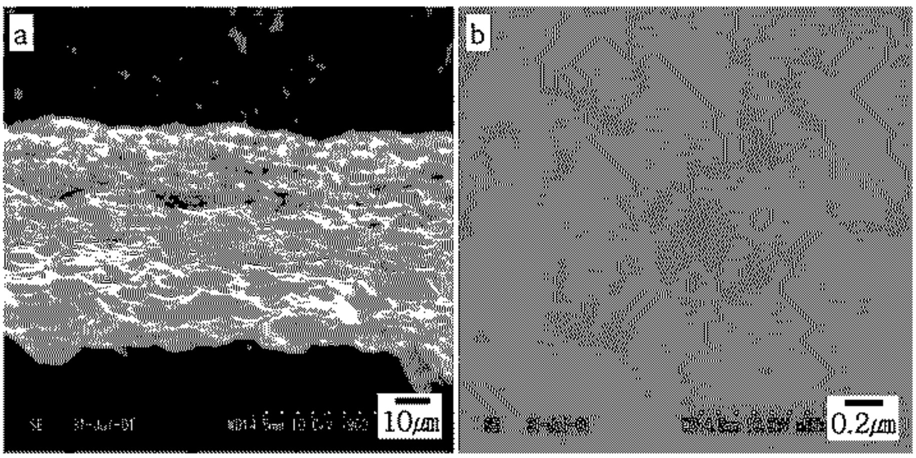

Fig. 2. FESEM images of the iridium-catalyzed carbon nanofilaments on MgO substrate under -50 V bias voltage application condition: (a) side area and (b) plane surface area of the substrate.

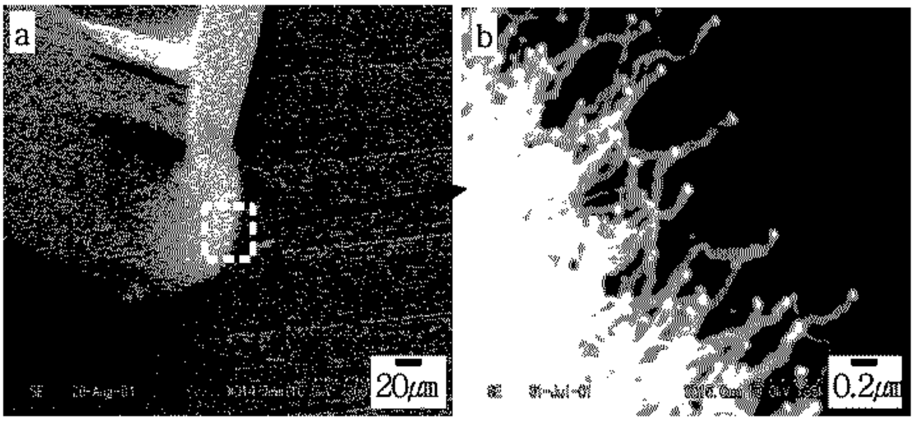

Fig. 3. FESEM images showing (a) the deposition of the iridium-catalyzed carbon nanofibers on the protruded area of the MgO substrate edge under -150 V bias voltage application condition and (b) the magnified image of Fig. 3a.

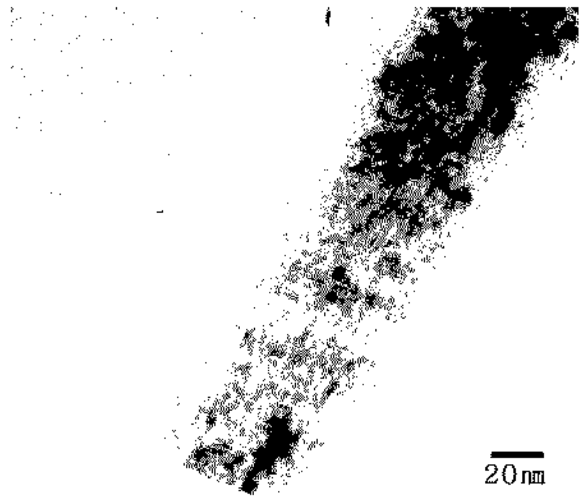

Fig. 4. TEM image of the carbon nanofiber.

we carried out TEM study. Fig. 4 shows the detailed structure of the carbon nanofilaments. From the stacking lattices, the protrusions of the lattices to the outside of the filaments and the filled image at the inside of the filaments, we confirmed that these filaments were carbon nanofibers. The diameters of the carbon nanofibers in this work were measured in the range of between 20 and 70 nm.

With increasing the bias voltage up to -250 V, we could observe the confinement of the deposition area of the carbon nanofibers within the limited area of the substrate edge as shown in Fig. 5.

At-350 V, the maximum bias voltage application condition in this work, the vertical growth of the carbon nanofibers could be observed at the whole area of the substrate side (see Fig. 6).

From the combined results of Figs. 3~6, it was considered that the carbon nanofibers could not be formed on the smooth top plane area of the substrate, irrespective of the applied bias voltage value. However, on the substrate side, edge and corner areas, the growth of the carbon nanofibers could be well observed above the -150 V applied

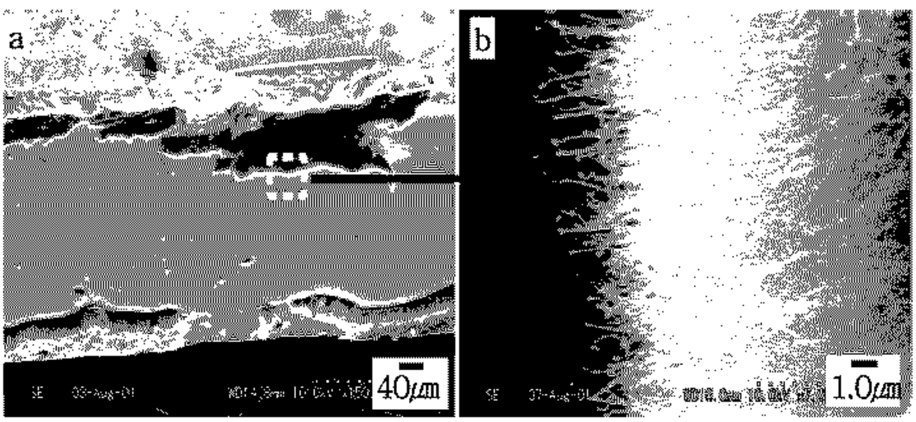

Fig. 5. FESEM images showing (a) the deposition of the iridium-catalyzed carbon nanofibers on the limited area of the MgO substrate edge under -250 V bias voltage application condition and (b) the magnified image of Fig. 5a.

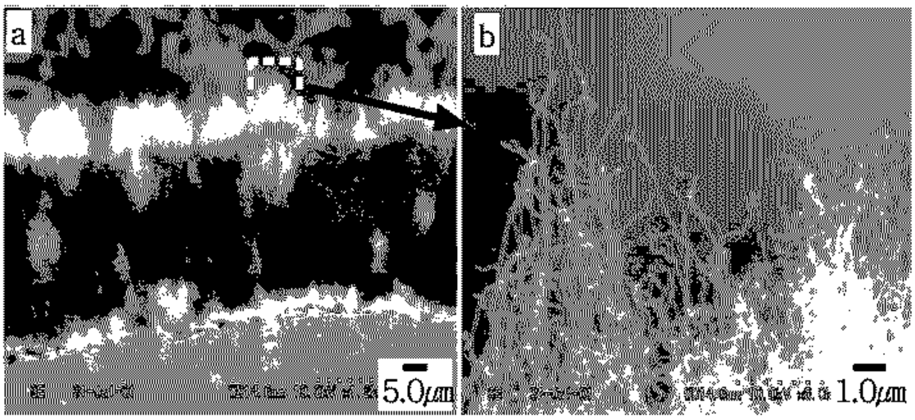

Fig. 6. FESEM images showing (a) the deposition of the iridium-catalyzed carbon nanofibers on the whole area of the MgO substrate side under -350 V bias voltage application condition and (b) the magnified image of Fig. 6a.

bias voltage. Furthermore, it seems that the carbon nanofibers deposition area is becoming more and more confining, from side into corner areas of the substrate, with decreasing the applied bias voltage from -350 V to -150 V. Compared with the smooth top plane area of the substrate surface, the edge or corner of the substrate might have the higher electric field. Because the local electric fields are different according to the surface roughness and/or shape, although the macro applied voltages from the out side may similar over the whole substrate. Thus we suggest that the growth of the iridium-catalyzed carbon nanofibers favors the higher electric field at the edge or corner areas of the substrate, instead of the smooth top plane surface morphologies. Based on these results, it is suggested that the iridium catalyst could give rise to the selectivity for the growth of the carbon nanofibers according to the surface morphologies.

The cause for the selectivity of the iridium-catalyzed carbon nanofilaments was understood as follows. The growth of the carbon nanofilaments was known to be initiated by the formation of the nano-sized metal catalyst grain.[12] Choi et al. reported that the formation of carbon-metal eutectic alloy enhanced the diffusion of carbon in the metal alloy. And then carbon aggregated and acted as a nucleation seed for the carbon nanofilaments growth.[13] Therefore the formation of catalytic metal-carbon eutectic characteristics is essential for the carbon nanofilaments formation. In this viewpoint, Iridium would be acceptable as the metal catalyst for the carbon nanofilamets formation because it was known to form iridium-carbon compound.[14,15] Furthermore, iridium was known to have the refractory characteristics.[16] Compared with the conventional iron-family group catalyst (Fe, Co, Ni) for the growth of the carbon nanofilaments, iridium-carbon eutectic characteristics might require the higher substrate temperature to form the carbon aggregation as a nucleation seed for the carbon nanofilaments growth.

Regarding the induced bias voltage, the rough edge or corner area, compared with the smooth top plane area, can induce a higher bias voltage even under the same applied bias voltage condition. Higher induced bias voltage at the edge or corner area can invoke the higher induced local temperature.

In consequence, the formation of the iridium-catalyzed carbon nanofibers would be dominantly formed at the edge or corner areas of the substrate due to the higher induced local temperature. With increasing the applied bias voltage value, the growth selectivity according to the surface morphologies was diminished because the side, edge or corner areas of the substrate might possess a sufficient applied bias voltage for the carbon nanofibers formation.

Therefore the growth position of the carbon nanofibers at the substrate seems to be controlled simply by varying the applied bias voltage during the deposition reaction.

4. Conclusions

The vertical growth of the iridium-catalyzed carbon nanofibers could be formed by MPECVD system. At -150 V, the carbon nanofibers were confined within the protruded area of the substrate corner. By increasing the applied bias voltage from -250 V to -350 V, the deposition position of the carbon nanofibers were varied from the limited area of the substrate edge to the whole area of the substrate side.

The higher temperature of the catalytic iridium-carbon eutectic characteristics, compared with the conventional iron-family group catalyst, to form the nucleation seed for the carbon nanofibers seems to be associated with the cause for the variation of the carbon nanofibers deposition position according to the applied bias voltage.

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