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RAMAN ANALYSIS OF SINGLE-WALLED CARBON NANOTUBE GROWN FROM SPIN-COATED COBALT CATALYST AT DIFFERENT TEMPERATURES

Nor Najihah Zulkapli, Nur Azura Ithnin, Nik Mohd Azren and Mohd Asyadi Azam
Carbon Research Technology Research Group, Faculty of Manufacturing Engineering, UniversitiTeknikal Malaysia Melaka, Hang Tuah Jaya, Durian Tunggal, Melaka, Malaysia
E-Mail: asyadi@utem.edu.my

ABSTRACT

Single-walled carbon nanotubes (SWCNTs) were grown from spin coated Co catalyst thin films using the alcohol catalytic chemical vapor deposition (ACCVD) method for different CVD processing temperatures and at a fixed 15 min CVD processing time. The presence of SWCNT was confirmed by Raman radial breathing mode peak confirmation. The Raman intensity of G band over D band for the as-grown SWCNTs was decreased with increasing CVD processing temperatures. Raman intensity analysis in the radial breathing mode region shows a relatively wide distribution of SWCNTs grown for all CVD processing temperatures, but, owing similar trend of G band and D band intensity decrement as increasing the CVD processing temperatures. In this paper, it was suggested that Co catalyst poisoning and SWCNT burning occurred when the CVD processing temperature was more than 700 °C. The structural properties of the SWCNTs grown have been investigated by Raman spectroscopy with 532 nm laser excitation.

Keywords: single-walled CNT, Raman analysis, spin coating, co catalyst,CVD temperatures.

INTRODUCTION

Ever since the world knows about the existence of carbon nanotube (CNT), it has been a spark to initiate the desire of researcher to know in deep the ability of this tiny and seamless structure. People are experimentally trying to grow and apply this unique structure in many methods; arc discharge, laser ablation and chemical vapour deposition, and applications; energy storage devices and nanocomposites (Frackowiak and Beguin, 2001) (Hiraoka *et al.*, 2010). However, single-walled carbon nanotubes (SWCNTs) have attracted more interest rather than multi-walled carbon nanotubes (MWCNTs) due to their physical properties originating from their electronic and molecular structures. The novel properties belong to SWCNTs hence lead to extensive study on that particular structure worldwide.

The common characterization methods used to study the CNT structure are using Raman spectroscopy and scanning electron microscopy (SEM). After all, Raman spectroscopy is the most chosen method to study the structure whereas it is a non-destructive, simple sample preparation and easily detect the presence of CNT. The crucial characteristic to determine the existence of SWCNTs is radial breathing mode (RBM). In fact, there is another characteristic that can be counted to detect the presence of SWCNT, but it is infrequently used in scientific reports. Therefore, that characteristic will be discussed in this paper.

Furthermore, commercial method for catalyst deposition is by physical method like sputtering and electron-beam deposition. Despite, these methods will lead to efficient use of production energy and materials, and the usability of production facilities (Miyasako *et al.*, 2010). For this reason, a new approach of catalyst thin film formation by using solution process was proposed to substitute the commercial method owing to low equipment costs, process simplicity and direct patternability by using printing techniques (Azam *et al.*, 2014).

Hence, in this paper, spin-coated Co catalyst thin films were used to study the dependency of growth temperature on the quality and structure of as-grown CNT. Raman spectroscopy was used to perform this study.

EXPERIMENTAL

Alcohol catalytic chemical vapour deposition (ACCVD) method was used to grow CNTs from spin-coated Co catalyst (Azam *et al.*, 2010). A 300-nm-thick thermally oxidized SiO_2 layer on p-type silicon wafer (100±0.5mm) was used as the substrate. By spin coating process, Co catalyst thin films were deposited on (15 x 15) mm^2 Si/SiO_2 substrate (Zulkapli *et al.*, 2014) (Azam *et al.*, 2014). The spin coated Co catalyst subsequently transferred and placed in an ultra-high-vacuum CVD furnace (MILA-3000). The quartz tube used for this furnace was in dimension of 1200 mm length and 26 mm in inner diameter. The tube was then evacuated using oil-free scroll pump to 0.4 Pa. In order to prevent the oxidation of Co, Ar gas was injected into the system at a pressure of 400 Pa concurrently with 5 min rapid heating. Once the growth temperature was reached, quickly the Ar gas flow was stopped and ethanol vapour was immediately lead off into the system at flow rates of 100-150 sccm. The growth process was fixed at 1.5 kPa internal pressure and 15 min CVD processing time. After the growth process, the ethanol gas flow was stopped and the samples were left for cooling to room temperature. Raman spectroscopy (UniRAM-3500) with laser excitation of 532 nm was used to characterize the as-grown SWCNTs.

RESULTS AND DISCUSSIONS

Raman intensity analysis between graphitic structure mode (G band) and Disorder-Induced Mode (D band)

G band, D band and I_G/I_D ratio are important characteristics to determine the quality of carbon nanotubes (CNTs) produced. Disorder-induced mode so-called D-band is a characteristic of disordered features in graphite sheets which involve phonons from the graphite K-point (Terrado et al., 2006). Normally, it lies between 1200 and 1400 cm^-. The D-band observed in Raman spectra of as-grown CNT was found at range of 1319-1330 cm^-(Figure 1-a). As the CVD processing temperature increased from 700 ºC to 850 ºC, the D-band intensities were decreased. Moreover, the peaks were rather blunt as compared to G-band. These characteristics indicated that the as-grown CNT had low content of amorphous in which the carbon atoms were fully graphitized into CNT structures.

Besides, high-energy mode is indicates original graphite features in which corresponds to the tangential modes of the graphitic planes in the CNTs. The analyzed result revealed that the G-band was optimum at CVD processing temperature of 700 °C and diminished up to 850 °C (Figure-1-a). It also can be seen that the G-band at all CVD processing temperatures consist of shoulder at the left side of peaks. The presence of shoulders denoted to as semiconductor and metallic properties of the tubes. This corresponding signal happened due to the electronic density of states of semiconducting (Lorentzian lineshape) and metallic (Breit–Wigner–Fano lineshape). In addition, like radial breathing mode, this structure also can be used to reveal the presence of single-walled CNT; due to the vibrations of carbon atoms along the circumferential direction of the SWNT (TO phonon) (M.S.D resselhaus *et al.* 2005; Pimenta *et al.*, 1998; Brown *et al.*, 2001).

Other than disorder-induced and high-energy modes, I_G/I_D ratio is also crucial and can be taken into account to measure the quality of as-grown CNT. It is also an indicator for structural order of CNT. As the growth temperature was increased from 700 to 850 ºC, the I_G/I_D ratio kept on decreasing from 6.23 down to 2.48 (Figure-1-b). This trend explains that by adding more heat to the growth process will reduce the quality of as-grown CNT. The optimum ratio at 700 ºC was also an indication of the presence of high-quality SWCNTs. Thus, an early conclusion can be made that high quality of SWCNTs can be grown at temperature of 700 ºC by alcohol catalytic chemical vapor deposition (ACCVD) system. It is also suggested that Co catalyst poisoning and SWCNT burning occurred when the CVD processing temperature is more than 700 ºC.

Radial breathing mode

Radial breathing mode (RBM) is the easiest indicator and most frequent method used to detect the presence of SWCNTs. Raman shift corresponding to RBM normally in range of 100 to 400 cm^{-1} (Saito, Dresselhaus and Dresselhaus, 1998; Dresselhaus and Eklund, 2000; Dresselhaus *et al.*, 2005). The Raman analysis of the RBM region showed that there were 6 strong RBM peaks exhibited at CVD processing temperature of 700 ºC and 750 ºC in which the RBM peaks that exhibited at 700 ºC were higher and narrower than at 750 ºC (Figure-2). However, as the CVD processing temperature increased to 800 ºC, there were only 5 strong RBM peaks left, including the third RBM peak that has been split into two. The presence of strong RBM peak kept on decreasing to 4 peaks at CVD processing temperature of 850 ^{0}C. Based on this trend, it can be suggested that the suitable temperature for SWCNT growth was at 700 ^{0}C. On the other hand, since the presence of SWCNTs were confirmed by the presence of RBM peaks, therefore, it can strengthen the indication on the presence of shoulder at the left side of G-band also can be used to reveal the presence of SWCNTs. The blank SiO_2/Si substrate was measured as reference. Si peak was clearly observed at around Raman shift of 302 cm^- for all samples growth at various CVD processing temperatures.

The possibility of Si peak detection was due to the reflected from the SiO2 underlayer; the presence of Si peak confirmed the nano-scale of spin coated Co catalyst thin film onto SiO2/Si substrate. Hence, it was proof that spin coating process is able to substitute the common conventional deposition techniques so that the amount of wasted expensive materials and production cost can be cut-off. Spin coating process is not only able to deposit nano-scale of catalyst thin film, but also able to produce good quality of SWCNTs by controlling the size of catalyst nanoparticles (Azam *et al.*, 2015).

Correlation between the RBM frequency with SWCNT diameter is well describes using empirical relationship of;

$$d_{tube} = \frac{248}{\omega_{RBM}}$$

where λ is the Raman shift (cm^-) and d_{tube} (nm) is the SWCNT diameter (Cui *et al.*, 2003; Takagi *et al.*, 2006; Ghoranevis *et al.*, 2008; Azam *et al.*, 2010). Other than using the equation, it would be interesting to confirm the morphology of single walled CNT using microscopic technique. As shown in Figure-2, it can be seen that the dominant peak that appeared at every CVD processing temperatures was at the 4th peak. The diameters of SWCNT calculated by the mentioned equation at that

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particular peak were 0.91, 0.91, 1.04 and 0.92 nm, accordingly. It can be observed that increased in CVD processing temperature lead to an increase in the diameter of the as-grown SWCNT. However, the measured tube diameters were less than 2 nm. The observation indicated that the diameter of SWCNTs was quite sensitive on CVD processing temperature. Therefore, to obtain desired diameter of SWCNTs, selection of CVD processing temperature is very crucial.

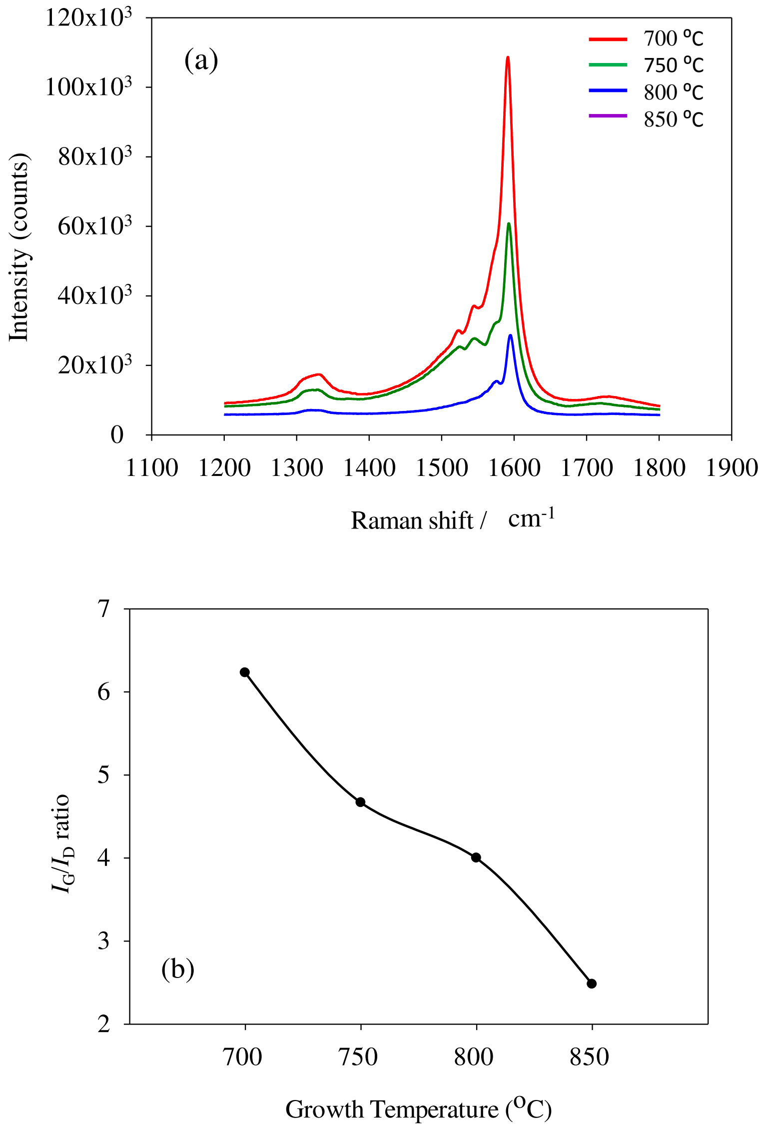

Figure-1. (a) D-band and G-band spectra, and (b) I_G/I_D ratio of as-grown CNT from spin coated cobalt catalyst after different growth temperature on SiO_2/Si bulk substrate.

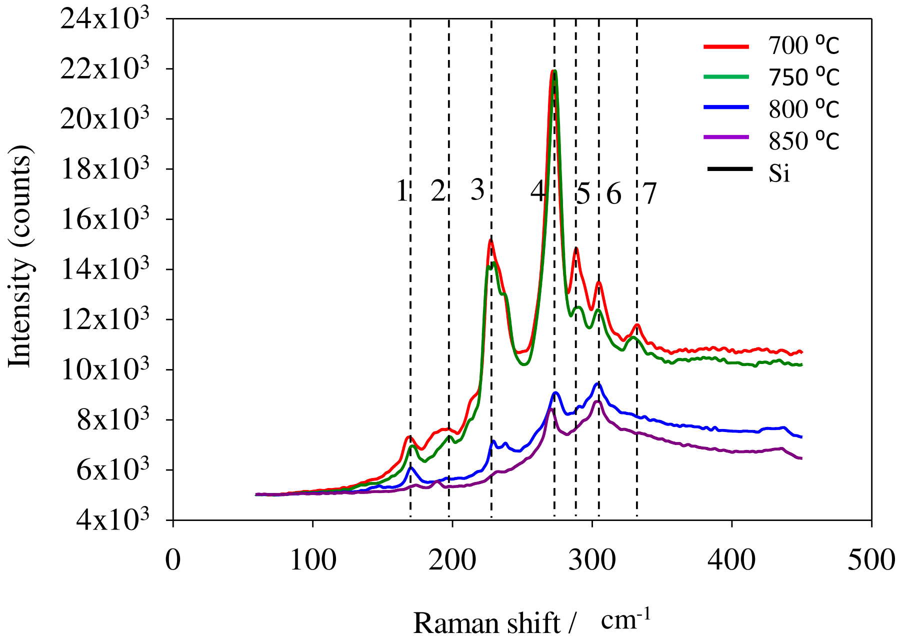

Figure-2. Raman spectra analysis at RBM spectra for samples growth at various CVD processing temperatures.

CONCLUSIONS

SWCNT growth from spin-coated Co catalyst thin films at different CVD processing temperature (700 ^{0}C, 750 ^{0}C, 800 ^{0}C and 850 ^{0}C) using the alcohol catalytic CVD method has been investigated. Structural analysis by Raman scattering measurement wih laser excitation of 532 nm was used to determine the quantity and quality of as-grown SWCNTs. It was confirmed that SWCNTs can be effectively grown at 700 ^{0}C using the alcohol catalytic CVD (ACCVD) system. High amount of SWCNTs was found at that CVD processing temperature based on the number of strong RBM peaks exhibited in RBM region. The as-grown SWCNTs at 700 ^{0}C also have good quality based on the highest value of I_G/I_D ratio measured at that temperature. The smallest mean diameter as compared to other growth temperature also can be a proof that 700 ^{o}C is the optimum temperature to grow SWNTs by ACCVD system. Therefore, it is suggested that CVD temperature of 700 ^{o}C is the optimum temperature to grow SWCNT from the spin-coated Co catalyst by ACCVD technique.

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