Morphology and Structural Characterization of Carbon Nanowalls Grown via VHF-PECVD

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Abstract. A 150 MHz very high frequency plasma enhanced chemical vapor deposition (150 MHz VHF-PECVD) system was utilized to fabricate two-dimensional carbon nanostructure from the mixture of methane and hydrogen. Morphology and structural properties of the grown nanostructure were investigated by FESEM imaging and Raman spectroscopy. Carbon nanowalls (CNW) with dense and wavy-like structure were successfully synthesized. The wavy-like morphology of CNW was found to be more distinct during growth at small electrode spacing and denser with increasing deposition time due to better flux of hydrocarbon radicals to the substrate and higher rate of reaction, respectively. Typical characteristics of CNW were observed from strong D band, narrow bandwidth of G band and single broad peak of 2D band of Raman spectra indicating the presence of disordered nanocrystalline graphite structure with high degree of graphitization.

1. Introduction

Since the breakthrough made by Novoselov et al. [1], graphene-based carbon nanostructures also known as two-dimensional carbon nanostructures (2DCN) have been extensively studied due to their excellent intrinsic properties. Recently, 2DCN have found their application in variety of fields including biosensor, field emission, supercapacitor, blackbody absorber and hydrophobic coating [2-6]. The versatility of 2DCN has offered many development and improvement in engineering field as the next generation superior material in nanoelectronics, energy storage and solar device [7,8].

In principal, 2DCN are a self-organized, stacked flat graphene sheets forming graphitic building block of walls or petal-like structure and have been known by several names such as carbon nanosheets (CNS), carbon nanoflakes (CNF) and carbon nanowalls (CNW). Their structure exhibits thin sharp edges with high aspect ratio that is typically in the range of few nanometers to tens of nanometers [9-11]. For example, CNW is composed of combination of planar graphene layers, stacking towards each other to form almost vertical graphitic walls, with thin sharp edges of the wall determine its aspect ratio.

There have been numerous reports regarding the growth method of CNW found in the literature. In general, chemical vapor deposition (CVD) method such as hot filament CVD (HFCVD), microwave plasma enhanced CVD (MPCVD), MPCVD with hydrogen radical injection and radio frequency plasma enhanced CVD (RFPCVD) have been adopted to synthesize CNW [3,11-14]. Carbon
precursors such as methane, acetylene and tetrafluorocarbon have been widely employed. Each of these methods owned different advantages in terms of film density, wall size and film controllability.

To date very few reports have managed to produce CNW with controllable film morphology. This feature is crucial since its application is highly dependent on film density and structural arrangement of the walls. Current researches on the fabrication of CNW often employed a highly modified PECVD system such as MPCVD and RFPCVD with hydrogen radical injection. Their system configuration is more complex and expensive compared to conventional PECVD 13.56 MHz RF plasma due to presence of magnetron component, and requires two-stage plasma source to operate. In addition, the synthesis of CNW employing a VHF-PECVD system is less to be found in the literature. In most reports, the plasma regions of either direct or remote plasma setup are not stated.

In this paper, the synthesis of CNW by using a capacitively coupled VHF-PECVD with working frequency at 150 MHz has been reported. The studied parameters were electrode separation (anode to sample stage), deposition time and type of substrates. This work focused on the investigation of surface morphology and structural properties of the grown CNW. The potential of capacitively coupled PECVD employing VHF radio frequency with remote plasma setup was elucidated in this report.

2. Experimental works
2.1. Sample preparation and materials
Fused silica (quartz) glass and Si crystal (University Wafer Inc.) were used as substrate throughout this study. All substrates were cut into a square dimension of 10 mm x 10 mm. The substrates were cleaned by immersion in acetone (Merck Company), ethanol (HACH Company) and deionized water with ultrasonic bath for 15 minutes to eliminate oil, dirt and debris originated from substrate cutting. High purity methane (CH\textsubscript{4}) and hydrogen (H\textsubscript{2}) of 99.999% were utilized as the carbon source and carrier gas for the nucleation of the CNW film.

2.2. Nickel catalyst deposition
A RF magnetron sputtering system (Penta Vacuum Inc.) was utilized to deposit nickel (Ni) thin film on quartz substrate. The sputter pressure for Ni deposition was fixed at 6.0 x 10\textsuperscript{-3} Torr. 50 W of RF power was set and the RF impedance matching were adjusted until a purple glow-discharge of plasma can be seen through the chamber viewport. Sputtering parameters were fixed at 50 W of RF power, 5.0 sccm of argon supply, 6.0-6.5 x 10\textsuperscript{-3} Torr of deposition pressure and base pressure of 1.0 x 10\textsuperscript{-5} Torr. Sputtering time was set to 105 seconds. Sputtering parameters were maintained at low power and low argon flow rate in purpose to induce low deposition rate and high uniformity of Ni thin film.

2.3. Synthesis of carbon nanowalls with varying electrode separation
A 150 MHz VHF-PECVD system was equipped with a linear motion feed through attached to the anode, thus enabling the adjustment of substrate position relative to the anode. The gas flow rate was set at 17.0 sccm (CH\textsubscript{4}) and 5.0 sccm (H\textsubscript{2}) with deposition time of 3000 s. RF power and temperature were kept constant at 20 W and 750 °C, respectively. The electrode separation was varied from 25 mm to 55 mm; with a certain electrode distance was set for each run. After the introduction of CH\textsubscript{4} and H\textsubscript{2} into the reactor, the linear motion feed through knob was adjusted to the desired substrate position before the growth process was initialized.

2.4. Synthesis of carbon nanowalls with varying deposition time
Flow rate of CH\textsubscript{4} and H\textsubscript{2} were maintained at 17.0 and 5.0 sccm, respectively. For this experiment, the growth time was varied from 20 minutes to 50 minutes with each run was set at a specific growth pressure. Reactor pressure was maintained at 7.7 x 10\textsuperscript{-2} Torr, with substrate temperature of 750 °C, RF power of 20 W and electrode distance at 30 mm.
2.5. Investigation of surface morphology and structural properties of carbon nanowalls

FESEM from Zeiss (SUPRA 35VP) was utilized to gather information on topographical (in 2D image), surface area coverage (CNW density) and size of the deposited CNW films. The CNW length and wall width were estimated by using the built-in software from the FESEM controller. Raman spectrometer (Renishaw inVia Raman Microscope) was utilized to investigate CNW film structural properties. This model is equipped with He-Cd laser for the monochromatic light source. In this study, a 514 nm laser source was utilized as light excitation of the sample. All samples were scanned in the range of 1000 cm\(^{-1}\) to 3500 cm\(^{-1}\) at five different spots with three repetitions to minimize error in signal count.

3. Results and discussion

3.1. Influence of electrode separation and deposition time on CNW surface morphology

Figure 1(a-c), provides the aerial view of SEM images of grown CNW at various electrode separations. Figure 1(a) and 1(b) shows that the CNW have been successfully grown with a wavy-like structure. Denser CNW is achieved as electrode distance increases from 25 mm to 45 mm with more distinct shape at smaller spacing. However, the morphology changed drastically during growth at 55 mm.

Figure 1. SEM images of CNW grown at different electrode separation: (a) 25 mm, (b) 45 mm, and (c) 55 mm with growth condition of 17:5 (CH\(_4\):H\(_2\)) sccm; 20 W RF power; temperature of 750°C and growth time of 3000 s. All images were captured at 20000 times magnification.

Figure 2 (top) verifies the average wall density and size of CNW grown at different electrode separation. They are found to be ranging from 11 wall/μm\(^2\) to 24 wall/μm\(^2\) and 0.46 μm to 0.48 μm, respectively, with highest density is obtained during separation of 45 mm. It is clear that wall size does not affected during growth at small spacing.

In contrast, during growth at largest electrode separation, 55 mm, dramatic change in morphology was observed thus causing the wall size to increase 115.52 μm. Figure 1(c) shows agglomeration of graphene flakes characterized by its round shape attributes and absence of vertical nanowalls. The growth of CNW is directly influenced by the supply of carbon species to the surface [17]. Thus, in a VHF-PECVD that employs remote plasma setup, the directed flux of C\(_2\) hydrocarbon species or radicals towards the substrate surface may be varied by distance.

Figure 3(a-d) presents the top view SEM images of CNW morphology grown at different deposition time. It can be noted that CNW density increases with deposition time. It also can be noticed that wall spacing becomes smaller as the deposition time increases.
Figure 2. Relationship of wall density and size at varying electrode separation (top) and deposition time (bottom).

Figure 2 (bottom) shows the average wall density and sizes were found to be ranging from 24 wall/μm² to 38 wall/μm² and 0.17 μm to 0.48 μm, respectively. The highest average density is obtained during growth at 3000 s with value of 38 wall/μm². In contrast, largest average wall size is observed during growth at 2400 s with value of 0.48 μm. This distinct change in morphology is due to higher rate of surface reaction of hydrocarbon radical species at an elevated temperature [16].
Figure 3. SEM images of CNW grown at varying deposition time: (a) 1200 s, (b) 1800 s, (c) 2400 s and (d) 3000 s with growth condition of 17:5 (CH₄:H₂) sccm; 20 W RF power; and temperature of 750°C. All images were captured at 20000 times magnification.

3.2. Influence of nickel catalyst and substrate type on CNW surface morphology

Figure 4 shows a comparative top view SEM image of grown CNW on Ni-catalyzed Si and silica substrate. It was found that the CNW is denser during growth on single crystal (sc)-Si substrate compared to silica. The average length and width of CNW were also drastically reduced. It also can be noted that, the morphology of CNW grown on sc-Si was composed of higher number of vertically standing walls compared to silica where a wavy and slightly inclined structure is dominant. The calculated average density of CNW grown on silica and sc-Si is 24 wall/μm² and 37 wall/μm², respectively (results not shown here). No noticeable change in average wall size as the value slightly changed from 0.63 to 0.64 μm. This result suggests that the density of CNW has increased approximately 37% during growth on sc-Si while maintaining its size. Presence of Ni catalyst catalyst (top) and single crystal p-type Si coated with Ni catalyst (bottom) somehow did not influence the growth morphology of CNW. Still, it can be claimed that the growth rate of CNW is higher compared to silica.
3.3. Raman scattering of grown CNW

Raman spectra of grown CNW are represented in figure 5(a-c). It was found that all experimental sets inherit similar bands located at peak position of acceptable range as has been reported in many literatures [18,19]. These bands are D (at ~ 1347 cm\(^{-1}\)), G (at ~ 1575 to 1577 cm\(^{-1}\)), D’ (at ~ 1609 cm\(^{-1}\)), 2D (at ~ 2683 to 2687 cm\(^{-1}\)) and D+G (at ~ 2925 cm\(^{-1}\)). The existence of D and G band can be considered as the molecular fingerprint of carbon-based materials and were observed in all poly-aromatic hydrocarbons.

The occurrence of D band in CNW is mainly due to disorder that corresponds to crystallographic or lattice defects of the structure [8]. It also can be related to the disorder, induced by finite crystallite size in nanocrystalline graphite (nc-graphite) [15]. Furthermore, the D band is always absence in the Raman spectra of graphene and defect-free graphite [11]. Thus, the high intensity of D band obtained in every experimental set was originated from the disorder activated by lattice defects, small crystallite size and density of edges of the grown CNW.

For the G band or graphite band, its bandwidth, \(W_G\) is prone to crystal imperfections of the graphite regions and has been a measure of graphitization of graphite-based structure [8,11]. A narrow bandwidth of the G band can be considered as a graphitic structure that possesses high degree of graphitization or in other words, low disorder nc-graphite.

The occurrence of D’ peak is also due to the imperfection or disorder of nc-graphite regions in the CNW film. Interestingly, the D’ peak is only revealed in a low disorder graphite structure and is absent in highly ordered graphite. In the case of disordered graphite, the peak broadening of G and D’ band often represents disorder where broader G band will be accompanied by the elimination of the D’ band and shifts into a broad single line G peak. Cho et al. [14] suggest that the D’ band is originated from the breaking of symmetrical bonding due to finite crystalline size of the graphite regions representing a highly ordered nc-graphite region constituting the CNW.

Second order D peak known as 2D band was observed in every sets of experiment. This 2D band is due to stacking behavior of sp\(^2\) orbitals in planar periodic arrangement in graphite, a misaligned stacking behavior is known as turbostratic (without AB stacking). For CNW the 2D peak is a single line with broader bandwidth approximately nearly two times compared to a sharp single line obtained in Raman spectra of a monolayer graphene [20]. This indicates that CNW is composed of 2D graphite structure.
3.4. **CNW film quality during growth at varying electrode separation and different substrate type**

For growth at various electrode separation, no significant change can be observed in value of $I_D/I_G$ (refer Table 1). Still, higher crystallinity of CNW can be achieved during growth at 45 mm electrode separation due to its lower defect density. This also can be supported its $I_D/I_G$ value however, too large electrode separation may promote growth of CNW with high crystallographic disorder. This may be due to the limited supply of radicals flux and higher collision between radical species as the space or distance between anode and cathode become larger thus inducing low quality of nanocrystalline graphite. It also can be derived that as the electrode distance grew larger, the $W_G$ slightly increases. This indicates that at larger electrode distance, CNW with lower degree of graphitization are produced.

Raman spectra obtained from the synthesis of CNW on different substrate with the presence of Ni catalyst. Still, it was found that all five main bands ($D$, $G$, $D^*$, $2D$ and $D+G$) were detected for all samples. Strong $D$ band is collected during growth on sc-Si compared to silica with a value approximately twice as much. This may be related to the high thermal conductivity of Si and the
number of vertically grown CNW on sc-Si [16], where higher fractions of edges were involved thus inducing stronger D band signal. In addition, the $I_D/I_G$ (refer Table 2) ratio during growth on sc-Si revealed that even though the structure is high in defect, it exhibits better crystallinity due to smaller grain size. Based on the $W_G$ value, it can be stated that the degree of graphitization is comparable between growth on sc-Si and silica at an equal amount of deposition time. Thus, it can be claimed that CNW grown on both sc-Si and Silica are constitute of highly graphitized nanocrystalline regions as has been suggested by [15]. However, the nanographite regions will be smaller during growth on sc-Si. It is also important to note that responses obtained during growth on Ni-catalyzed silica were in line with growth without catalyst. Thus, this revealed that the presence of Ni catalyst had no influence on the structural characteristics of CNW. This claim was also suggested by [3].

**Table 1.** Intensity ratio and bandwidth of Raman signal during growth at varying electrode separation

| Electrode separation (mm) | $I_D/I_G$ | $I_D'/I_G$ | $I_{2D}/I_G$ | $W_G$ (cm$^{-1}$) | $W_{2D}$ (cm$^{-1}$) |
|---------------------------|-----------|------------|--------------|------------------|---------------------|
| 25                        | 1.66      | 0.29       | 0.53         | 38               | 83                  |
| 45                        | 1.55      | 0.28       | 0.56         | 42               | 86                  |
| 55                        | 2.04      | 0.31       | 0.48         | 50               | 104                 |

**Table 2.** Intensity ratio and bandwidth of Raman signal during growth of CNW with the presence of Ni catalyst.

| Type of Substrate | $I_D$ (cts) | $I_D/I_G$ | $I_D'/I_G$ | $W_G$ (cm$^{-1}$) | $W_{2D}$ (cm$^{-1}$) |
|------------------|-------------|-----------|------------|------------------|---------------------|
| sc-Si, $G_t=20$ min | 22652       | 2.77      | 0.41       | 52               | 93                  |
| Silica, $G_t=20$ min | 13040       | 1.81      | 0.32       | 50               | 91                  |
| Silica, $G_t=40$ min | 25160       | 1.67      | 0.26       | 42               | 85                  |

**4. Conclusion**

A capacitively coupled 150 MHz VHF-PECVD with remote plasma setup is a promising technique to synthesize CNW structure. From this method, a dense wavy-like CNW structure was successfully grown. Morphology of CNW is possible to be controlled by varying the electrode distance and deposition time. Apart from that, the quality of the CNW structure can be claimed as highly graphitized which composed of finite size of nanocrystalline graphite regions. In summary, CNW can be considered as a unique 2D carbon nanostructure due to its composition of less ordered graphite made up of small nanocrystalline graphite domain with a high degree of graphitization.

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