Effect of the growth temperature on carbon nanotubes grown by thermal chemical vapor deposition method

M. AKSAK*, S. KIR, Y. SELAMET
Department of Physics, Izmir Institute of Technology, Urla, 35430, Izmir, Turkey

We studied the effects of temperature on the growth of carbon nanotubes (CNTs) produced by thermal chemical vapour deposition technique. Very thin Co catalyst films with 3.5 nm thickness were deposited on SiO₂/Si substrates by DC magnetron sputtering. CNT growth was performed in the flow of methane gas at growth temperatures of 825, 850, 875, 900 and 925°C. Our as-grown CNTs were characterized under scanning electron microscopy to study the morphological properties of CNTs. The topography of the as-grown CNTs at was also examined by AFM. We observed that as the growth temperature was increased from 850°C to 925°C, the average diameter of the carbon nanotubes was decreased continually from 20.4 nm to 10.5 nm. We also observed that the length of the CNTs was increasing, while radial distribution decreasing with the increasing temperature.

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1. 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], sensors [4], etc. Due to its very small diameter, which is on the order of few nanometers with the length up to centimeters [5], perfect electrical and thermal conductance properties [6], CNTs are expected to find applications in all industrial areas, also provide rich research subjects. CNTs can be produced by different techniques; among them most widely used ones are arc-discharge [7], laser ablation [8], and chemical vapor deposition (CVD) [7] methods. We chose thermal chemical vapor deposition (TCVD) technique which has some distinct advantages [7] over other techniques, such as production cost, scalability, and growth onto various substrates and it can accommodate more than one sample in one run in supported catalyst case. There is variety of parameters which affect the morphology of CNTs: temperature and catalyst particle formation being the most important two of them.

There are several efforts in the literature about growth time and/or temperature effect on the radius of the CNTs. Most of the results which are done with acetylene (C₂H₂) CVD support the idea that the diameter of the CNTs increases with the increasing the temperature [9-11]. It was generally thought that the increase in diameter is due to the extra concentric cylinders in multwall CNTs. However, recent study shows that the increase in the diameter is due to nanocrystalline carbon or glassy carbon sheath which expands exponentially with time [11]. On the contrary, there were some reports indicating that the growth at higher temperatures yields thinner and longer CNTs in methane (CH₄) CVD [12].

Compare to C₂H₂, CH₄ has different growth dynamics. In CH₄ reaction with H₂ to produce carbon, more H₂ results in compare to that in C₂H₂ reaction. H₂ is thought to help make catalyst particles smaller by an etching reaction [13]. For this reason, we studied the radius and the length of the nanotubes at different temperatures in methane CVD, keeping all the other parameters constant. We used Co catalyst thin films as they are known for their well-behavior for the growth of CNTs [14] with high catalytic activity [15]. Co shows high carbon solubility at high temperatures [16] at which we can expect to have more H₂ in the growth zone due to effective disassociation of CH₄.

2. Experimental

We used Si substrates deposited with 1 µm SiO₂. We utilized a DC magnetron sputtering system to deposit very thin Co films on SiO₂/Si substrates. The sputtering system used for depositing our catalyst thin films is AJA ATC Orion 5 UHV sputtering system with four 2-inch magnetron heads. The system includes a substrate holder which is able to rotate, a heater, and a load-lock chamber. The chamber base pressure was 10⁻⁶ Torr before the catalyst film growth. The substrates were cleaned chemically in methanol for 15 min in ultrasonic bath and rinsed with ultra-pure water for 15 min. After loading
substrates into the growth chamber, the plasma cleaning was applied to them for 2-3 minutes. Furthermore, we presputtered the target for 1 min. to clean the target surface before Co deposition. The distance between substrate and target was kept at 7cm. We carry out DC sputtering at 20 W, with a growth rate 0.1 Å/sec at pressure 0.5 mTorr. The catalyst film thickness was measured by a thickness monitor as 3.5 nm. The samples were cut into small pieces before the CNT growth. They were kept under vacuum conditions until their turn to protect their surface from contamination and oxidation. The TCVD system used for this study consists of a hinged furnace with a quartz tube of 1200 mm in length and 25 mm in diameter. The system was evacuated by a mechanical pump down to mTorr scale. We controlled the flow rate of the gases by electronic mass flow meters. The system was always kept under vacuum while not in use, and high purity Ar flow was used to bring it to the atmospheric pressure for sample loading. After reaching sufficiently low vacuum, we set the growth temperature with the temperature increase rate of about 30°C/min. The argon flow was kept constant at 120 sccm until the growth temperature was reached. We sent H2 gas with 120 sccm flow rate for 5 minutes before letting CH4 in. For CNT growth we used CH4/H2 at 100/50 sccm for 30 minutes under system pressure of ~350 Torr. The growth was terminated by turning off CH4 flow and the samples were allowed to cool down to room temperature under Ar gas flow. We characterized our as-grown CNTs by SEM (Phillips XL-30S FEG) to study their morphology and to obtain the length and diameter of these as-grown CNTs. We used a multimode SPM to investigate the topography of our CNTs the growth mechanism [17]. Energy dispersive X-ray (EDX) measurements were done to investigate the elemental composition of our samples.

### Table 1. Growth conditions and average diameters of the CNTs grown on Co catalyst film.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>T (°C)</th>
<th>CH4:H2 (sccm)</th>
<th>P (Torr)</th>
<th>Time (min)</th>
<th>Catalyst film thickness (nm)</th>
<th>Average CNT diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSiOCNT2</td>
<td>825</td>
<td>100:50</td>
<td>350</td>
<td>30</td>
<td>3.5</td>
<td>NA</td>
</tr>
<tr>
<td>CoSiOCNT3</td>
<td>850</td>
<td>100:50</td>
<td>350</td>
<td>30</td>
<td>3.5</td>
<td>20.4</td>
</tr>
<tr>
<td>CoSiOCNT4</td>
<td>875</td>
<td>100:50</td>
<td>350</td>
<td>30</td>
<td>3.5</td>
<td>15.4</td>
</tr>
<tr>
<td>CoSiOCNT5</td>
<td>900</td>
<td>100:50</td>
<td>350</td>
<td>30</td>
<td>3.5</td>
<td>14.2</td>
</tr>
<tr>
<td>CoSiOCNT6</td>
<td>925</td>
<td>100:50</td>
<td>350</td>
<td>30</td>
<td>3.5</td>
<td>10.5</td>
</tr>
</tbody>
</table>

All SEM pictures shown in Fig. 1 are representative ones for uniform formations at their respective temperatures.

From the SEM analysis, we deduce that the diameter decreases with the increasing growth temperature (Fig. 2). We also observed that the radial distribution gets narrower as we go to higher temperatures. The straight line in that figure is a linear fit in \( A+BT \) form with \( A=120.18 \) nm and \( B=-0.1185 \) nm/°C illustrating the tendency with the temperature.

3. Results and discussion

All the growth conditions other than temperature for the samples studied here were kept constant to study only the temperature effect (Table 1). Analyzing SEM results we find the average diameters of the CNTs grown on Co catalyst film. Study of SEM images of the CNTs grown on Co/SiO2/Si thin films at 825 °C reveals that no CNT formation was occurred even though we sent methane gas at this temperature (Fig. 1 (a)). In fact, in our efforts with other Co thin films, not presented here, resulted with no CNT growth at temperatures at and lower than 825 °C. We observed uniform formation of catalyst nanoparticles with average diameter of about 25 nm with number density of about 2.5x10¹⁰ (catalyst/cm²). Although no CNT growth was observed, uniform formation of catalyst nanoparticles are so important in the growth of carbon nanotubes as they controls the diameter of nanotubes [18]. For the growth at 850 °C, CNT formation was rather bulky and short, with average diameter of 20.4 nm (Fig. 1 (b)). For the CNTs grown at 875 °C (Fig.1(c)), we obtained carbon nanotubes with average diameter of 15.4 nm and they were longer than the previous CNTs grown at 850 °C. At these two temperatures we also observed wide radii distribution. The CNTs grown at 900 °C had an average diameter of about 14.2 nm (Fig. 1 (d)).

When we increased the growth temperature to 925°C, we observed very thin and longer nanotubes (Fig. 1 (e)), whose average diameter were about 10.5 nm. At these last two temperatures, the radial distributions were much narrower compare to those of at temperatures 850°C and 875°C.
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Fig. 1. SEM images of as-grown CNTs grown on Co/SiO2/Si thin films at (a) 825 °C; (b) 850 °C; (c) 875 °C; (d) 900 °C; (e) 925 °C. Scale bars a: 1 μm b and c: 100 nm d and e: 200 nm.

We also studied AFM imaging of the CNTs grown at 850°C and 925°C (Fig. 3). Both AFM and SEM results provided us with the growth mechanism of carbon nanotubes. The growth mechanism of carbon fibers was first predicted by Baker et al [20] who assumed that this growth mechanism constituted the dissociation of hydrocarbon gases by the catalyst material, and then carbon atoms would diffuse into the catalyst nanoparticles, following which they would saturate, precipitate, and end up with carbon nanotubes while cooling the system down to room temperature. According to our results, we observed that the catalyst nanoparticles are at the tip of the carbon nanotubes, and so-called tip growth mechanism, of which results were very compatible with the literature [19, 20].

![AFM image of as-grown CNTs grown on Co/SiO2/Si thin films at a) 850°C and b) 925°C. Scans: a) 12.5x12.5 μm², b) 12.5x12.5 μm², height-color codes: a) 0-120 nm, b) 0-1.05 μm.](image)

![Graph showing decrease in the average diameters of CNTs with the growth temperature.](image)

We also did EDX analysis on these samples in order to obtain the elemental compositions. We observed that our film consisted of small amount of carbon (2.1, 3.1, 4.3, and 3.7 wt% for the temperatures 850, 875, 900, and 925 °C, respectively) and mostly of oxygen and silicon. These results were expected since CNTs are nanometer sized tubular structures with small substrate surface coverage. The major source of silicon and oxygen observed in our analysis is due to the SiO₂ layer on our substrates. Observed decrease in the wt% of carbon at 925 °C might be due to very fine structure of the nanotubes (diameter = 10.5 nm).

A simple argument could be reasoned to explain observed behavior with the growth temperature: At low temperatures (below 850°C), supplied energy is not enough to decompose all methane into carbon and hydrogen. Added hydrogen at 50 sccm is effectively shaping catalyst film into desired nanoparticles but they are not effectively catalyzing methane to initiate CNT growth. At moderate temperatures (850°C - 875°C) most of the methane is disassociated supplying carbon for CNT
formation and extra hydrogen for catalyst shaping. However, at these temperatures available H$_2$ is not efficiently shaping nanoparticles within narrow size distribution so that we observe wide CNT radii distribution. At high temperatures (above 900°C) supplied energy is enough to disassociate methane into carbon and hydrogen. Now available carbon is abundant to have longer CNTs and added hydrogen with hydrogen coming from methane disassociation is effectively shaping catalyst film into desired smaller nanoparticles.

From both the AFM results and SEM results, we observed that our NTs grew with the tip growth mechanism [20] as the catalyst nanoparticles are seen from the both AFM and SEM images that they are at the tip of the CNTs with brighter color than the nanotubes.

4. Conclusions

In this work we demonstrated how temperature affected the growth of carbon nanotubes in methane CVD. We changed the growth temperature while keeping other parameters strictly constant. We observed that there was no CNT formation below 850°C, yet there were uniform formation of Co catalyst particles with average diameter 25 nm. At and above 850°C we have seen CNT formation with average radius and radii distribution decreasing while their length is increasing with the increasing temperature. This tendency let us to conclude that methane CVD growth conditions can be adjusted to control nanotube radius and length. We observed that the temperature affected the as-grown CNTs diameter inversely.

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References


*Corresponding author: meralaksak@iyte.edu.tr