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# Bridge-type formation of iridium-catalyzed carbon nanofibers across the Gap on MgO substrate and their electrical properties

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Abstract We could achieve the bridge-type formation of the iridium-catalyzed carbon nanofibers across the gap on the MgO substrate using microwave plasma enhanced chemical vapor deposition method. On the plane surface area of the MgO substrate, the iridium-catalyzed carbon nanofibers were grown as a lateral direction to the substrate. The bridge-type formation and/or the lateral growth of the iridium-catalyzed carbon nanofibers were interconnected with each other. Finally, they could form an entangled network having the bridge-type formation of the carbon nanofibers across the gap on the substrate and the laterally-grown carbon nanofibers on the plane surface area of the substrate. The entangled network showed the semiconductor electrical characteristics.

Key words Carbon nanofibers, Iridium catalyst, Bridge-type formation, Interconnection network, Semiconductor characteristics, Microwave plasma

## 1. Introduction

Carbon nanofilaments (CNFs), called carbon nanotubes if hollow and carbon nanofibers if filled, have regarded as the promising material candidate for the elements of nanoelectronic devices, especially for the interconnection lines, due to their fascinating shape of the micrometer scale length and the nanometer scale diameter [1-3]. Among the CNFs, the electrical properties of carbon nanotubes have been known to be varied as metallic, insulating, or semiconductor characteristics according to their diameter, wrapping angle, or post-growth treatment [4, 5]. Therefore the control of the electrical properties of carbon nanotubes would be indispensable for the application in the practical electronic devices. On the other hand, for the carbon nanofibers, although not much studied, solely the semiconductor electrical characteristics were reported up to the present [6, 7]. In this respect, carbon nanofibers, instead of carbon nanotubes, might be regarded as the promising elements of nanoelectronic devices for practical application.

For an application of CNFs to interconnection lines, the alignment of CNFs growth as a lateral direction would be required because this direction makes connection plausible [3]. For aligning CNFs, Jang *et al.* [8] reported that multi-walled carbon nanotubes were laterally aligned by an electric field. Zhu *et al.* [9] reported the different growth direction of carbon nanotubes on substrates according to their gravity factor.

Previously, the feasibility for the bridge-type interconnection of the laterally grown carbon nanofilaments could be shown in the etched area of the substrate [10]. In this work, we intentionally make the gap on MgO substrate surface and confirm the solely bridge-type formation of carbon nanofibers across the gap on MgO substrate. The bridge-type interconnection lines would be essential for the achievement of three-dimensional interconnection lines. In this respect, the bridge-type interconnection lines would be the primary factor to achieve the nanoelectronic devices via the three-dimensional interconnection. In addition, we propose the simple mechanism for the growth mode of the bridge-type formation of carbon nanofibers across the gap on MgO substrate. A thin iridium layer was used to catalyze the growth of carbon nanofibers [11]. The iridium-catalyzed carbon nanofibers could form an entangled network of the self-assembled laterally-grown carbon nanofibers with bridge-type connections. The electrical characteristics of the entangled network were also studied by measuring the surface electrical resistivities and the scanning tunneling spectroscopy as the previous work [10].

## 2. Experimental Section

Iridium coated $1.0 \times 1.0\ \mathrm{cm}^2$ MgO substrate was pre-

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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 |

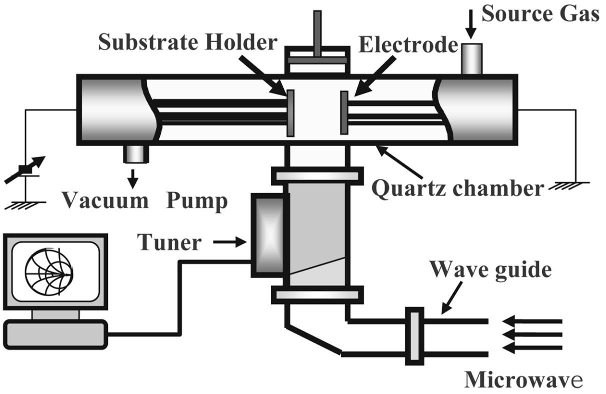

Fig. 1. Systematic diagram of a horizontal-type microwave plasma-enhanced chemical vapor deposition (MPECVD) system.

pared 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 20 W RF power condition. Detailed experimental conditions for the iridium catalyst coating were shown in Table 1.

For CNFs 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 CNFs as shown in Fig. 1. Table 2 shows the detailed experimental conditions for CNFs depositions.

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

The surface electrical conductivities of laterally-grown CNFs were measured as a function of the substrate temperature. The laterally-grown CNFs formed a self-assembled interconnection network. Thus, the electronic transport properties of the self-assembled lateral CNFs network could be readily investigated without the time-consuming alignment step for electrical contacts [12, 13]. For the electrical contact, gold-dot contacts were affixed at the corner on the surface of each sample using vacuum evaporator with mask. The diameter sizes of dots were approximately 1 mm. The change of surface electrical resistivities was measured as a function of surface temperature by the four-probe method. An I-V analysis revealed that these contacts displayed near-ohmic contact characteristics throughout all of the experiments.

A scanning tunneling spectroscopy (STS) measurement for the self-assembled lateral CNFs network was also carried out by scanning tunneling microscopy under atmospheric pressure condition.

## 3. Results and Discussion

The gap on the substrate seems to be generated by the application of higher negative bias voltage (about −350 V) and gas plasma during the CNFs deposition reaction. The higher negative bias voltage seems to manipulate the gas plasma (mainly hydrogen ion) discharge between the plasma and the substrate. By the gas plasma discharge reaction, the surface of the substrate might be etched away and then the gap could be created onto the substrate surface. Indeed, we could find the deep cracks of the substrate surface after intentional 20 minutes pure hydrogen plasma discharge reaction under the higher (−350 V) bias voltage application condition as shown in Fig. 2.

The surface morphologies of the substrate, particularly around the gap areas were intensively investi-

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 | $CH_4$,<br>$H_2$ | $CH_4$ : 2.5 sccm<br>$H_2$ : 47.5 sccm | 900°C | 80 Torr | 5 min | −350 V |

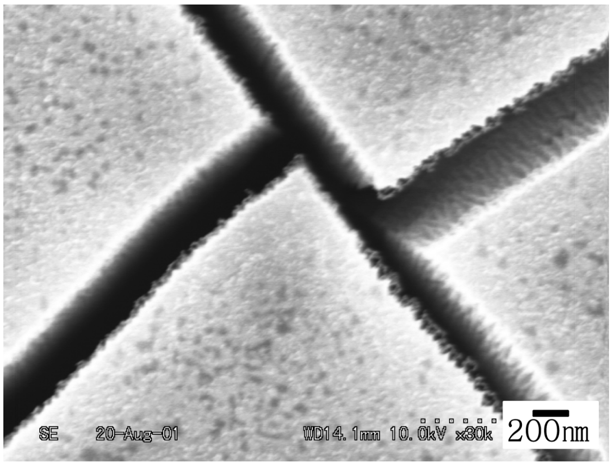

Fig. 2. The deeply-cracked image on the substrate by 20 minutes pure hydrogen plasma discharge reaction under the higher (−350 V) bias voltage application condition.

gated. As shown in Figs. 3a and 3b, the lateral growth of CNFs could be observed around the gap areas. In the gap, however, CNFs were interconnected as a bridge-type configuration (see Figs. 3a and 3c). They traversed the gap on the substrate as shown in Fig. 3c. Indeed, CNFs were interconnected with each other. Finally, they could form the entangled networks interconnected by the self-assembled carbon nanofibers having the laterally-grown and/or bridge-type CNFs.

Based on the results shown in Figs. 3a~3c, the followings were suggested for the causes of the entangled network including the bridge-type connection. Compared with the conventional catalyst such as iron family materials (Fe, Co, Ni), iridium has been known as refractory material having a high melting point [10]. The refractory characteristics of iridium would require a higher substrate temperature to melt the metal catalyst layer. Compared with the smooth plane surface morphology, the rough edge area of the gap might induce a relative high negative bias voltage even under the same applied bias voltage condition. It was reported that high negative bias voltage favors the vertical growth of CNFs [14]. These results gave one of the possible explanations as to why the gap area favors the bridge-type configuration of CNFs, on the other hand the plane surface area favors the lateral growth of CNFs. The simple mechanism for this growth mode was proposed as follows (see Fig. 4).

Step 1: Lateral growth of CNFs would proceed on the

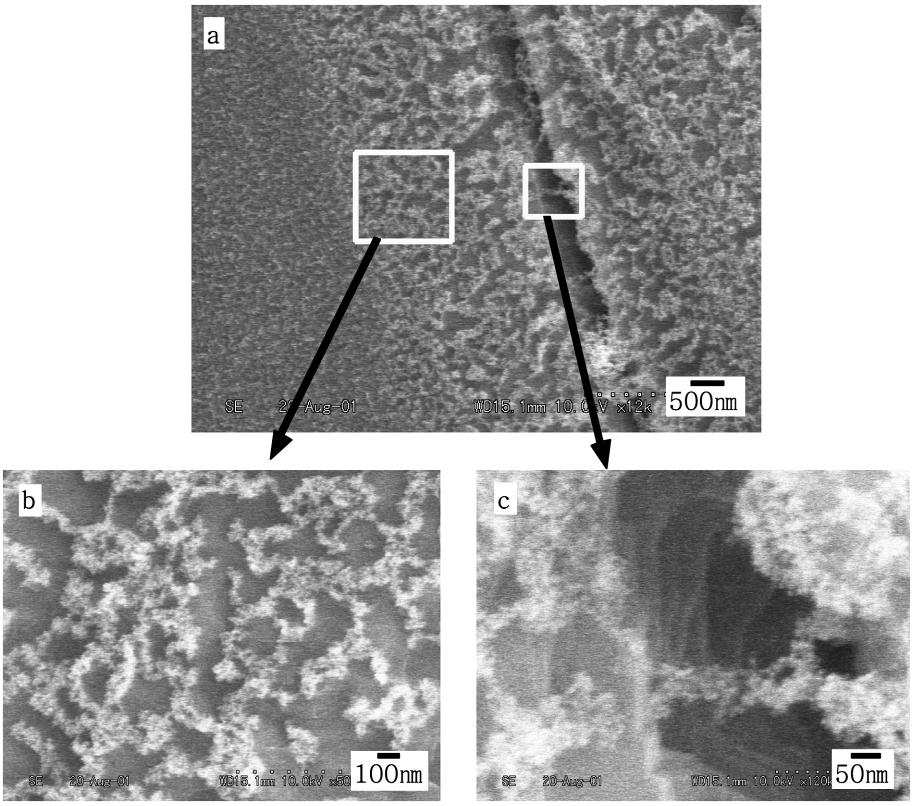

Fig. 3. (a) FESEM image showing the entangled network having the bridge-type formation of the carbon nanofibers across the gap on the substrate and the laterally-grown carbon nanofibers on the plane surface area of the substrate, (b) the magnified image of Fig. 2a focused on the plane surface area on the substrate, and (c) the magnified image of Fig. 2a focused on the gap on the substrate.

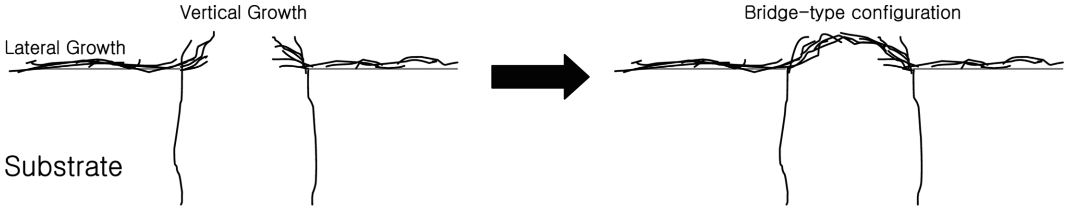

Fig. 4. A simple mechanism for the growth mode of the bridge-type formation of the carbon nanofibers across the gap on the substrate.

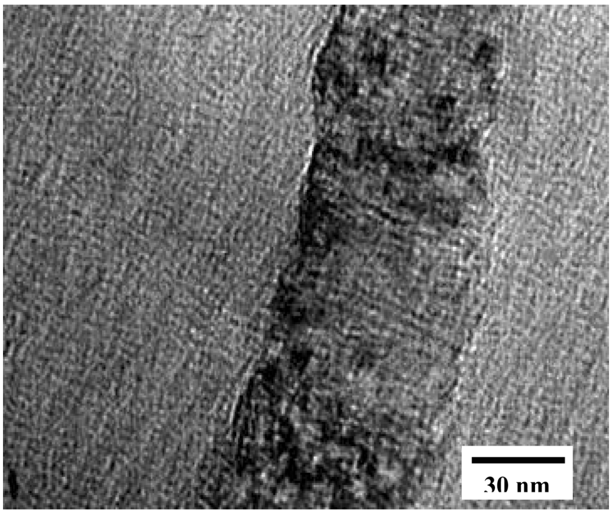

Fig. 5. TEM image of the carbon nanofiber.

plane surface area, while vertical growth of CNFs would proceed at the edge area of the gap.

Step 2: Vertically grown CNFs at the edge area of the gap would meet together at the inner position of the gap and finally they could form the bridge-type configuration.

To identify whether these CNFs are carbon nanotubes or carbon nanofibers, we carried out TEM study. Fig. 5 shows the detailed structure of CNFs. From the stacking lattices and the filled image at the inside of the filaments, we confirmed that these CNFs were carbon nanofibers [15]. The diameters of the carbon nanofibers in this work were measured in the range of between 20 and 80 nm.

The surface electrical resistivities of the entangled network including the bridge-type connection decreased with increasing the substrate temperature (see Fig. 6). This behavior of the entangled network including the bridge-type connection confirms the semiconductor characteristics. At the high temperature range (over 400$^{o}$C), the decrement of surface electrical resistivities with increasing the substrate temperature seemed to be reduced. The cause for this behavior is possibly attributable to the electron colliding effect at the high temperature range.

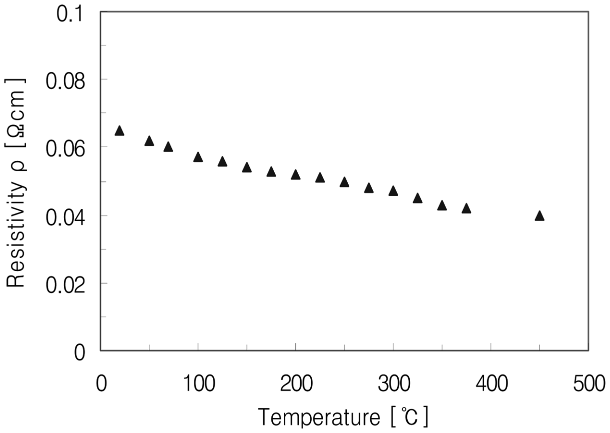

Fig. 6. The surface electrical resistivities of the entangled carbon nanofibers network as a function of the substrate temperature.

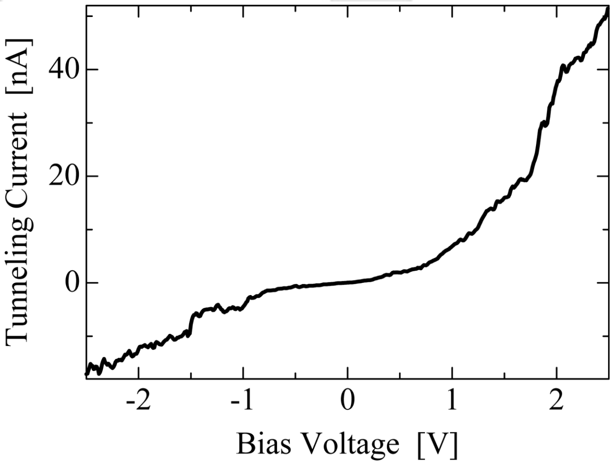

Fig. 7. The scanning tunneling spectrograph of the entangled carbon nanofibers network.

The tunneling current of entangled network as a function of the bias voltage was also confirmed by STS measurement, which revealed the band-gap existence between −1 and 1 V (see Fig. 7). The STS data in Fig. 7 imply that there is a structure near the band edge. From the results of the Figs. 6 and 7, we suggest that the entangled network including the bridge-type connection has the semiconductor electrical characteristics as the previous work [10].

## 4. Conclusions

We could achieve the bridge-type formation of the self-assembled laterally-grown carbon nanofibers interconnected as an entangled network onto the substrate. The causes for the entangled carbon nanofibers network including the bridge-type connection at the gap of the substrate were explained via the intrinsic characteristics of iridium catalyst. The entangled network including the bridge-type connection has the semiconductor electrical characteristics.

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