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Investigation of the growth of carbon nanofilaments over a wide temperature range

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Carbon nanofilaments could be formed on silicon oxide substrates over a wide temperature range of 350-1050°C by a thermal chemical vapor deposition system. Using a vacuum-sublimation method, we deposited Fe metal catalyst nanograins on the substrate and carried out carbon nanofilament depositions as a function of the substrate temperature. The diameters of the carbon nanofilaments increased at a higher substrate temperature range. At 350°C, the diameters of carbon nanofilaments were measured to be around 50 nm. At 850°C, however, they seemed to be above 150 nm. Above 850°C, the carbon nanofilaments seemed to be transformed into amorphous carbon. The cause for the variation of the carbon nanofilament diameter as a function of temperature is discussed in association with the surface migration of Fe metal catalyst nanograins and their agglomeration.

Key words: carbon nanofilaments, thermal chemical vapor deposition, temperature effect

Introduction

Recently, carbon nanofilaments, called carbon nanotubes if hollow and carbon nanofibers if filled [1-3], have been regarded as promising materials for the fabrication of nanoelectronic devices because of their unique electrical properties and geometries [4-8]. Despite the fascinating materials characteristics of carbon nanofilaments, their electrical properties were known to be uncontrollable, because they varied with metallic, insulating, or semiconductor characteristics according to their diameters [9, 10]. For their practical applications, therefore, it would be indispensable to achieve a reproducibility of a single electrical property by controlling the diameters.

The diameter of carbon nanofilaments is known to be related to the catalyst particle size and also depends on the substrate temperature [11-13]. To achieve a reproducibility of a single electrical property, therefore, the first consideration would be the investigation of the substrate temperature effect on the diameter of the carbon nanofilaments. Up to the present, several studies of the substrate temperature effect on the characteristics of carbon nanofilaments have been carried out [13-15]. However, the commonly used temperature ranges have been limited from 600 to 1000°C.

In this study, we carried out carbon nanofilament depositions over a wide temperature range from 350 to 1050°C. Using the precursor $Fe(CO)_5$ of the Fe metal catalyst and a vacuum-sublimation process as a catalyst deposition technique, we could achieve a low temperature deposition down to 350°C [16]. The morphologies, the densities, and the diameters of the carbon nanofilaments were investigated as a function of the substrate temperature. Before the deposition of carbon nanofilaments, the surface morphologies of Fe metal catalyst nanograins deposited on the substrate were also investigated as a function of the substrate temperature. The cause for the variation of the carbon nanofilament diameter as a function of the substrate temperature is discussed in association with the surface migration of Fe metal catalyst nanograins and their agglomeration.

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Experimental Procedure

The SiO_2 substrates were prepared by the thermal oxidation of $2.0\times2.0\ cm^2$ p-type Si (100) substrates. The thickness of the silicon oxide (SiO_2) layer on the Si substrate was estimated to be about 300 nm. A 7.18 mol iron pentacarbonyl, $Fe(CO)_5$, solution was prepared as the Fe metal catalysts source solution. In the vacuum sublimation process (see Fig. 1), a 7.18 mol $Fe(CO)_5$ solution was frozen using liquid air and Fe metal catalyst nanograins were deposited on the substrate as in the previous study [16]. Detailed experimental condition for the Fe metal catalyst, $Fe(CO)_5$, deposition are shown in Table 1.

For carbon nanofilament deposition, C_2H_2 and H_2 were introduced to the deposition system after precleaning the substrate. A thermal chemical vapor deposition system was employed for the formation of carbon nanofilaments as shown in Fig. 2. Table 2 gives

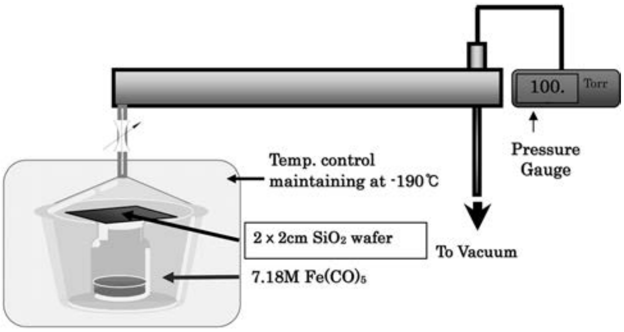

Fig. 1. Schematic diagram of vacuum-sublimation process for $Fe(CO)_5$ deposition on the SiO_2 substrate.

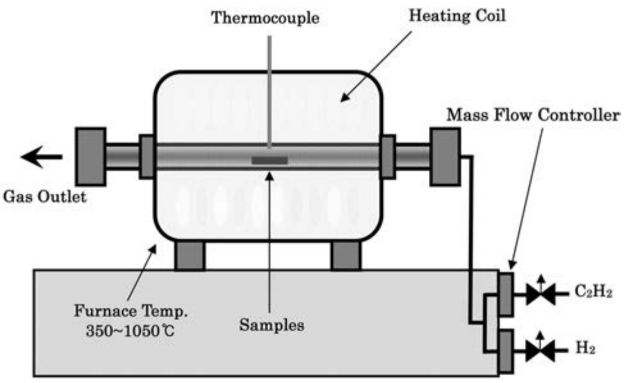

Fig. 2. Schematic diagram of the thermal chemical vapor deposition system for the carbon nanofilaments deposition.

the detailed experimental condition for carbon nanofilaments deposition.

Detailed morphologies of Fe metal catalyst nanograins deposited substrates and carbon nanofilaments deposited substrates were investigated using field emission scanning electron microscopy (FESEM). Transmission electron microscopy (TEM) and Raman spectroscopy (wavelength = 488 nm) were employed to identify the characteristics of these carbon nanofilaments. The samples for TEM were prepared by dispersing carbon nanofilaments using acetone in an ultrasonic bath. A drop of suspension was dropped onto a carbon film which was supported by a Cu grid. Then the Cu grid was placed into the TEM chamber and the detailed morphologies of carbon nanofilaments were investigated.

Results and Discussions

We first investigated the surface morphologies of as-deposited substrates as a function of the wide substrate temperature range. Figures 3a-h show FESEM images of the as-deposited substrates at 350 (Fig. 3a), 450 (Fig. 3b), 550 (Fig. 3c), 650 (Fig. 3d), 750 (Fig. 3e), 850 (Fig. 3f), 950 (Fig. 3g) and 1050°C (Fig. 3h). At a substrate temperature of 850°C, the densities of carbon nanfilaments were higher than those of any other temperature. This result reveals that the optimal substrate temperature for the densities of carbon nanofila-

Table 1. Experimental conditions for the deposition of Fe metal catalyst nanograins on silicon oxide substrate

Metal catalyst source	Concentration of metal catalyst source solution	Total pressure during the sublimation process	Freezing method for $Fe(CO)_5$	Total sublimation time
$Fe(CO)_5$	7.18 mol	10 Torr (0.001333 μPa)	By liquid air (about −190°C)	2 h

Table 2. Experimental conditions for the deposition of carbon nanofilaments

Source gases	Flow rates	Total flow rates	Total pressure	Deposition temp.	Reaction times
C_2H_2, H_2	C_2H_2 : 15 sccm H_2 : 35 sccm	50 sccm	100 Torr (0.01333 μPa)	350-1050°C	90 minutes

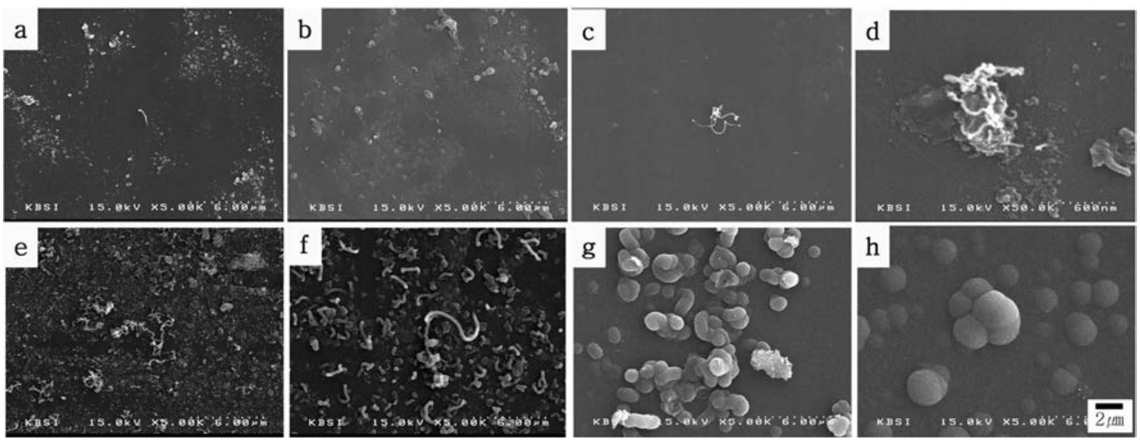

Fig. 3. FESEM images of the substrate surfaces deposited carbon nanofilaments at (a) 350, (b) 450, (c) 550, (d) 650, (e) 750, (f) 850, (g) 950 and (h) 1050°C.

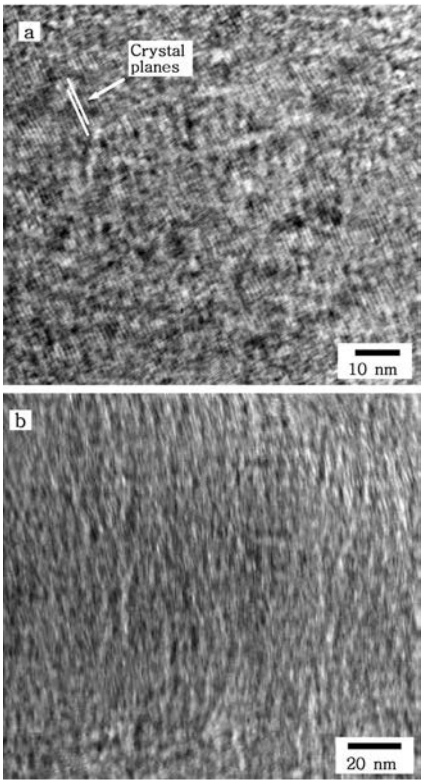

Fig. 4. TEM images for one of the carbon nanofilaments deposited at (a) 850 and (b) 950°C.

ments would be around 850°C.

To identify whether these carbon nanofilaments are carbon nanotubes or carbon nanofibers, we carried out a TEM study. Figure 4a shows the detailed structure of carbon nanofilaments deposited at the optimal temperature (850°C). From the stacking lattices and the filled image inside the filaments, we confirmed that these carbon nanofilaments were carbon nanofibers [1, 17]. However, we found amorphous, instead of carbon nanofibers, features (see Fig. 4b) of carbon nanofilaments deposited at a higher temperature (950°C). These results reveal that, above 850°C, the carbon nanofibers seemed

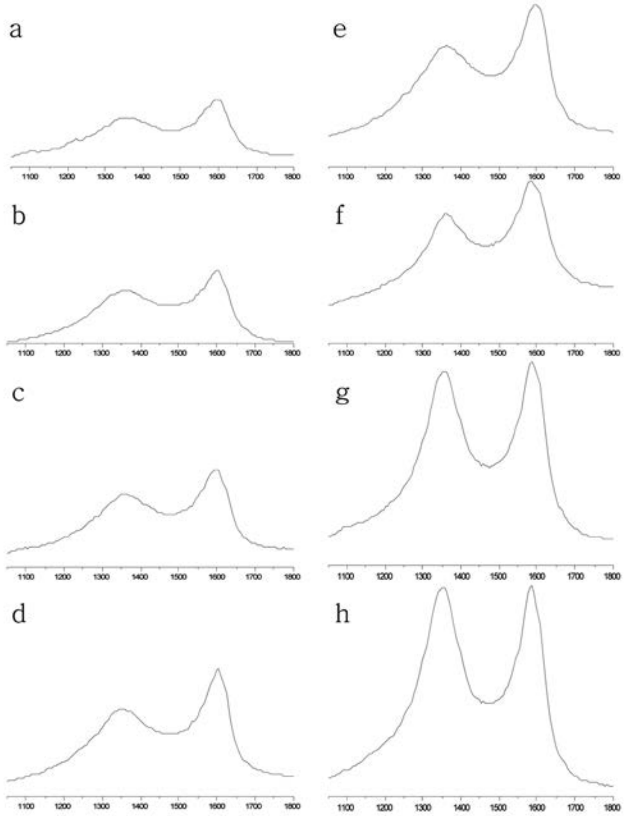

Fig. 5. Raman spectra of the substrate surfaces deposited carbon nanofilaments at 350, (b) 450, (c) 550, (d) 650, (e) 750, (f) 850, (g) 950 and (h) 1050°C.

to be transformed into amorphous carbon.

The amorphous characteristics of the carbon nanofilaments at the higher temperature range (above 850 °C) could also be verified by the first-order Raman spectra of the carbon nanofilaments. As shown in Fig. 5, two distinct Raman bands of the typical graphite structure features at ~1335 cm^{-1} (D band) and ~1580 cm^{-1} (G band) could be seen in these spectra [18, 19]. Above 850°C, the peaks of D-band increase with an increase in the substrate temperature. Because the D-

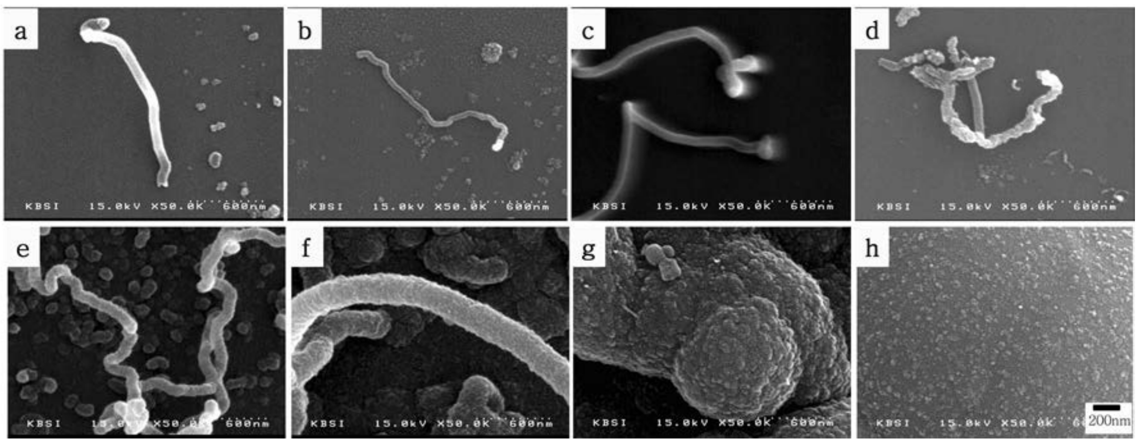

Fig. 6. High magnification FESEM images of the substrate surfaces deposited carbon nanofilaments at (a) 350, (b) 450, (c) 550, (d) 650, (e) 750, (f) 850, (g) 950 and (h) 1050°C.

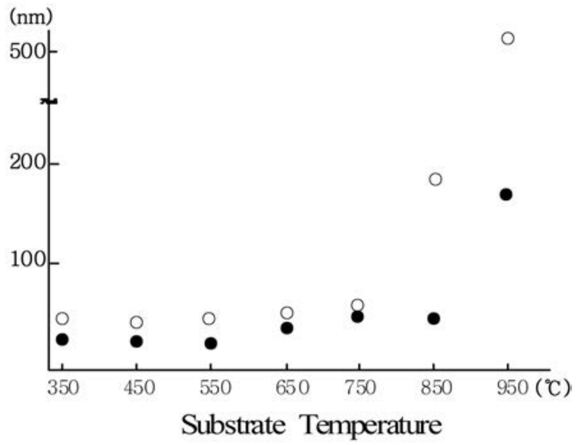

Fig. 7. Variations of the diameter (open circles) of carbon nanofilameters and the grain sizes of Fe metal catalyst particles (black circles) as a function of the substrate temperature.

band is normally known to be associated with the presence of amorphous carbon [20], we consider this result as an indication of an increase in the amount of amorphous carbon in the film at the higher temperature range (above 850^{o}C). Furthermore, the higher values of I(D)/I(G) at the higher temperature range also confirms the deterioration of the crystallinity [13, 14].

Figures 6a-h show highest-magnified FESEM images of Figs. 3a-h. As shown in Fig. 6, the diameters of carbon nanofilaments are almost invariable in increasing the substrate temperature from 350 up to 750^{o}C. Above 750^{o}C, however, they rapidly increase with an increase in the substrate temperature (see the open circles in Fig. 7). These results reveal that the diameters of carbon nanofilaments increase with an increase in the substrate temperature prominently in the higher temperature range (above 750^{o}C).

To elucidate the cause of the increase in the diameters of carbon nanofilaments with an increase in the substrate temperature, we carried out a 10 minute heating of the substrate deposited Fe metal catalyst nanograins under vacuum. And then we examined the surface morphologies as a function of the substrate temperature. As shown in Fig. 8, the change in the grain size with an increase in the substrate temperature are quite similar to those of the diameters of carbon nanofilaments (compare the open circles with the black circles in Fig. 7). Namely, at the lower temperature ranges (350-850^{o}C), the grain sizes of Fe catalyst particles very little with an increase in the substrate temperature (see Figs. 8a-f). In the higher temperature range (above 850^{o}C), however, they steeply increased with an increase in the substrate temperature (see the Figs. 8g and h).

The combined results of Figs. 6-8 confirm that the variations of the diameters as a function of the substrate temperature are in association with those of the Fe metal catalyst nanograins sizes. Basically, the increment of the grain size would be dependent on the surface migration of the grains and their agglomeration. And the surface migration of the grains and their agglomeration would be favored in the higher temperature range [13]. Therefore the increment in the grain size would be facilitated in the higher temperature range. Consequently, this may give rise to the increase in the diameters of carbon nanofilaments.

Conclusions

We could achieve the deposition of carbon nanofilaments over a wide temperature range (350-1050^{o}C) using vacuum-sublimated Fe metal catalyst nanograins and a thermal chemical vapor deposition technique. Above 850^{o}C, we found that the carbon nanofibers transformed into amorphous carbon. At the lower temperature range (350-750^{o}C) the diameters of carbon nanofilaments very little with an increase in the substrate temperature. In the higher temperature range (above 750^{o}C), however, they steeply increased with an increase in the substrate temperature. The surface migration of Fe metal catalyst nanograins and their agglomeration are regarded as the reason for this steep increment.

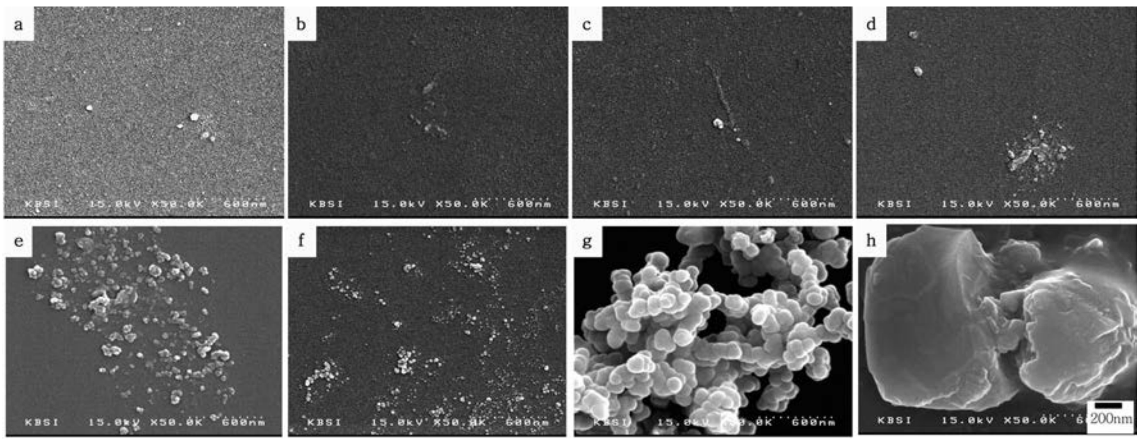

Fig. 8. FESEM images of the substrate deposited Fe metal catalyst nanograins after heating for 10 minutes in a vacuum at (a) 350, (b) 450, (c) 550, (d) 650, (e) 750, (f) 850, (g) 950 and (h) 1050°C

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