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M. Ghoranneviss & A. Salar Elahi

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Review of carbon nanotubes production by thermal chemical vapor deposition technique

M. Ghoranneviss and A. Salar Elahi

Plasma Physics Research Center, Science and Research Branch, Islamic Azad University, Tehran, Iran

ABSTRACT

We have reviewed carbon nanotubes (CNTs) production on a silicon wafer by thermal chemical vapor deposition (TCVD) using acetylene as a carbon source, cobalt as a catalyst and ammonia as a reactive gas. The DC-sputtering system was used to prepare cobalt thin films on Si substrates. Energy Dispersive X-ray (EDX) measurements were used to investigate the elemental composition of the Co nanocatalyst deposited on Si substrates. Atomic Force Microscopy (AFM) was used to characterize the surface topography of the Co nanocatalyst deposited on Si substrates. The as-grown CNTs were characterized under Field Emission Scanning Electron Microscopy (FESEM) to study the morphological properties of CNTs.

KEYWORDS

Carbon nanotubes; cobalt nanocatalyst; TCVD

Introduction

Nanotechnology based on CNTs is developing very fast leading to decrease in the dimensions of electronic devices used in today's technological applications, such as field effect transistors [1], field emitters [2], flat panel displays [3,4], sensors [5], etc. Due to its very small diameter, which is on the order of few nanometers with the length up to centimeters [6], perfect electrical and thermal conductance properties [7], CNTs are expected to find applications in all industrial areas, also provide rich research subjects. CNTs have been grown by various methods, such as laser ablation, thermal decomposition of hydrocarbons, and Chemical Vapor Deposition (CVD). These three methods have been used the most for producing CNTs. Among them, CVD has been shown to be the best method in producing vertically aligned CNTs uniformly in large quantities due to the ease in controlling the catalysts and temperature [8,9]. Transition metals such as Fe, Ni, Co and their compounds or alloys have been widely used as the catalysts [10]. CVD with these transition metals as a catalyst has several advantages over other deposition methods [11]. CVD with a catalyst can be used to grow single-walled, double-walled, or multi-walled CNTs by controlling the particle size and chemical nature of the catalyst. The adhesive force between the catalyst and the substrate has been often attributed as an important factor in determining the growth mechanisms of CNTs. While weak contact between the catalyst and substrate favors a tip-growth mechanism, a strong interaction promotes base-growth [12,13]. The growth of CNTs can be divided into four steps: (1) supply of carbon source on the catalyst surface by adsorption and the subsequent catalytic decomposition of the adsorbed carbon by carbon atoms; (2) desorption of

CONTACT A. Salar Elahi salari_phy@yahoo.com
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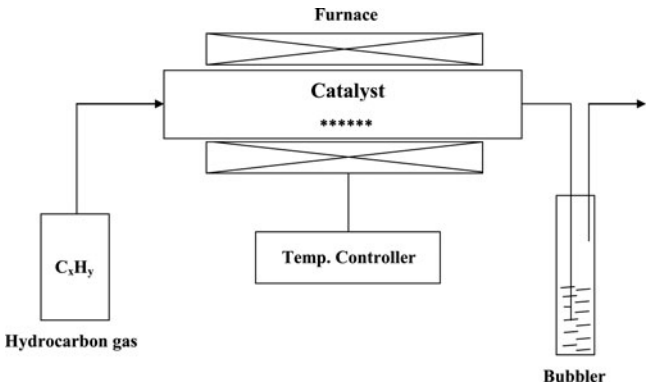

Figure 1. Schematic diagram of TCVD system of nanotube synthesis.

the carbon atoms into a gas phase; (3) diffusion of the carbon atoms away from the catalyst surface through bulk or surface diffusion; and (4) precipitation and formation of a graphite structure [14]. In this paper, we have systematically investigated the effects of growth temperatures and deposition time on carbon nanotubes grown by thermal chemical vapor deposition using cobalt nanocatalyst.

Experimental setup

In the present investigation, p-type Si (400) wafers with the size of 1 cm × 1 cm were used as substrates. The wafers were cleaned by ultrasonic method in acetone and ethanol solutions to remove potential residual contaminants prior to deposition. The samples were introduced into the planar DC-sputtering system and then pumped down to a base pressure of 4 × 10–1 Pa. A cobalt plate was used as a cathode and was placed in parallel with the oven which was grounded. The distance between the cathode and anode was about 1 cm. Argon was introduced into the chamber with a flow of 200 standard centimeter cubic per minutes (sccm). The cobalt nanocatalysts were sputtered on Si substrates when the substrate temperature gradually increased up to 100°C. Deposition time for cobalt sputtering was 30 min. The thermal chemical vapor deposition (TCVD) system in the experiment (Fig. 1) was an electric furnace composed of a horizontal quartz glass tube with an internal diameter of 7.5 cm and a length of 80 cm which was operated at atmospheric pressure. Argon gas with a flow rate of 200 sccm was supplied into the CVD reactor to prevent the oxidation of catalytic metal while raising the temperature to 750°C. The samples were placed in the chamber and the temperature increased to 850°C. After that, Ar flow was switched off. For CNT growth, we used C2H2 / NH3 at 35 / 60 sccm for 15 min. The growth was terminated by turning off C2H2 / NH3 flow and the samples were allowed to cool down to room temperature under Ar gas flow. Same experiments were repeated at growth temperatures of 850°C, 900°C, 950°C, and 1000°C during the deposition time of 15 min and again at the deposition time of 25 min while keeping other growth parameters constant.

Results and discussions

In each of the deposition times (15 and 25 min), all the growth conditions except the growth temperature of the samples studied here constant to study only the temperature effect. Prior to

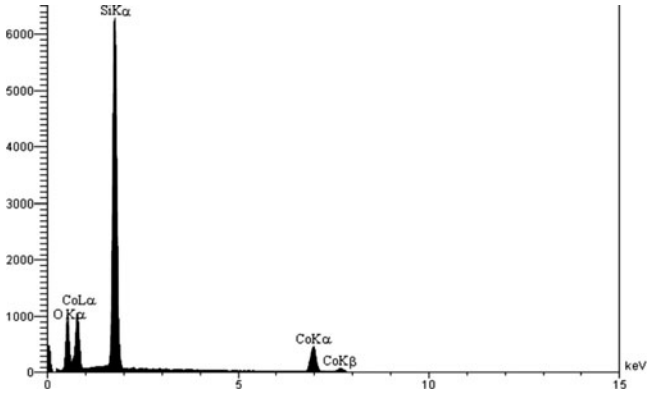

Figure 2. Energy Dispersive X-ray (EDX) measurements show the elemental composition of the cobalt-nanocatalyst deposited on Si substrates.

carbon nanotube growth, Energy Dispersive X-ray (EDX) measurements were done to investigate the elemental composition of the cobalt catalyst deposited on Si substrates (Fig. 2). Atomic force microscopy (AFM) in contact mode was used for analyzing the surface morphology of Co film deposited on Si substrates (Fig. 3 (a,b)). AFM images have been obtained in a scanning area of 3 μm × 3 μm. As it is clear, the formation of catalyst particles with a relatively smooth surface can be observed. For the analysis of the uniformity of catalyst distribution along the substrate surface, it is helpful to calculate the roughness value. The average roughnesses is 1.91 nm. Root-Mean-Square (RMS) roughnesses was measured over the whole area and it was 2.44 nm. The RMS roughness of a surface is similar to the roughness average, with the only difference being the mean squared absolute values of surface roughness profile. The effect of deposition temperature on CNTs as a function of growth time was investigated. FESEM images of CNTs grown on the cobalt catalyst at growth temperatures of 850°C, 900°C, 950°C, and 1000°C during the deposition time of 15 min have been shown in Fig. 4 (a–d). For comparison purposes, the FESEM images of CNTs grown at growth temperatures of 850°C, 900°C, 950°C, and 1000°C during the deposition time of 25 min have been shown in Fig. 5 (a–d). As can be seen in Fig. 4 (a), the CNTs grown at 850°C have smaller diameters and production yield is very high. When the temperature enhanced and reached to 900°C, the CNTs diameters have been increased and the efficiency was very low (Fig. 4 (b)). At 950°C, the yield slightly increased (Fig. 4 (c)) and at 1000°C, the efficiency enhanced again but CNTs

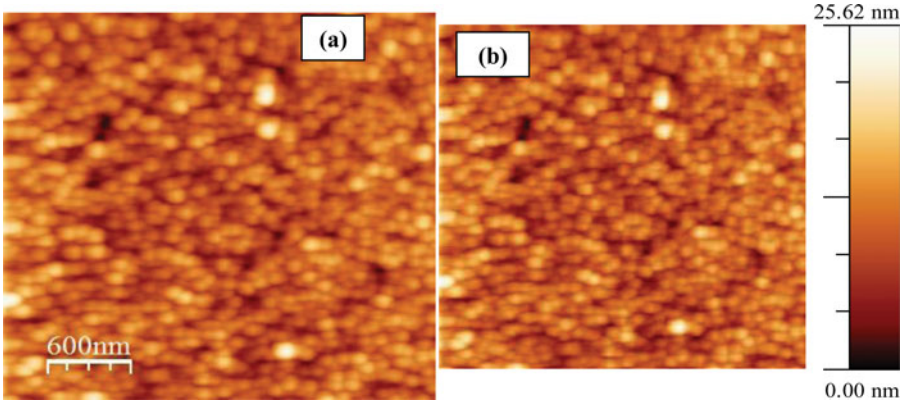

Figure 3. (a) 2D and (b) 3D AFM Images of Co film deposited on Si substrates.

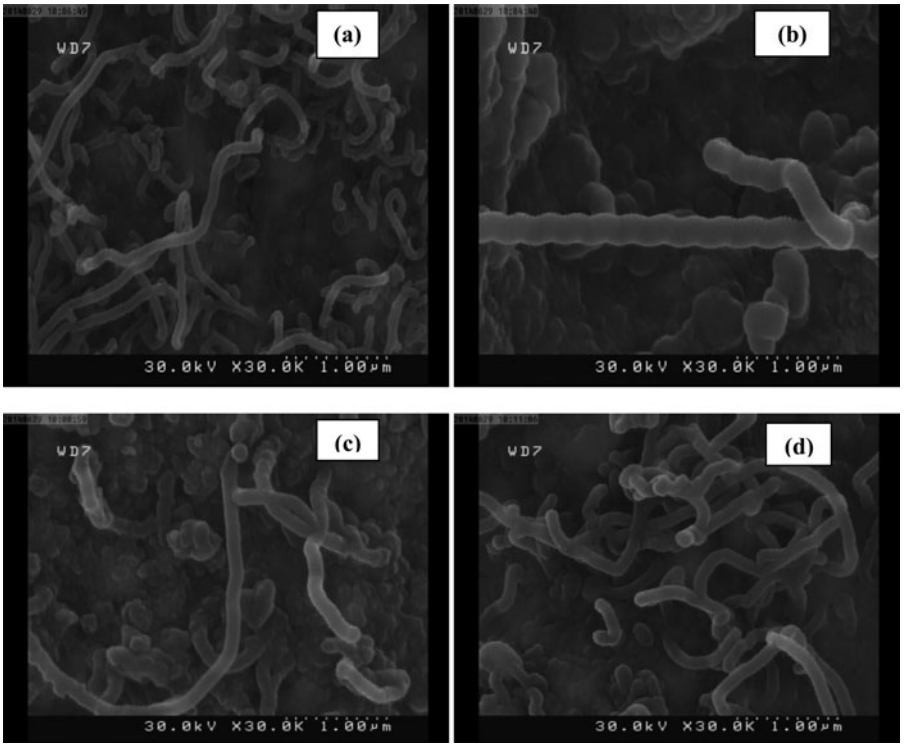

Figure 4. FESEM images of CNTs grown on the cobalt catalyst at growth temperatures of (a) 850°C, (b) 900°C, (c) 950°C, and (d) 1000°C during the deposition time of 15 min.

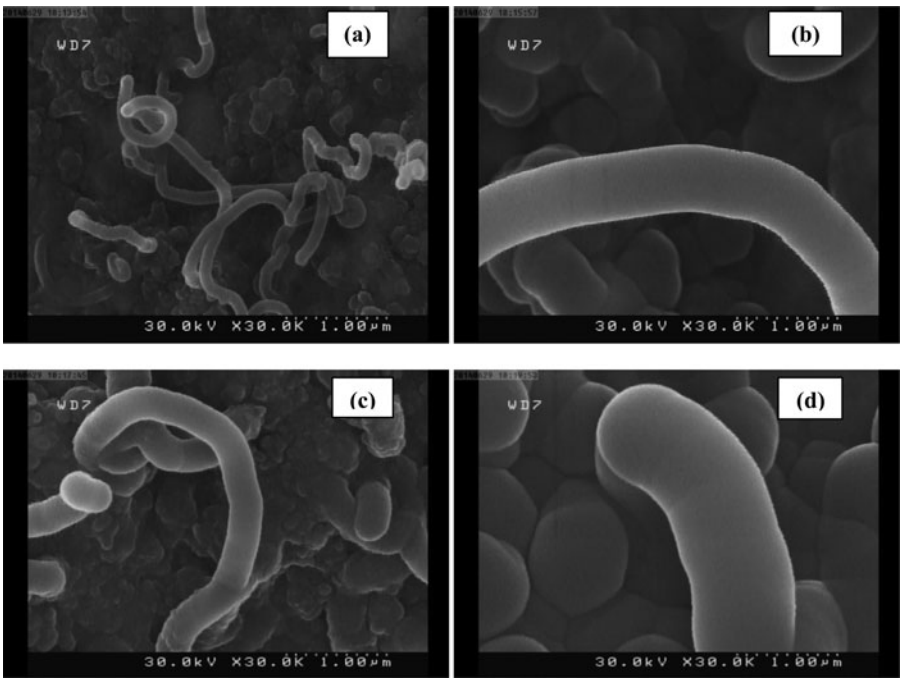

Figure 5. FESEM images of CNTs grown on the cobalt catalyst at growth temperatures of (a) 850°C, (b) 900°C, (c) 950°C, and (d) 1000°C during the deposition time of 25 min.

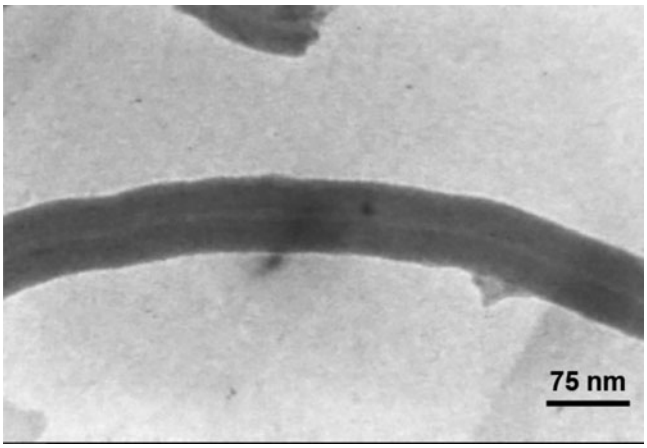

Figure 6. The HRTEM image of the grown CNT at a growth temperature of 850°C during the deposition time of 15 min using Co as catalyst.

have large diameters. From the Fig. 5 (a-d), it is found that the deposition time of 25 min gave less CNTs population particularly for 900°C, 950°C, and 1000°C where large catalyst particles that remained un-reacted amidst the carbon nanotubes were seen. At the temperatures of 900°C and 1000°C, nucleation was performed but the growth has not taken place. On the other hand, the grown CNTs at the temperature of 850°C among all of the samples during deposition time of 25 min have a minimum diameter and maximum efficiency (Fig. 5). It is supposed that at high temperature, the metal atoms agglomerate into bigger clusters leading to thick carbon nanotubes. Simultaneously, high temperature promotes acetylene decomposition leading to more carbon generation and hence more wall formation. Since agglomeration of catalyst particles produces greater particles with lower activities, the number of active sites decreases and the density of grown CNTs is reduced. Thus, The CVD temperature plays the central role in CNT growth. Figure 6 shows the HRTEM image of the grown CNT at a growth temperature of 850°C during the deposition time of 15 min using Co as catalyst, which confirms that the morphology seen in the FESEM image (Fig. 4 (a)) have tubular structure, i.e. they are multi-walled carbon nanotubes (MWCNTs). The grown CNTs were then characterized by Raman spectroscopy. The Raman spectrum of the produced CNTs at different growth temperatures during deposition time of 15 min is shown in Fig. 7. The well separated two Raman peaks at 1500–1605 cm-1 for G peaks (graphite band) and at 1250–1450 cm-1 for D peaks (disorder induced band) was observed for all samples. Also, there is a signal peak in the region of the radial breathing mode (RBM), i.e. below 300 cm-1 of the spectrum. The RBM Raman features correspond to the atomic vibration of the C atoms in the radial direction. The G'-band frequency is close to twice that of the D band and is found from 2500 to 2900 cm-1. The G' band is an intrinsic property of the nanotubes and graphite and present even in defect –free nanotubes for which the D-band is completely absent. Also, the Raman spectrum of the produced CNTs at different growth temperatures during deposition time of 15 min is shown in Fig. 8. The IG /ID ratios were calculated to estimate the variation of CNT crystallinity at different growth temperatures during the deposition time of 15 and 25 min using Co catalyst (Table 1).This reveals that the trend of CNT crystallinity varies with synthesis temperature and deposition time. Here, the ratio of IG /ID is greater than others for the grown CNTs at growth temperature of 950°C and deposition time of 25 min which indicates that these CNTs have good crystalline graphite structure, while from FESEM results found that the diameters

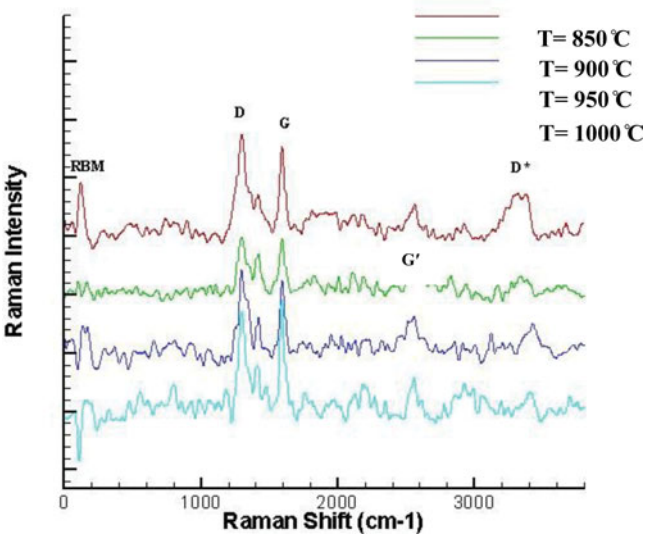

Figure 7. The Raman spectrum of the produced CNTs at different growth temperatures during deposition time of 15 min.

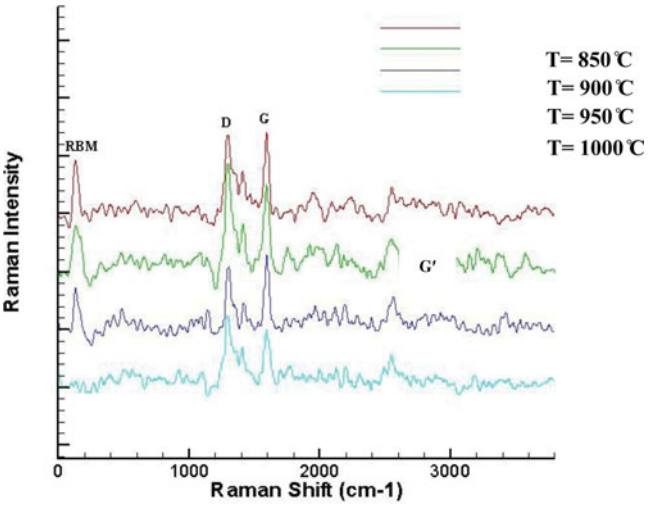

Figure 8. The Raman spectrum of the produced CNTs at different growth temperatures during deposition time of 25 min.

Table 1. The ratios of the intensities of G and D peaks,IG/ID for produced CNTs at different growth temperatures during deposition time of 15 and 25 min.

Deposition Time	Growth temperature	G band (cm-1)	D band (cm-1)	IG / ID
15 min	850°C	1594.56	1300.73	0.8982
15 min	900°C	1595.69	1294.29	0.9563
15 min	950°C	1594.56	1293.00	0.9155
15 min	1000°C	1586.82	1293.00	1.0444
25 min	850°C	1594.56	1293.00	1.0266
25 min	900°C	1594.56	1300.73	0.8102
25 min	950°C	1595.69	1302.01	1.1986
25 min	1000°C	1586.82	1293.00	0.7904

of CNTs are raised and density is decreased. From the FESEM results, we observed that our CNTs grew with the tip growth mechanism as the catalyst nanoparticles are seen from FESEM images that they are at the tip of the CNTs with brighter color than the nanotubes [15].

Conclusions

In this work, we demonstrated how growth temperature and deposition time affected the growth of carbon nanotubes using the TCVD technique. In both of deposition time (15 and 25 min), we changed the growth temperature while keeping other parameters strictly constant. It was found that by raising the growth temperature, the degree of crystallinity of grown CNTs increases however agglomeration of nanocatalysts reduces their catalytic activities, which enhance graphite sheet defects.

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