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Conference Paper · March 2014

DOI: 10.13140/RG.2.1.4375.3447

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Effect of Growth Temperature on Vertically-Aligned Carbon Nanotubes Prepared by Radio-Frequency Plasma-Enhanced Chemical Vapor Deposition

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ABSTRACT

Vertically-aligned carbon nanotubes (VACNTs) were synthesized by radio-frequency plasma enhanced chemical vapor deposition (RF-PECVD), using CH_4/H_2 as a feeding gas mixture. Stainless steel substrate, coated with cobalt catalyst was used for the growth of VACNTs. The effect of growth temperature was examined in the range of 450 °C to 750 °C. The synthesized VACNTs were characterized by scanning electron microscopy (SEM), laser microscope, X-ray diffraction (XRD), and infrared (IR) spectroscopy. The development of VACNTs is optimized at 650 °C and further increase in temperature lead to randomly oriented CNTs.

Keywords

Vertically-aligned carbon nanotubes (VACNTs); radio-frequency plasma enhanced chemical vapor deposition (RF-PECVD); stainless steel substrate; spin coater; characterization.

INTRODUCTION

Carbon nanotubes (CNTs) have attracted special attention among scientists and engineers since their discovery in 1991 [1]. CNTs possess ultimate mechanical and physical properties due to their strong carbon-carbon covalent bonds and unique atomistic structures. Their elastic modulus and strength are in the order of 1 TPa and 50 GPa, respectively [2], their electrical conductivity ranges from about 3×10^4 S/cm to 10^6 S/cm, which is higher than that of copper [3,4], and their room-temperature thermal conductivity ranges from about 3000 W/m.K to 3500 W/m.K, which is higher than that of bulk-graphite which its conductivity is about 2000 W/m.K [5].

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Among various CNTs synthesis methods, chemical vapor deposition (CVD) is widely used due to the following: (1) its capability to produce dense and uniform deposits, (2) ability to grow CNTs on the desired substrate, (3) ability to control growth sites by arranging the catalyst, (4) reproducibility, (5) good adhesion, adjustable deposition rates, (6) ability to control crystal structure, (7) surface morphology and orientation of the CVD products, (8) wide scope in selection of chemical precursors and ability to be produced on an industrial scale efficiently and economically [6].

Plasma enhanced CVD (PECVD) has been known as one of the applicable fabrication techniques to produce vertically aligned nanotubes on various substrates at relatively low temperature. A variety of plasma reactors have been used to grow carbon nanotubes. Radio frequency inductively coupled plasma (ICP) CVD, provides high-density plasma source with 13.56 MHz power supply for CNTs growth [7]. The main advantages of PECVD processing are: its low deposition temperature to avoid defect formation, diffusion and degradation of the metal layer (great for temperature sensitive materials), good dielectric properties of the films, low mechanical stress, and good conformal step coverage [8,9].

There are several routes for catalyst preparation used in the development of CNTs, including physical deposition methods and wet chemical processes [10]. Among wet chemical processes, spin coating was used for the preparation of cobalt catalyst over the stainless steel substrate due to the ease and simplicity of producing large and uniform catalyst thin-film. As consequence it could be used as an economic method for mass production of carbon nanotubes using CVD technique.

Moreover, due to limited studies that have been conducted on the growth of CNTs using different catalysts prepared by spin coating technique, further research will be necessary in order to well understand all the variables affecting the CNTs. Among of these variables temperature strongly affects the growth kinetics and subsequently morphology of grown CNTs. Therefore, this study is focused on examining the effect of growth temperature on CNTs production using radio frequency-inductively-coupled plasma-enhanced chemical vapor deposition (RF-ICPECVD).

EXPERIMENTAL

Materials and chemicals

All the chemicals used in the present investigation are analytical reagent grade. Titanium diisopropoxide bis-(acetyl acetonate), cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), isopropanol were purchased from Fisher scientific. Gases used for PECVD were methane (99.99%) and Hydrogen (99.99%).

Preparation of cobalt nanoparticles on a stainless steel (SS 316) substrate

Prior to coating the catalyst, the SS plate was washed in an ultrasonic cleaner using ethanol as cleaning agent. In this method, titanium precursor mixed with cobalt (II) nitrate solution which consists of $Co(NO_3)_2.6H_2O$ and isopropanol and then spread uniformly on substrate using spin coater at 2000 rpm and 20 s. Then the coated substrate heated to 500 °C for 2hrs.

Growth of CNTs

The synthesis of CNTs by radio frequency plasma enhanced chemical vapour deposition (RF-PECVD) shown in Fig. (1) under the conditions listed in table (1).

Table 1: PECVD operating conditions

Reduction Conditions	
H_2 Pressure (torr.)	5
H_2 Flow Rate (sccm)	50
Power (W)	300
Time (min.)	20
Temperature (°C)	550
Growth Conditions	
Total Gas Pressure (torr.)	10
CH_4 Flow Rate (sccm)	9
H_2 Flow Rate (sccm)	1
Power (W)	300
Time (min.)	60
Temperature (°C)	450, 550, 650, and 750

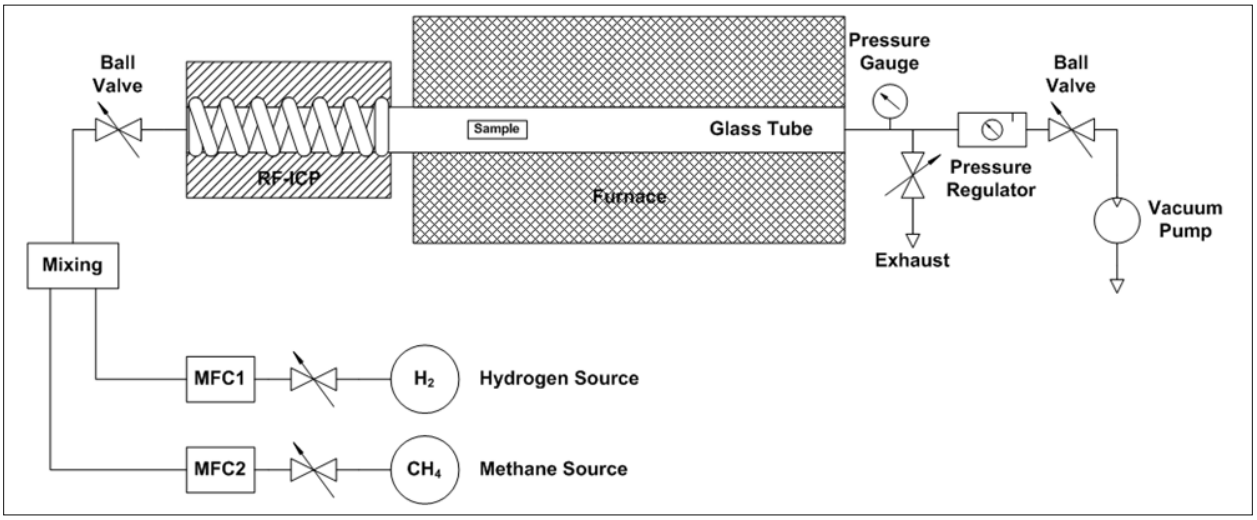


Fig.1: Schematic diagram of PECVD

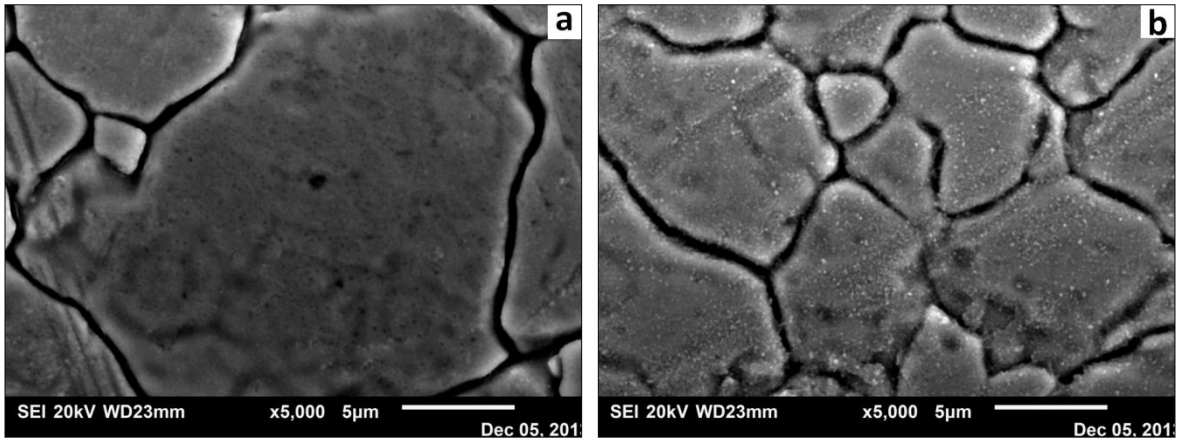
Characterization

Morphology and topography of the coated catalyst and synthesised CNTs were characterized by Scanning electron microscopy (SEM) (JEOL JSM-6010LV) and 3D LASER scanning microscope (Keyence VK-X100). X-ray diffraction (XRD) was operated using (Shimadzu XRD-6100) and functional group characterized by Fourier Transform Infrared (FTIR) spectrometer was completed using (Brucker Vertex 70).

RESULTS AND DISCUSSION

Scanning Electron Microscope (SEM) and 3D LASER microscope Results

Fig. (2) shows the SEM images of the CNTs grown on SS316 substrate at four different temperatures of 450, 550, 650, and 750 °C after 30 min. Compared to free substrate, no CNTs grow at 450 ^{0}C, this could be the reason that the temperature at 450 ^{0}C is not sufficient to make the reaction between the cobalt nanoparticles and the carbon source (CH_4) gas. However a dense vertically aligned arrays was grown at 650 ^{0}C. Further increase in temperature leads to curl like structure indicating a complete saturation of carbon nanotubes. Due to the force of gravity, the grown CNT cannot withstand vertically with the increase in growth temperature.



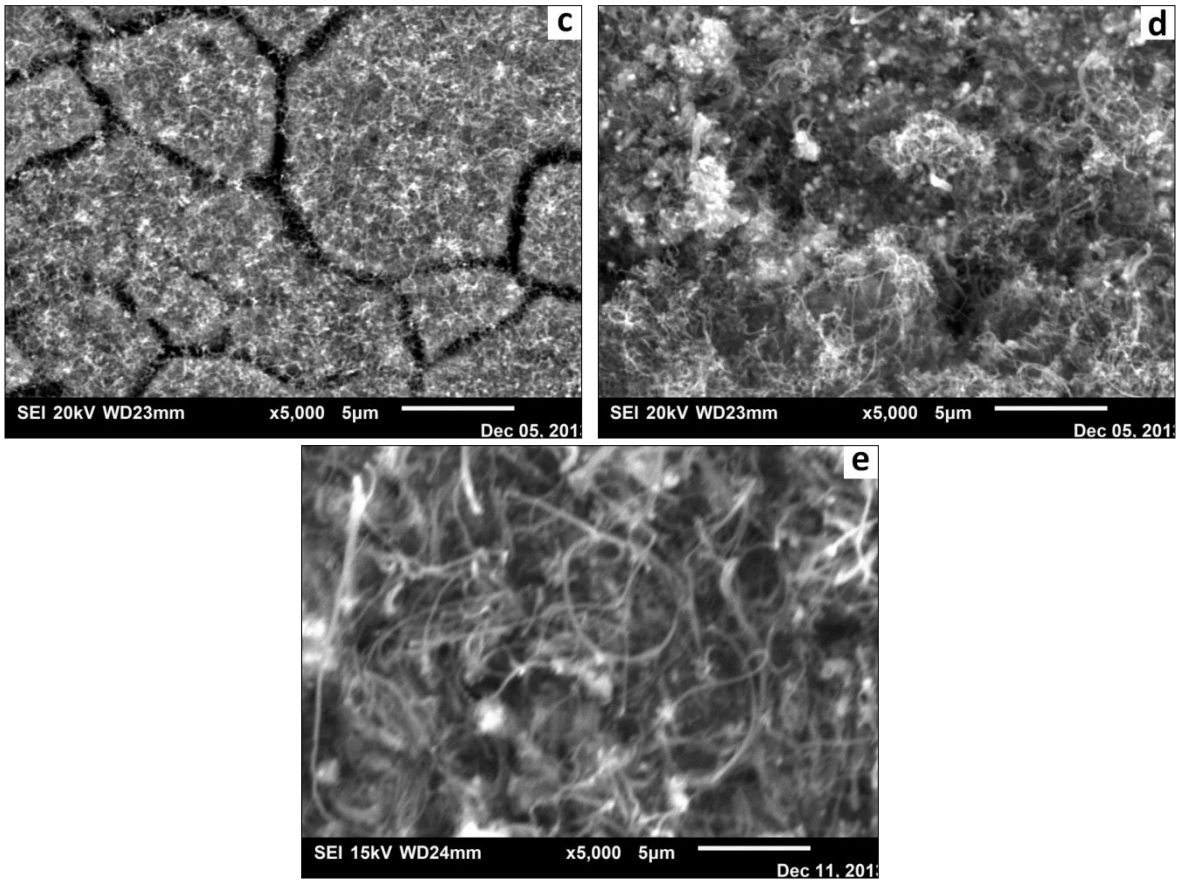
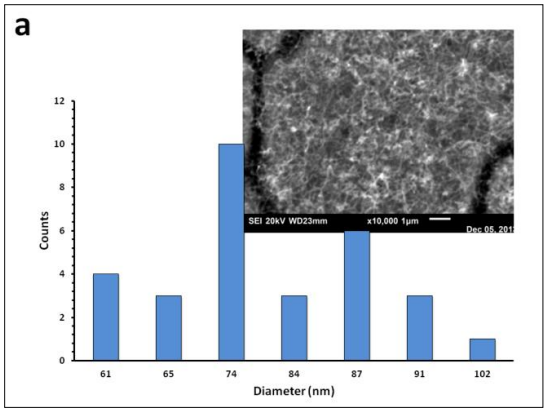


Fig. 2: SEM images of samples obtained at different temperatures: (a) catalyst-coated substrate; (b) 450 °C; (c) 550 °C; (d) 650 °C; and (e) 750 °C.

Fig. 3 shows the statistical variation of grown CNTs diameters with growth temperature. It is clearly seen that CNTs diameter tends to increase with growth temperature. There are no carbon nanotubes grown on the substrate at 450 °C, however, at temperatures of 550, 650 and 750 °C, CNTs were successfully grown with diameters ranging from 61~102 nm, 83~133 nm, and 119~275nm, respectively.



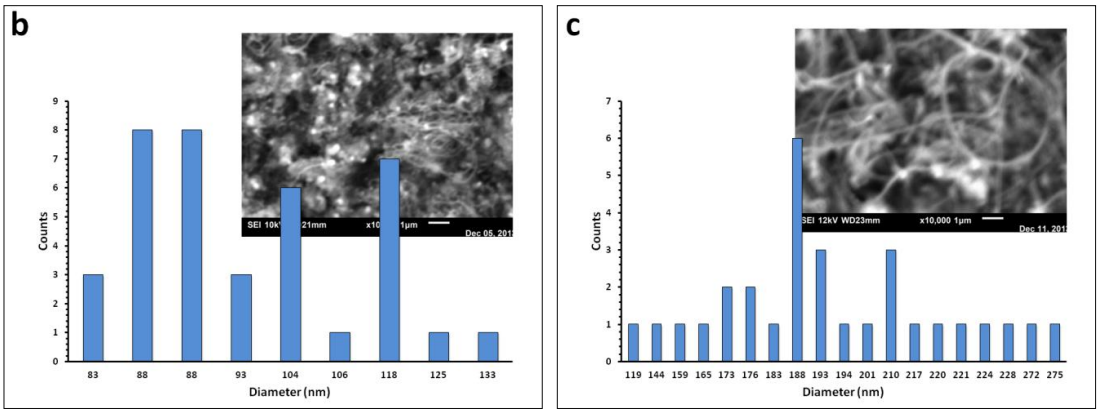
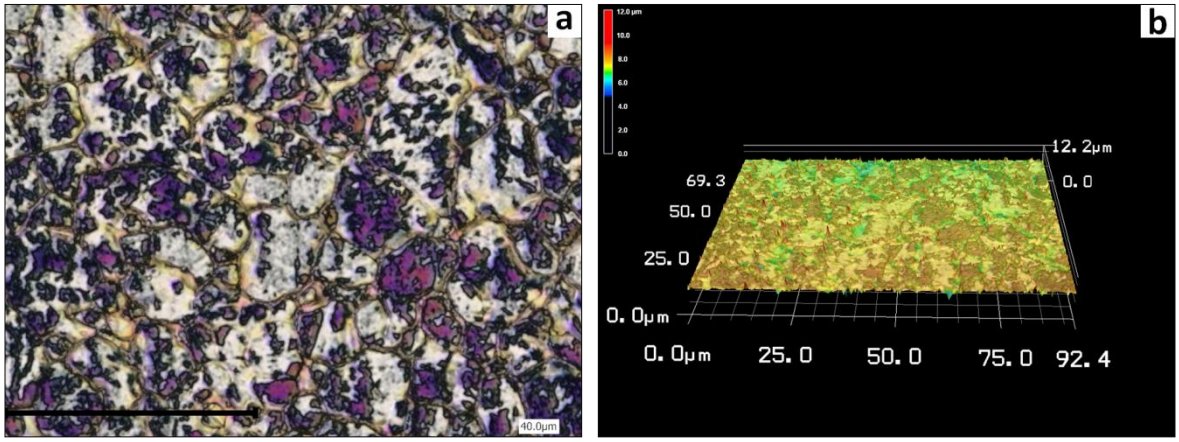
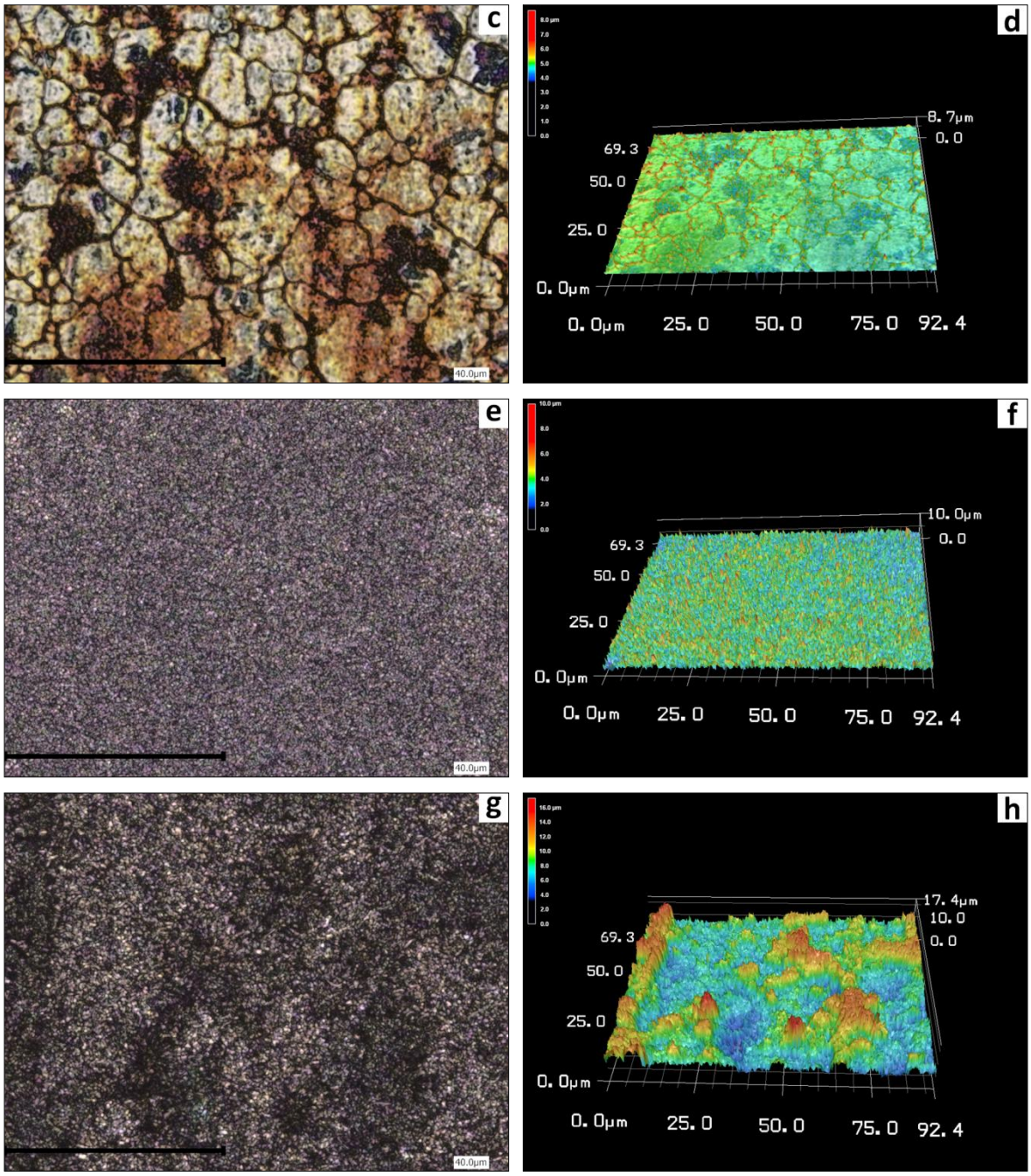


Fig. 3: Diameters variation of: (a) CNTs at 550 °C; (b) CNTs at 650 °C; (c) CNFs at 750 °C.

In order to determine the average length of the grown CNTs, 3D LASER microscope images were used taken at different temperatures as shown in Fig.4. The height contour increases with increasing growth temperatures in addition the amount of curl CNT tends to increase with increasing. Fig.4, (a, b) show the stainless steel (316) coated with cobalt catalyst only, while (c, d) show the sample at 450 °C however at this temperature the CNTs was not grown because the reaction temperature was not sufficient. In another hand Fig.4, (e, f) shows CNTs growth at 550 °C, in which CNTs started to grow uniformly and reached to heights in the range of 7.4~12.9 μm. Moreover, Fig.4, (g, h) CNTs grow longer to heights in the range of 14~20.2 μm at 650 °C and the CNTs formed appeared to be vertically aligned carbon nanotubes. Finally in Fig.4, (g, h), CNTs grown reached to heights in the range of 21~33.2 μm at 750 °C and the CNTs produced at this temperature appeared to be mostly randomly-oriented carbon nanotubes.




c
d
8.7µm
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25.0
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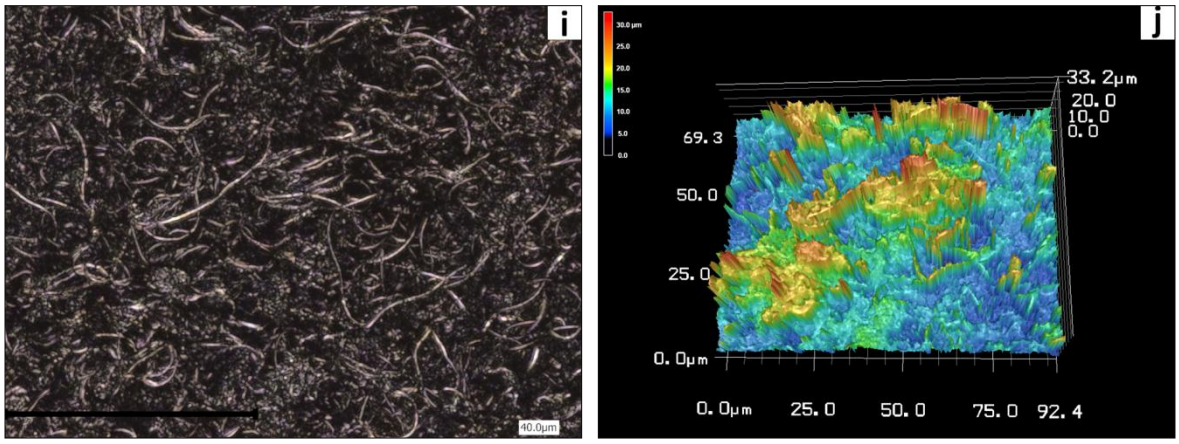

Fig. 4: 3D laser confocal scanning microscope images of: (a,b) sample before growth; (c,d) CNTs at 450 °C; (e,f) CNTs at 550 °C; (g,h) CNTs at 650 °C; (i,j) CNFs at 750 °C

X-Ray Diffraction

This characterization method is not sample destructive and is used to obtain some information on the interlayer spacing, the structural strain and the impurities. However, carbon nanotubes have multiple orientations compared to the X-ray incident beam. The main features of X-ray diffraction pattern of CNTs are close to those of graphite as shown in (Fig. 5): (i) a graphite-like peak (0 0 2 l) is present (ii) a family of (hk 0) peaks due to the honeycomb lattice of single graphene sheet. Moreover, the line shape of the (0 0 2 l) peaks is weakened and somewhat broadened on its low diffraction angle part. The decrease of the interlayer spacing with the increase of diameter of the shells [11] and the inner diameter distribution [12] modify also the shape of the (0 0 2 l) peaks. The intensity and width of the (0 0 2 l) peaks are related to the number of layers, to the variations of interlayer spacing, to the lattice distortions [13,14] and to the carbon nanotube orientation compared to the X-ray incident beam [15-17]. Some studies on the alignment of CNTs have been done using X-ray diffraction. Cao et al. [15] have shown that no (0 0 2) peak can be measured by X-ray diffraction with well aligned straight nanotubes on the substrate surface. In the case of carbon nanotubes with tube axis perpendicular to the substrate surface, the X-ray incident beam is scattered inside the sample and is not collected. Consequently, the intensity of the (0 0 2) peak decreases monotonically as CNTs are better aligned.

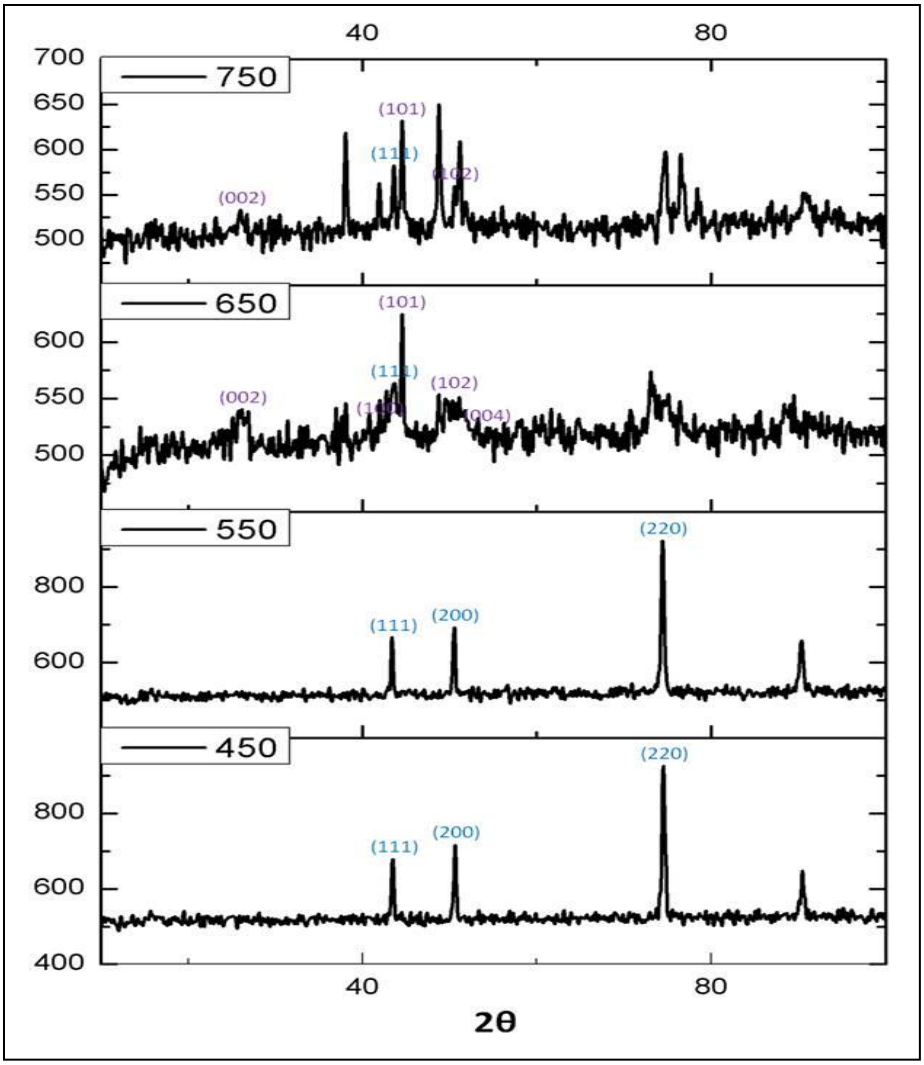

Fig. 5. XRD pattern of CNTs synthesized by PECVD at different growth temperature

FT-IR Results

FTIR is mainly used as qualitative technique for evaluation of functional groups. The FTIR spectra of prepared CNT at different growth temperatures are compared in Fig. (6). The spectra indicates intensive bands at wave numbers 3450 cm^{-1} (stretching vibrations of isolated surface –OH moieties). The bands in the 1750-1550 cm^{-1} range can be assigned to C=C in aromatic rings and unsaturated structural of C=C bonds [18-20]. In addition, Kastner et al. [21,22] found that phonon modes of MWNTs at about 868 and 1575 cm^{-1}, respectively. Kuhlmann et al. [23] noticed that these modes (around 850 and 1590 cm^{-1}) appear in all CNTs symmetry independently of the diameters.

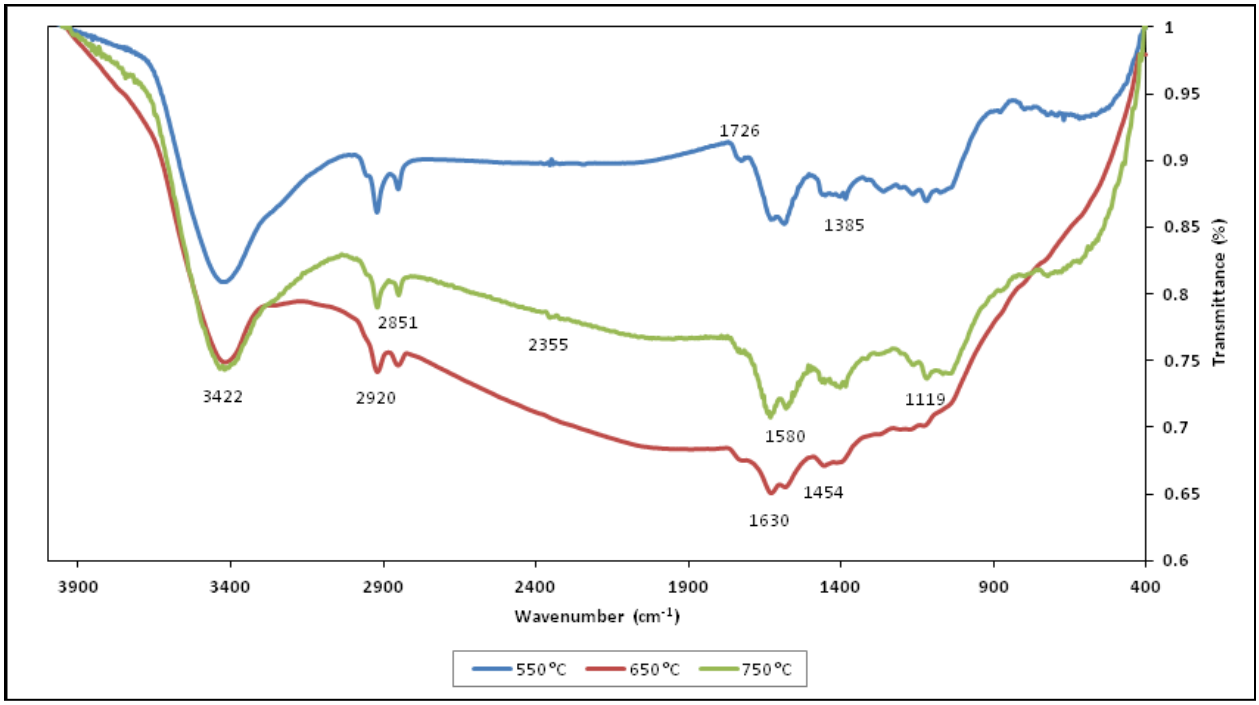

Fig. 6. FTIR spectra of as prepared CNTs at different growth temperatures

CONCLUSION

It has been found that the preparation of cobalt catalyst over the stainless steel substrate via spin coating process is simple, reproducible, economic and very efficient, as consequence it could be used as an economic method for mass production of carbon nanotubes using PECVD technique. Moreover, temperature optimization is obtained at 650 ºC led to production of a well-aligned CNTs array. In conclusion, both of diameter and length of the synthesized CNTs are increasing with increasing temperature indicates the importance of controlling growth temperature of CNTs in order to obtain the desired morphology and topography of the synthesised CNTs.

ACKNOWLEDGMENT

The authors would like to acknowledge the Missions Sector-Higher Education Ministry, Egypt (MOHE), International Cooperation Agency (JICA) and Egypt – Japan University for Science and Technology (E-JUST), for their supports through this work.

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