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Selective Growth of the Carbon Nanofibers at the Groove Area of the MgO Substrate by the Iridium Catalyst

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ABSTRACT

Carbon nanofibers could be selectively formed at the groove area of the MgO substrate using microwave plasma-enhanced chemical vapor deposition system. Iridium metal was used as a catalyst layer for the formation of the carbon nanofibers. The growth direction of the carbon nanofibers was vertical to the substrate surface. The selectively grown iridium-catalyzed carbon nanofibers show around 1.8 V/μm turn-on voltage and 1.0 mA/cm^2 field emission current density at 2.65 V/μm in the field emission measurement.

Key words* : *Carbon nanofibers, Iridium catalyst, Selective growth, Field emission characteristics

1. Introduction

Recently, carbon nanofilaments, called carbon nanotubes if hollow and carbon nanofibers if filled, have been regarded as high potential materials for the elements of nano-electronic devices, especially for the electron emitters and the interconnection lines of transistors because of their unique electrical properties and geometries.[1-6] To apply the carbon nanofilaments for the nanoelectronic devices, the aligning and/or the patterning them for the interconnection lines or the electron emitters were essential.

For aligning the carbon nanofilaments, Terrones *et al.* have reported the formation of the well-aligned carbon nanotubes by the pyrolysis method using a triazine compound and Co particles catalyst.[7] Ren et al. have reported the well-aligned carbon nanotubes by plasma-enhanced hot filaments chemical vapor deposition using a nickel layer catalyst.[8]

To enlarge the application area of the well-aligned carbon nanofilaments to various shapes, the patterning of the carbon nanofilaments would be required. For patterning the carbon nanofilaments, the formation of the interconnection lines using the selectively grown lateral carbon nanofilaments have been reported by a selective deposition of the metal catalyst.[9-11]

Recently, the application of the negative bias voltage during the plasma reaction has been known to facilitate the well-aligned carbon nanofilaments as a vertical direction to the substrate surface.[12,13] 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.[13]

Despite these efforts, the manipulating their growth alignment and/or the patterning them via the selective growth technique are still required to maximize their applicable purpose.

This work presents the selective growth of the carbon nanofibers merely at the groove area of the substrate. Iridium thin layer was used to catalyze the carbon nanofilaments growth. Compared with the conventional catalyst for carbon nanofilaments, iridium was known to a more hard and dense material.[14] Therefore, a high negative bias voltage of −400 V was applied to nanocrystallize the iridium metal. Finally, we could achieve the growth of vertically well-aligned carbon nanofibers merely at the groove area of the substrate. Field emission characteristics of the selectively grown carbon nanofibers at groove areas were also investigated.

2. Experimental Procedure

Iridium coated 1.0 × 1.0 cm^2 MgO substrate was prepared by iridium coating on a MgO substrate using a Radio Frequency (RF) sputtering. Detailed experimental condition for the iridium catalyst coating was shown in Table 1. For carbon nanofilaments deposition, 5% CH_4 and 95% H_2 were introduced to the deposition system after pre-cleaning the substrate with pure H_2 plasma for a few minutes. Microwave plasma-enhanced chemical vapor deposition system was employed for the formation of carbon nanofilaments as shown in Fig. 1. Table 2 shows the detailed experimental condition for carbon nanofilaments deposition.

Detailed morphologies of carbon nanofilaments were

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Table 1. Experimental Condition for the Iridium Catalyst Layer Deposition

RF power	Injection gas	Flow rate of injection gas	Substrate temp.	Total pressure	Reaction time
20 W	Ar	10 sccm	25°C	30 mTorr	5 min

Table 2. Experimental Condition for the Carbon Nanofilaments Formation

Microwave power	Source gases	Flow rate of source gases	Substrate temp.	Total pressure	Reaction time	Bias voltage
600 W	CH_4, H_2	CH_4 : 2.5 sccm H_2 : 47.5 sccm	900°C	80 Torr	5 min	–400 V

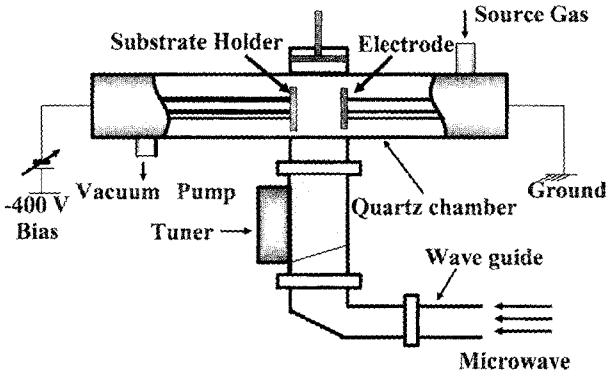

Fig. 1. Schematic diagram of microwave plasma-enhanced chemical vapor deposition system.

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 supported by a Cu grid. Then Cu grid was place into TEM chamber and the detailed morphologies of carbon nanofilaments could be investigated.

The field emission measurement was carried out in a diode type field emission measuring system under the ultra high vacuum condition as shown in Fig. 2. The emission current density at the anode was measured as a function of the applied bias voltage between anode and cathode. Quartz

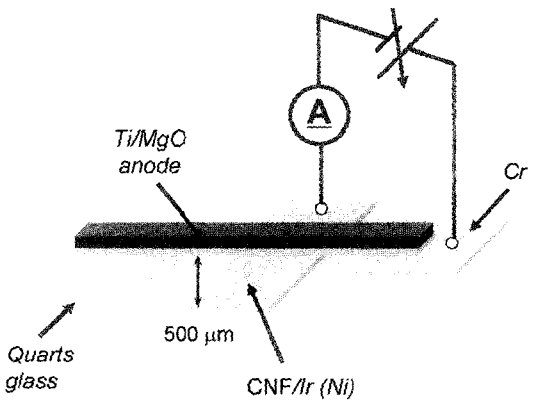

Fig. 2. The schematic diagram of the field emission measurement system.

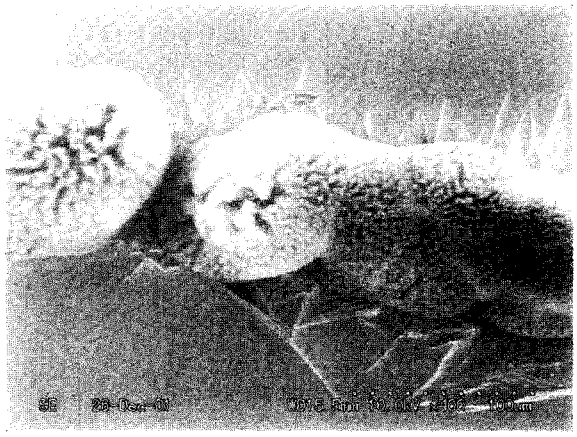

Fig. 3. FESEM image of the iridium-catalyzed carbon nanofilaments on the substrate surface with the groove area.

having around 500 μm thickness was used as a spacer between anode and cathode.

3. Results and Discussion

Grooves were intentionally made on the substrate surface by scratching and then coating the iridium catalyst layer on the substrate surface before the carbon nanofilaments deposition reaction. After 5 min $CH_4 + H_2$ plasma reaction under the –400 V voltage condition (see Table 2 for the detailed experimental condition), the surface images of the substrate were investigated using FESEM. As shown in Fig. 3, the formation of the carbon nanofilaments couldn't be observed on the smooth plane area of the substrate. However, at the groove area on the substrate, the growth of the carbon nanofilaments could be well-observed. Compared with the substrate surface, the inner area of the groove of the substrate has rough surface morphology state. Thus we suggest that the growth of the iridium- catalyzed carbon nanofibers favors the rough surface morphology state of the substrate.

Contrary to this phenomenon, in the case of the nickel-catalyzed carbon nanofilaments, the formation of the vertically grown carbon nanofilaments could be well observed even on the smooth plane area of the substrate as shown in Fig. 4. Based on the results of Figs. 3 and 4, it was suggested that the iridium catalyst could give rise to the selectivity for the formation of the carbon nanofilaments according to the surface morphology states.

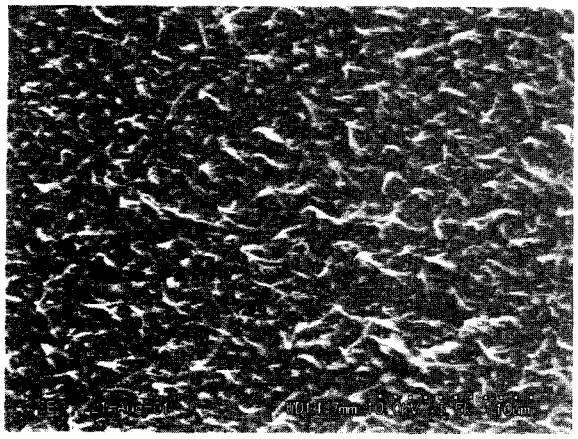

Fig. 4. FESEM image of the nickel-catalyzed carbon nano- filaments on the substrate surface.

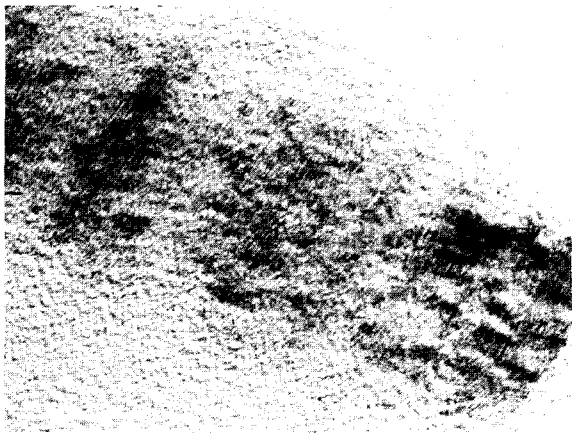

Fig. 6. TEM image for one of the carbon nanofibers.

The cause for this selectivity was understood as follows. Compared with the conventional iron-family group catalyst (Fe, Co, Ni) for the formation of the carbon nanofilaments, iridium was known to a more hard and dense material.[14] Actually, the formation of the carbon nanofilaments was known to be initiated by the formation of the nano-sized metal catalyst grain.[13] The refractory characteristics of iridium, compared with the conventional catalyst, would require the higher substrate temperature to form the nano-sized iridium grains by melting the iridium catalyst layer. Due to the tendency of the higher induced bias voltage at the rough morphology state, compared with the smooth one, the groove area can induce the higher substrate temperature. Consequently, the formation of the iridium-catalyzed carbon nanofilaments would be dominantly formed at the groove areas.

Fig. 5 shows the magnified image of Fig. 3. It reveals the bush-like formation of the individual carbon nanofilaments. The growth of these carbon nanofilaments seems to be vertically well-aligned to the substrate surface. It also shows the metal existence (the bright dot) on the top position of the individual carbon nanofilaments. The metals presence at the top position indicates the tip growth mode for the iridium-catalyzed carbon nanofilaments.[15]

To identify whether these carbon nanofilaments are carbon nanotubes or carbon nanofibers, TEM study were carried out. Fig. 6 shows the detailed structure of one of these carbon nanofilaments. From the stacking lattices and the filled image at the inside of the filaments, we confirmed that these filaments were carbon nanofibers.[16] The diameters of the carbon nanofibers in this work were measured in the range of between 20 and 100 nm.

Fig. 2 shows the schematic diagram of the field emission measurement system. The vertically grown carbon nanofibers were separated from titanium/MgO anode using a quartz spacer. To obtain the field emission characteristics of the iridium-catalyzed carbon nanofibers selectively deposited at the groove area of the substrate, the variation of the anode current density were measured as a function of anode to cathode voltages as shown in Fig. 7. Turn-on voltage of the field emission current and the emission current density were measured around 1.8 V/μm and around 1.0 mA/cm^2 at 2.65 V/μm, respectively. This turn-on value is one of the

Fig. 5. The magnified FESEM image of Fig. 3.

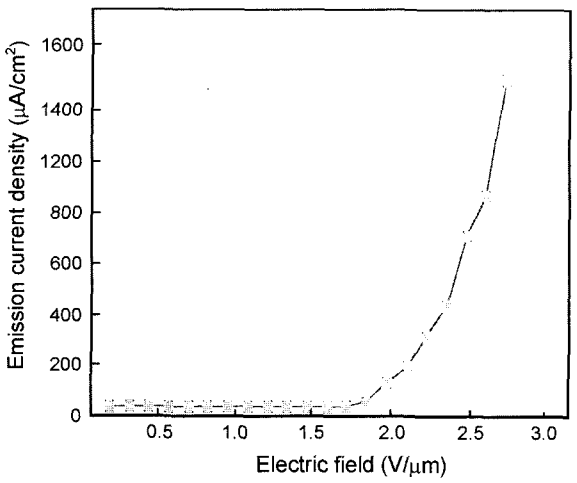

Fig. 7. The measured field emission current density as a function of anode to cathode voltage.

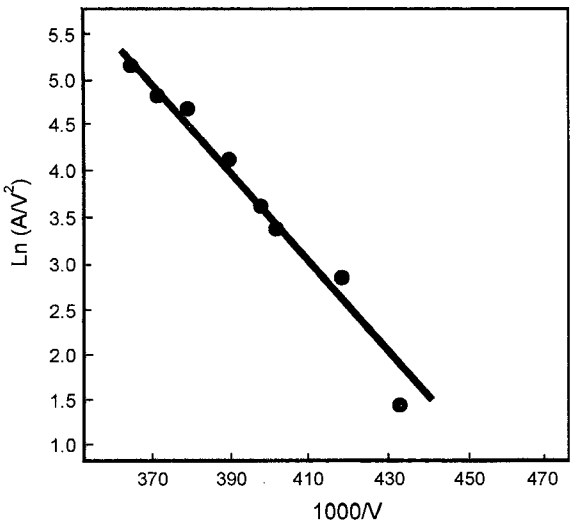

Fig. 8. Fowler-Nordheim plot for Fig. 7.

lower values among the reported turn-on voltage using carbon nanotubes or nanofibers.[17] The geometry of carbon nanofibers seems to be the cause for the lower turn-on voltage value. Namely, the vertical direction of carbon nanofibers might have an advantage for the electron emission, as a straight line, from tip area of carbon nanofibers to the anode of Ti/MgO anode. We defined J_{max} as the maximal current obtained without the destruction of the emitter. As shown in Fig. 7, J_{max} was measured around 1.6 mA/cm^2 at 2.75 V/μm. These values indicate that the iridium-catalyzed carbon nanofiber is the promising material for the field electron emitter. Fig. 8 shows the corresponding Fower-Nordheim plot for Fig. 7. The straight line in Fig. 8 confirms that the emission current principally comes from field emission characteristics.

4. Conclusions

The iridium-catalyzed carbon nanofibers were selectively formed at the groove areas on the MgO substrate surface. The growth direction of the fibers was observed as a vertical to the substrate surface. The iridium-catalyzed carbon nanofibers show around 1.8 V/μm turn-on voltage and 1.0 mA/cm^2 field emission current density at 2.65 V/μm.

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