

Bamboo and Herringbone Shaped Carbon Nanotubes and Carbon Nanofibres Synthesized in Direct Current-Plasma Enhanced Chemical Vapour Deposition

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Carbon nanotubes with different structures were catalytically synthesized on Ni coated SiO_2/Si substrate in a Direct Current Plasma Enhanced Chemical Vapour Deposition system, in which C_2H_2 acted as the carbon source and NH_3 as the etchant gas. A Scanning Electron Microscope study showed that carbon nanotubes were all vertically aligned with respect to the substrate, with diameters ranging from 10 nm to 200 nm. Different sizes of Ni catalyst particles were observed on the tips of carbon nanotubes. Transmission Electron Microscopy was used to study the morphology of the grown tubes and the results obtained show that the diameters and structures of these carbon nanotubes were closely correlated to the sizes and structures of the Ni nanoparticles. Two main structures namely bamboo shaped carbon nanotubes and herringbone shaped carbon nanofibres were found on the same sample. It is suggested that by controlling the pre-growth condition, desired structure of carbon nanotubes or carbon nanofibres could be produced for practical applications.

Keywords: Carbon Nanotubes (CNTs), Carbon Nanofibres (CNFs), PECVD, SEM, TEM.

1. INTRODUCTION

Carbon nanotubes (CNTs) and carbon nanofibres (CNFs) have been studied for many years due to their unique electronic and extraordinary mechanical properties.^{1–3} Controllable growth conditions of different morphologies of CNTs and CNFs are of importance to realize various applications, such as field emission displays,⁴ cathodes for electron microscopy,⁵ sensors,⁶ and energy storage⁷ etc. Among the commonly used technologies of fabricating CNTs and CNFs, such as arc discharge,⁸ laser vaporization,^{9,10} and chemical vapour deposition (CVD)¹¹ etc, the plasma enhanced chemical vapour deposition (PECVD) based methods have been favoured over the others due to the advantages of low temperature processing, vertical structure alignment and large area growth capability.¹² All of these mentioned synthesis techniques use transition metals as the catalyst for growing CNTs and CNFs. Rodrigus et al.¹³ proposed that there are three structural forms of carbon nanofibers that were classified by the angle of graphene layers with respect to the filament axis, namely (a) stacked,

(b) herringbone and (c) nanotube. Another structure of CNTs, which called bamboo shape-like structure was also found by several other groups.^{14–16} These CNTs have more or less tilted graphite planes and graphite shells inside the hollow core of the tubes. Although it was widely recognised that the metal catalysts play an important role in controlling the growth features of CNTs and CNFs, there were few reports about the different structures of CNTs and CNFs synthesized from one sample.

This paper describes the growth of different structures of CNTs and CNFs on a thin Ni film coated SiO_2/Si substrate through DC PECVD processing. Inspection using Scanning Electron Microscopy (SEM) showed that different diameters of CNTs were perpendicularly grown on the SiO_2/Si substrate, with various sizes of Ni nanoparticles on top of the tips. Transmission Electron Microscopy (TEM) inspection confirms that these CNTs consist of bamboo shaped CNTs and herringbone like structures of CNFs. It clearly shows that the Ni catalyst particles correlate with the size and structures of the grown CNTs. Smaller Ni particles (below 50 nm) have pearl like structure, in which case bamboo shaped CNTs form through the particles. Larger Ni particles (i.e., sizes greater than 50 nm)

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normally form sharp tips at the bottom end, resulting in the herringbone structure of CNFs. On the other hand, CNTs with fewer bamboo structures, like compartments inside the core, are preferred to grow through quasi-spherical Ni nanoparticles below 20 nm. It is proposed in this paper that by controlling the pre-growth conditions, specific and desired structures of CNTs or CNFs can be synthesized for different applications.

2. EXPERIMENTAL DETAILS

In the experiment, *n*-type Si wafer with approximately 1 μm thick thermally grown SiO_2 layer was used as the substrate. After cleaning the wafer in Aceton, followed by IPA in an ultrasonic bath, the sample was dried using a nitrogen blow dry gun. A thin Ni film with a thickness of 4 nm was then deposited on top of the substrate using a thermal evaporator. The synthesis process was carried out in a modified DC PECVD apparatus (MPS1400, JLS). Prior to the PECVD growth, the sample was annealed at a ramping temperature up to 750 °C inside vacuum chamber for 30 minutes, with a pressure of 4×10^{-6} Torr. This was followed by a synchronized introduction of NH_3 and C_2H_2 into the chamber for CNT growth. Gas flow rates of 160 sccm and 40 sccm were used respectively, with an established pressure of 1.5 Torr. The deposition was carried out for 30 minutes in a stable glow discharge condition, with the current at 100 mA and the discharge voltage at 455 V, which gives a corresponding power of ~ 45 W. The sample was cooled down inside the chamber naturally before taking out for analysis. The morphology and density of the grown CNTs were studied using a Scanning Electron Microscopy (Tescan) and Transmission Electron Microscopy (TEM, JEOL 2010).

3. RESULTS AND DISCUSSION

Figure 1 shows an SEM image of the sample after a synchronization processing in DC-PECVD. Closely packed carbon nanotubes were observed perpendicularly aligned on the sample surface. All these CNTs have the catalyst particles shown in bright spots at their tips. Most CNTs have a diameter ranging from 20 to 50 nm. Some protruding structures are shown to have large diameters in the region of 100 to 200 nm. Figure 2 shows a chart of the dependence of nanotube dimensions with respect to the Ni particle size. It clearly illustrates that the diameters of the CNTs are approximately identical to the Ni nanoparticles sizes.

TEM images of CNTs from the sample are shown from Figures 3 to 5. Two main structures of CNTs were observed on the holey carbon film coated Cu grid. Most CNTs show bamboo like structures with more or less tilted graphite planes inside the hollow core of surrounding parallel planes (Fig. 3). The grown CNTs range from 20 nm

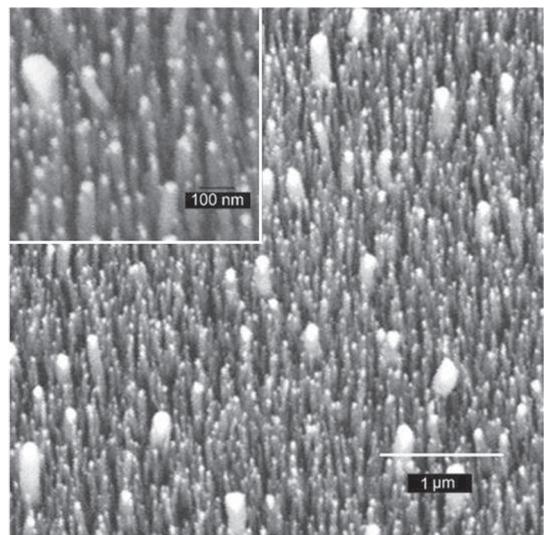


Fig. 1. SEM image of CNTs/CNFs prepared by DC PECVD. Inset shows the high magnification of CNTs/CNFs.

to 50 nm in diameter. Ni nanoparticles on the tips of the CNTs show pearl or droplet like shapes. It was found that the smaller Ni particles tend to have a quasi-spherical shape, which result in CNTs with smaller diameters and less tilted graphite planes inside the core than the larger diameter CNTs (Fig. 4). Herringbone like CNFs were also found on the same sample (Fig. 5). These CNFs have large diameter of more than 50 nm with conical shape Ni particles on the tips.

Several research groups have synthesized various morphologies of CNTs and CNFs using different growth conditions. Delzeit et al.¹⁷ illustrated the CNTs and CNFs transition by changing the plasma bias. Bartsch et al.¹⁵ proposed that deposition time controls the structure of CNTs. They demonstrated that the short deposition times of few minutes attain the tubular structure, whereas bamboo like structure was dominantly grown in a longer deposition time around 30 to 60 minutes. Zhao et al.¹⁸ realized the bamboo shaped CNTs and herringbone nanofibers synthesized at different temperature of 550 °C and 500 °C, respectively. Although most groups proposed the strong relationship of catalyst particles with the structure of CNTs, they only got one structure of CNTs at each condition. The difference with other groups is

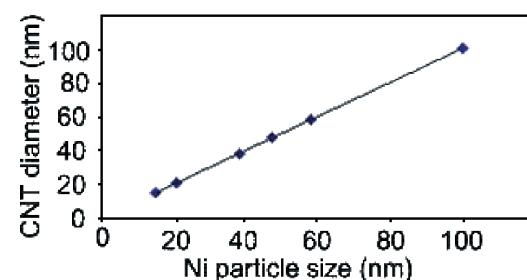


Fig. 2. Plot of CNT diameter as a function of Ni particle size.

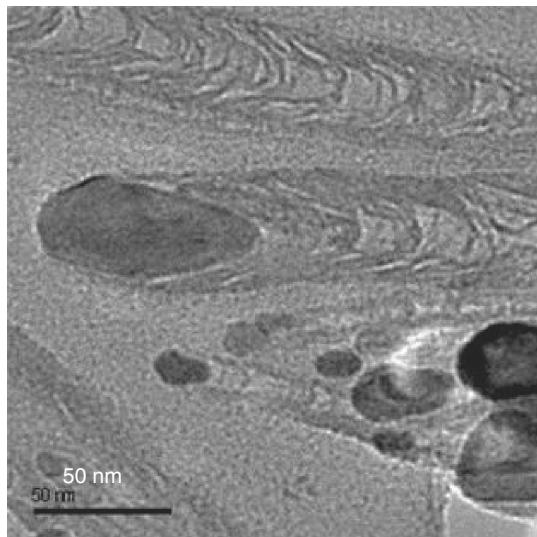


Fig. 3. TEM image of bamboo-shaped CNTs.

that we obtained different structures of CNTs and CNFs on one sample without changing the growth condition. Therefore, we considered that the growth condition is not the only parameter for controlling the structure of CNTs.

We suggest that the pre-growth process is an important factor in controlling the catalyst size and shape for CNTs structure. When the thin Ni film is heated, the mobility of the Ni atoms increases and the thin film then coalesces into small islands due to the surface tension and the compressive stress which result from the mismatch of the thermal expansion coefficients of Ni and SiO_2 .^{14,19} In the present case, the Ni film was thermally annealed to form the Ni nanoparticles as catalyst for CNTs growth in vacuum. Our results suggest that the various diameters and structures

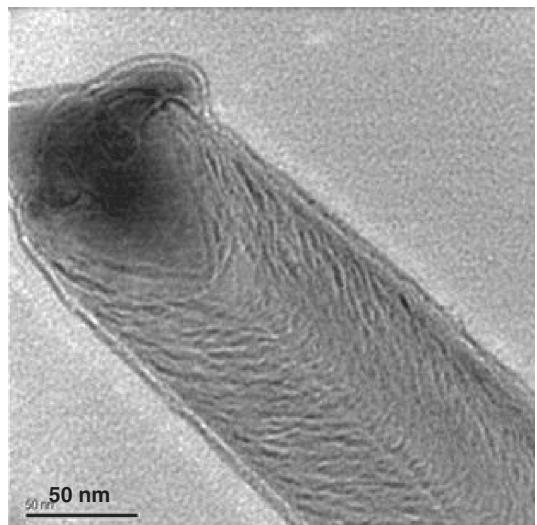


Fig. 5. TEM image of herringbone shaped CNF.

of CNTs are due to the non-uniform distribution of Ni particles formed during the annealing process. It is widely accepted that the different states of catalyst particles determine the CNT structure.¹⁵ Therefore, we considered that under vacuum annealing, the thin Ni film forming into small islands undergoes different states. Various sizes of Ni particles were formed possibly due to the local temperature difference and non-uniform distribution of the thickness deposited by thermal evaporation. The small sizes of Ni particles (under 50 nm) seem to be in the quasi-liquid state after thermal annealing, according to the pearl and quasi-spherical shape on the tip of CNTs.¹⁵ Large Ni particles with sizes above 50 nm were assumed to be in the solid state.

In order to prove our deduction, an experiment for CNT growth at the same conditions except for a thermal

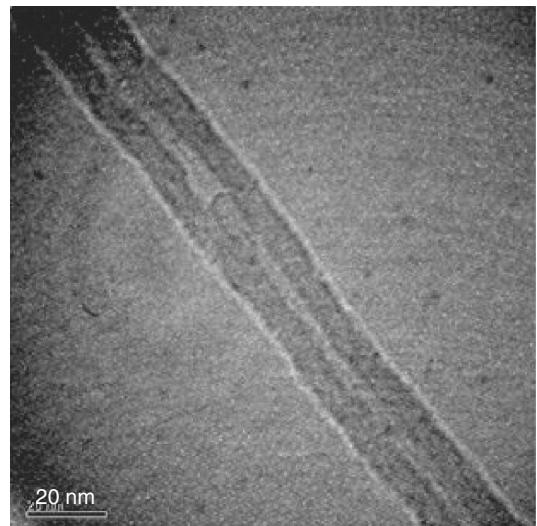


Fig. 4. TEM image of small diameter CNT with less tilted graphite planes inside the core.

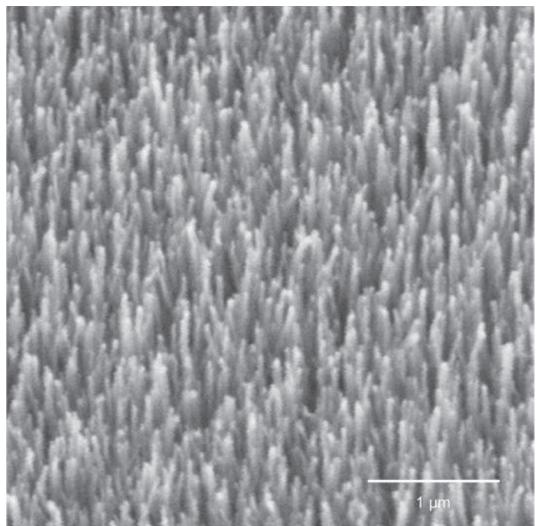


Fig. 6. SEM images of uniform CNTs grown on Ni coated substrate annealed in 1.5 Torr H_2 followed by PECVD process.

annealing in a 50 sccm flowing H₂ at 1.5 Torr was also carried out. Figure 6 is an SEM image showing that the CNTs have more uniform diameter at an average size of 35 nm. All of the CNTs have bamboo-shaped structure according to the Ni shape and size. Figure 7 shows the Ni nanoparticles distribution after the Ni thin films coated sample annealed in vacuum and in H₂. We observed that more uniform Ni nanoparticles were formed during the annealing process in H₂ (Fig. 7(b)) than annealing in vacuum (Fig. 7(a)), where the restructuring of the thin metal film is more effective in H₂. H₂ can minimize the oxidation of the metal at an elevated temperature, while higher gas pressure results in small islands height and uniform distribution.²⁰ Therefore, by increasing the H₂ pressure at the annealing process, more quasi-spherical Ni nanoparticles will be formed. The spherically shaped Ni nanoparticles under 20 nm are preferable for hollow CNTs synthesis. The pearl or droplet like shapes of Ni nanoparticles (i.e., between 20 to 50 nm) dominate the growth of bamboo shaped CNTs, while the large solid sharp end Ni

particles (i.e., more than 50 nm) promote the growth of herringbone shaped CNFs.

4. CONCLUSIONS

Bamboo shaped CNTs and herringbone shaped CNFs were synthesized on the same sample in PECVD at an elevated temperature of 750 °C using Ni as the catalyst. It is found that the size and structure of the Ni nanoparticles deeply influence the diameters and structure of the grown CNTs and CNFs. The diameters of the CNTs are close to the sizes of the Ni nanoparticles on the tips. CNTs with more or less compartments inside the hollow core (Bamboo shape) have a pearl shaped Ni on the tips. The diameter of bamboo shaped CNTs vary from 20 to 50 nm. Herringbone shaped CNFs with diameter larger than 50 nm have the solid sharp end Ni on the tips. We propose that by controlling the pre-growth condition, for example, annealing the sample in H₂ environment instead of annealing in high vacuum, would result in uniformly distributed CNTs formation and limit the CNFs (which are classified with diameter larger than 50 nm) growth.

Acknowledgments: The authors would like to acknowledge Mr. Ian Wright of the York-JEOL Nanocenter for TEM support. The authors would like to thank for Mr. Malcolm Law and Mr. Jonathan Cremer for the maintenance of the equipment and JLS for their support with the modification of the MPS1400.

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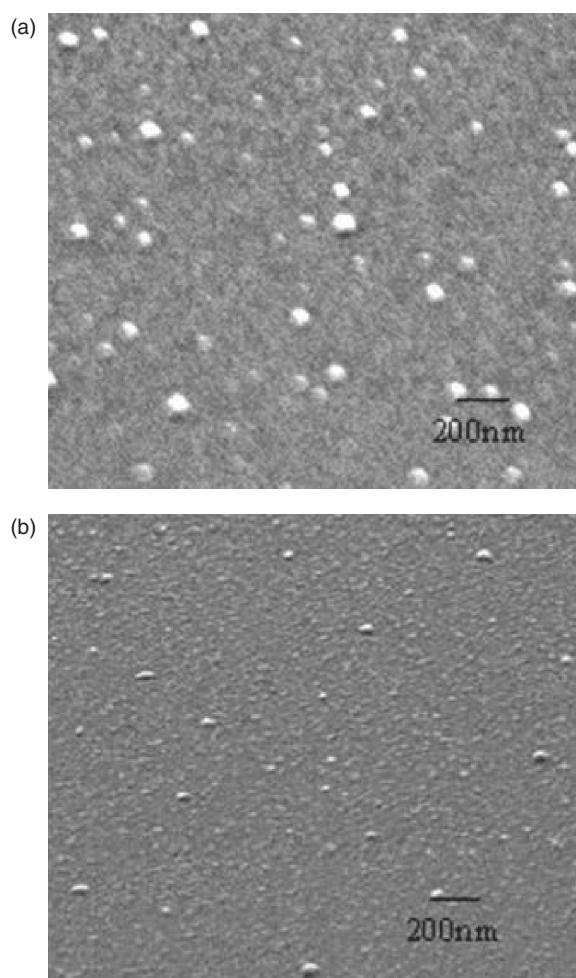


Fig. 7. SEM images of Ni nanoparticles after Ni thin film coated sample annealed in (a) 4×10^{-6} vacuum and (b) 1.5 Torr in H₂, at a ramping temperature up to 750 °C for 30 minutes.

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Received: 12 January 2008. Accepted: 20 July 2008.