Journal of the Korean Crystal Growth and Crystal Technology
Vol. 14, No. 1 (2004) 1-5

Growth of nickel-catalyzed carbon nanofibers using MPCVD method and their electrical properties

Sung-Hoon Kim†

Department of Nano Materials Science & Engineering, Silla University, Busan 617-736, Korea

(Received September 24, 2003)
(Accepted January 13, 2004)

Abstract Carbon nanofilaments were formed on silicon substrate via microwave plasma-enhanced chemical vapor deposition method. The structure of carbon nanofilaments was identified as the carbon nanofibers. The extent of carbon nanofibers growth and the diameters of carbon nanofibers increased with increasing the total pressure. The growth direction of carbon nanofibers was horizontal to the substrate. Laterally grown carbon nanofibers showed the semiconductor electrical characteristics.

Key words Carbon nanofibers, Microwave plasma, Total pressure effect, Semiconductor characteristics, Lateral growth

1. Introduction

Carbon nanofilaments (CNFs) have fascinating shape suitable for interconnecting with nanometer diameter and micrometer lengths were classified as carbon nanotubes (if hollow) and carbon nanofibers (if filled) [1-3].

For the nanowiring applications in nanoelectronic devices, the CNFs should show the reproducibility of the electrical properties. Unfortunately, the electrical properties of carbon nanotubes are uncontrollable, because they were known to be varied as metallic, insulating, or semiconductor characteristics according to their diameter, wrapping angle, or post-growth treatment [4, 5]. The formation of carbon nanotubes having the reproducible single electrical properties is too difficult to achieve. From the practical point of views, therefore, the nanowiring application of carbon nanotubes has been excluded.

On the contrary to carbon nanotubes, inside of carbon nanofibers was known to be filled by the stacking of carbon lattice structure [1, 6]. So the uncontrollable varied electrical characteristics of CNFs, due to the diameter and the wrapping angle, may be excluded. Consequently, the possibility to get the reproducible single electrical properties would be enhanced. This idea impels us to launch the fabrication of laterally grown carbon nanofibers for the nanowiring materials of the nanoelectronic device [7, 8].

We present the growth of lateral carbon nanofibers to the substrate. Ni thin layer was used to catalyze the carbon nanofibers growth. The growth of carbon nanofibers was investigated as a function of total pressure. The surface electrical resistivities of the laterally grown carbon nanofibers were measured as a function of the substrate temperature. Finally, we presented and discussed the fabrication of the laterally grown carbon nanofibers having the semiconductor electrical properties.

2. Experimental

We deposited CNFs films on the nickel layer-coated $1.0\times1.0\ cm^2$ 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 under 500 W RF power condition. We obtained around 50 nm film thicknesses after 5 min sputtering reaction.

Before the CNFs deposition reaction, we cleaned the substrate with H_2 plasma for a few minutes. CH_4 and H_2 were used as source gases. The substrate surface temperature during the plasma reaction was measured using optical pyrometer. The detailed experimental conditions of the CNFs formation under MPECVD were shown in Table 1.

The morphologies of CNFs were investigated using field emission scanning electron microscopy (FESEM). Carbon nanofibers were confirmed by the nanostructures via transmission electron microscopy (TEM) study. The samples for TEM were prepared by dispersing the

†Corresponding author
Tel: +82-51-309-5619
Fax: +82-51-309-5176
E-mail: shkim@silla.ac.kr

Table 1
Experimental conditions of carbon nanotubes formation

Microwave power	Source gases	Flow rates of source gases	Sub. Temp.	Total pressure	Reaction time
600 W	CH_4, H_2	CH_4: 2.5 sccm H_2: 47.5 sccm	750°C, 950°C, 1050°C	40 Torr, 60 Torr, 80 Torr	5 min

carbon nanofibers 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 carbon nanofibers were investigated.

The surface electrical resistivity measurement of carbon nanofibers was carried out by the two points probe as a function of the substrate temperature. The composition of carbon nanofibers was analyzed by electron probe-micro analysis (EPMA).

3. Results and Discussion

We first investigated the surface images of the substrate as a function of the total pressure. Figs. 1a~c show FESEM images of the nickel layer-coated Si substrates after CNFs deposition reaction under 40 (Fig. 1a), 60 (Fig. 1b) and 80 Torr (fig. 1c) experimental condition (see Table 1 for the detailed experimental condition). The increase of the substrate surface temperature with the increase of the total pressure was considered to be due to the change of plasma density and the chemical species, as the previous reports [9]. Figs. 2a~c show the magnified image of Figs. 1a~c, respectively. As shown in Figs. 1 and 2, we could observe the increase in the number density of CNFs on the substrate with increasing the total pressure. Under this condition, we could not obtain the vertical-type carbon nanotubes alignment onto the substrate surface. On the other hand, CNFs places parallel direction to the substrate surface.

We measured the variation in the diameter of CNFs as a function of the total pressure. As shown in Fig. 3, the diameters of CNFs decrease with increasing the total pressure.

From the combined results of Figs. 1~3, we may suggest that the low total pressure gave rise to the low number density of CNFs with the large diameter. The

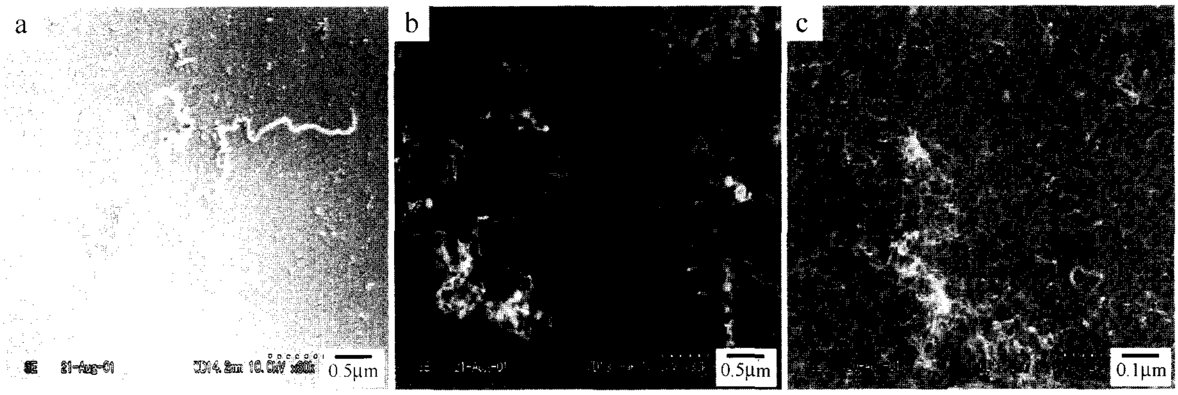

Fig. 1. FESEM images of the CNFs-deposited Si substrates under (a) 40, (b) 60 and (c) 80 Torr total pressure conditions.

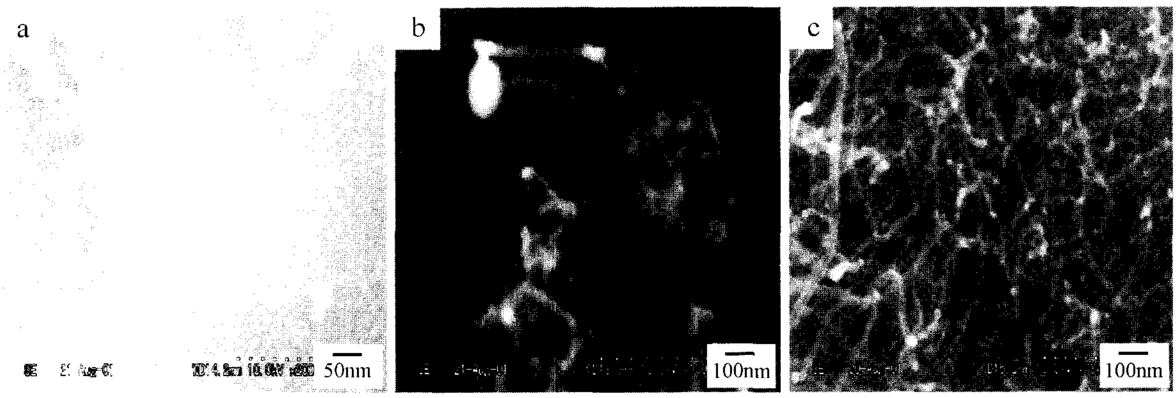

Fig. 2. The magnified FESEM images of Fig. 1.

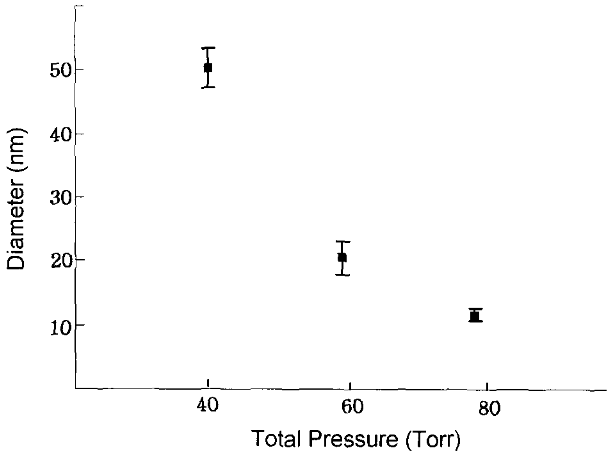

Fig. 3. The variation in the diameters of CNFs as a function of the total pressure.

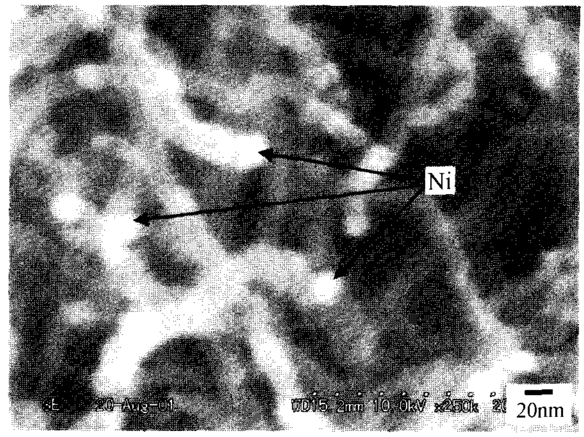

Fig. 5. The high-magnified FESEM images of Fig. 2c.

cause for these results may be attributed to the low induced temperature of the substrate caused by the relatively low pressure plasma (see the variation of the substrate temperature according to the total pressure in Table 1). It was reported that the diameter of carbon nanofilaments increased with increasing the metal catalyst grain size [10, 11]. Thin layer of metal catalyst was known to form the nano size grains by the plasma reaction during the initial plasma reaction [12]. In addition, the nano size grains of metals were known to melt at lower temperature, compared with the melting point of the bulk metals [13]. Consequently, Low temperature, compared with high temperature, may induce relatively large size metal grains. So, relatively large size nickel clusters, instead of small size nickel clusters, can be formed and they tend to participate in the formation of CNFs. Finally, the relatively large size diameters of CNFs can be produced. Furthermore, due to the lack of optimal size nickel clusters for CNFs formation, the number density of CNFs on the substrate would be low. Indeed, when we carried out CNFs formation reaction using around 1,000 nm nickel catalyst layer under the 15 Torr total pressure (~650°C substrate temperature) condition, we could obtain merely a few CNFs having the very large size (~70 nm) diameters as shown in Fig. 4. The cracked image in Fig. 4 indicates the damaged nickel layer by the plasma.

Figure 5 shows the high-magnified FESEM images of Fig. 2c. In this image, we could find the nickel on the end position of CNFs. The existence of the nickel on the end positions (see the arrow positions of Fig. 5) of CNFs was found as a result of detecting nickel and carbon using EPMA. It indicates that the CNFs growth would follow the tip growth mode [14], instead of base growth mode.

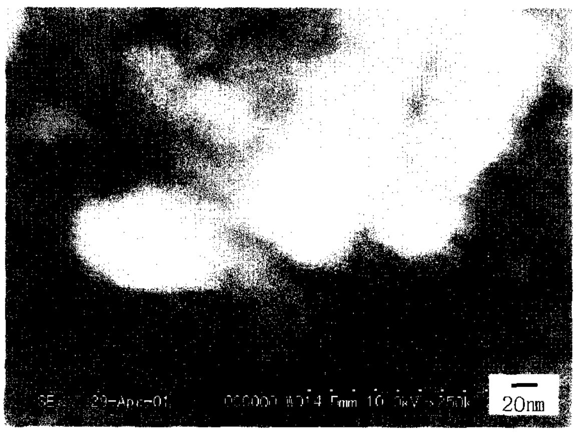

Fig. 4. FESEM images of CNFs on around 1000 nm nickel catalyst layer coated Si substrate under the 15 Torr total pressure (~650°C substrate temperature) condition.

Fig. 6. TEM image for one of the carbon nanofibers under 80 Torr total pressure condition.

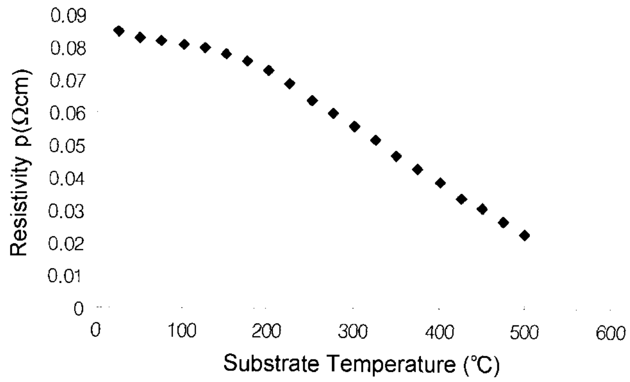

Fig. 7. The surface electrical resistivities of the self-assembled lateral carbon nanofibers network as a function of the substrate temperature.

To identify whether these bundles are carbon nanotubes or carbon nanofibers, we carried out TEM study. Fig. 6 shows the detailed structure of one of CNFs deposited by 80 Torr plasma reaction. From the stacking lattices (see the horizontal lines in Fig. 6), 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 CNFs were carbon nanofibers [1, 6].

Surface electrical conductivities of the laterally grown carbon nanofibers by 80 Torr plasma reaction were measured as a function of the substrate temperature. Laterally grown carbon nanofibers formed self-assembled lateral carbon nanofibers network as shown in Fig. 1c. We already reported that carbon nanofilaments had a self-assembled tendency [15]. So, the laterally grown carbon nanofibers in this work were regarded to form self-assembled lateral carbon nanofibers network. Consequently, the electronic transport properties of the self-assembled lateral carbon nanofibers network could be readily investigated without the time-consuming alignment step for the electrical contacts [16, 17]. For the electrical contact, we merely deposited two points of gold dot on the self-assembled lateral carbon nanofibers network. As shown in Fig. 7, the surface electrical resistivities of the self-assembled lateral carbon nanofibers network decrease with increasing the substrate temperature. Based on these results, the carbon nanofibers seemed to have the semiconductor characteristics.

4. Conclusions

Lateral carbon nanofibers were grown on Si substrate by the nickel catalyst. The extent of carbon nanofibers growth and the diameters of carbon nanofibers increased with increasing the total pressure. Laterally grown carbon nanofibers showed the semiconductor electrical characteristics.

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