Effects of the process parameters on the carbon nanotubes growth by thermal CVD


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ABSTRACT

Multiwall carbon nanotubes were grown by thermal chemical vapor deposition with a metal catalyst. This approach employs a metal film deposition onto a SiO2/Si substrate followed by a thermal annealing to generate metal particles able to convert carbon containing gas (methane or acetylene) into carbon nanotubes. Nickel was used as a metal catalyst, and the influence of different growth parameters on the CVD process was investigated. The studies have shown that the effect of the methane concentration depends essentially on the process temperature. We have also observed that the catalytic capacity of the nickel depends on the carbon gas precursor reactivity. Moreover, it is generally assumed that the metal particle size determines the carbon nanotube diameter but, according to our research, this seems to be valid only for relatively small metal particles when the tip growth mechanism predominates. For relatively large metal particles, a hybrid growth mechanism (probably involving both tip and base growth models) can be considered, and the size of the particle does not determine the diameter of the resulting nanotube.

Keywords: carbon nanotubes, CVD, metal catalysis, metal thin films, growth mechanism

1 INTRODUCTION

Carbon nanotubes (CNTs) have received much attention due to their extraordinary properties and potential technological applications [1]. The development of technologies involving carbon nanotubes can result in nanodevices characterized by high performance, low mass and low consumption of energy. Thermal chemical vapor deposition (CVD) has been shown to be an efficient and versatile technique for the carbon nanotubes synthesis [2,3,4,5]. However, many challenges (in particular, the lack of precise control of the nanotube growth during the CVD process) still have to be addressed.

The identification and control of numerous growth parameters is crucial for the development and optimization of the synthesis process, study of growth mechanisms and nano-devices fabrication. Therefore, the detailed study of the effect of experimental conditions such as time, temperature, metal catalyst, carbon gas precursor, among others, is of great relevance and now it is the subject of many experimental researches.

In this work, the influence of different experimental parameters on the carbon nanotube growth by thermal CVD using nickel metal catalyst was investigated.

2 EXPERIMENTAL

Electron beam evaporation was used for thin (6 nm) nickel film deposition onto silicon wafers covered by a 50 nm thick thermally grown silicon oxide layer. Then the wafers were cut in small (~5x5 mm) samples, followed by their annealing in a quartz tube furnace at 700 °C in a H2 flow of 400 sccm during 30 minutes. Two different CVD processes were used. In the growth method 1, the hydrogen was replaced by NH3 flow of 400 sccm during 5 minutes. Then, the temperature was raised to 800-950 °C, and the synthesis was started by addition of 25-100 sccm of CH4 for 30 minutes. Two other CVD processes were used. In the growth method 2, the hydrogen was replaced by the same flow of H2. When C2H2 was used as the carbon gas precursor (growth method 2), the flow of H2 was increased to 600 sccm after the annealing, and a flow of 6 sccm of C2H2 was introduced for 15 minutes keeping the temperature at 700 °C. A high resolution scanning electron microscope FEG-SEM JSM 6330F was used for structural analysis of samples. Raman spectroscopy was performed employing a Renishaw System 3000 Raman Imaging Microscope, using the 632.8 nm line of a He-Ne laser.

3 RESULTS & DISCUSSION

During the annealing process, nickel thin films supported on SiO2/Si substrates form isolated metal particles. The characteristic of this thermal treatment is that the variation of particle diameters is relatively wide, and thicker films lead to a wider distribution of particle sizes [3,4,5,6]. Scanning electron micrographs obtained for Ni film with a thickness of 6 nm annealed at 700 °C show round (disk-like) particles with diameters ranging from 10 to 100 nm (Figure 1). Different size distributions were
found for the catalyst particles located at the edge and in the center of the sample, with the distribution in the center being narrower (see Figure 1 A and B). The reasons for this are not clear at the moment. According to our observations (to be published elsewhere [7]), the metal film tends to break more readily (faster and at lower temperatures) at the edge of the substrate as compared with its center. This phenomenon could explain the different metal particle size distribution over the substrate.

After the annealing process, H₂ flow was replaced by NH₃ flow for cleaning of the metal particles before the CNT growth according to the method 1 described earlier. Then, the growth temperature was set and methane was introduced inside the furnace as the carbon precursor gas. In the beginning of the growth, NH₃ gas was employed to prevent a possible poisoning of the metal catalyst, and after that the NH₃ was replaced by H₂ again.

Scanning electron micrographs showed multiwall carbon nanotubes (MWNTs) with diameters larger than 20 nm for all samples. The characteristic profile of Raman spectra corroborates the formation of MWNTs (Figure 2). As expected, the Raman spectrum of MWNTs is similar to that of the polycrystalline graphite, since carbon nanotubes are constituted by graphene cylindrical walls. Therefore, spectra shown in Figure 2 consist of two bands, a G-line at 1579 cm⁻¹ associated to graphitic structure and a D-line near to 1330 cm⁻¹ accompanied by a second order D' band at 1612 cm⁻¹ related to disordered graphitic structure [8]. The ratio of the D- and G-lines intensities (I_D/I_G) is used to characterize the defects in carbon nanotubes. Higher I_D/I_G ratio implies in more structural defects in CNTs. As expected, sample prepared at lower temperature (850 °C – Figure 2 A) presented the highest I_D/I_G ratio (0.75), since lower temperatures do not lead to a high graphitization of the carbon walls structure. However, the smallest I_D/I_G ratio (0.52) was observed for the sample prepared at 900 °C whereas the I_D/I_G ratio for the sample prepared at 950 °C was slightly higher (0.65). Further investigations involving purification of the CNTs and TEM analysis, to provide additional information on the possible changes in CNTs structural properties, are in progress. Due to low thermal stability of methane, experiments at temperatures as high as 950 °C could result in decomposition of the gas and deposition of different amorphous carbon materials over the carbon nanotubes.

Regarding the influence of the main growth parameters on the CNT formation, the effect of the methane concentration depends essentially on the process temperature. In experiments at temperatures of 850, 900 and 950 °C, higher concentration of methane during the growth process resulted in a higher CNT density (Figure 3) indicating that the growth process is limited by carbon supply. At 850 °C, CNTs were not formed for the most diluted H₂/CH₄ mixture. Furthermore, the formation of CNTs was not observed at the lower temperature (800 °C), independently on the methane concentration. These results indicate the decrease of the catalytic capability of the metal with the growth temperature reduction when methane is used as a carbon feedstock gas.

Since the basic interest here is the development of procedures able to lead to a controlled synthesis of CNTs, it is important to describe a curious phenomenon observed for

![Figure 1](image1.png)  
Figure 1. SEM images of Ni film after annealing process: (A) edge and (B) center of the substrate. In the central region of the substrate (histogram B) 96 % of particles present diameters ranging from 27 to 74 nm against 43 % of particles at the edge (histogram A).

![Figure 2](image2.png)  
Figure 2- Raman spectra of CNTs grown using a gas ratio of H₂/CH₄ = 4:1 at different temperatures: (A) 850 °C, (B) 900 °C, and (C) 950 °C.
most of the samples while using methane and nickel as a catalyst (note that the effect is not observed for iron catalyst, see elsewhere [7]). The growth of CNT does not occur evenly over the entire substrate, but mainly in a region close to the edges. In fact, there is a gradient of the CNT nucleation density which decreases from the edge to the central region of the substrate, as shown in Figure 4. Investigations are in course to explain and overcome this phenomenon. A possible cause may be correlated with the presence of residual oxygen inside the furnace or the release of oxygen due to possible decomposition of SiO₂ layer catalyzed by the metal [9]. In this case, the metallic nickel could catalyze the following conversion: SiO₂ $\rightarrow$ O₂ + SiO, and the concentration of oxygen released from the silicon oxide could be higher at the center than at the edges. In turn, this would result in formation of the nickel oxide (which is known to be much less efficient as a catalyst as compared with the metallic nickel [10]), the process being stronger in the central part of the sample. Literature data also suggest that this non-homogeneity in the CNT growth may be caused by nickel oxidation. Yen et al [11] observed worm-like carbon fibers, similar to carbon structures shown in Figure 4 B, when nickel particles were partially oxidized.

In striking contrast to the case of methane as a carbon feedstock gas, experiments performed with acetylene (the growth method 2), led to a high density of CNTs grown evenly over the entire substrate. This result indicates the influence of the carbon precursor reactivity. Due to higher reactivity of acetylene compared to methane [12], essentially softened experimental conditions – such as lower growth temperature and concentration of carbon (H₂/CH₄ = 100:1) – also resulted in the CNT growth. Probably, the enhanced acetylene reactivity makes the whole growth process less sensitive to the metal catalytic capacity, thus resulting in more uniform CNT growth in all regions of the substrate.

The studies performed with methane also showed other interesting result. Under our experimental conditions, small Ni catalyst particles were usually observed at the tip of the CNTs suggesting the tip growth mechanism. However, in some cases, CNTs with diameters between 20-80 nm grown from metal islands of larger dimensions (up to ~300 nm) were observed with another metal particle at the bottom of the tube (Figure 5). This is in contrast to most observations where the catalyst particle is observed at either the tip or bottom of the nanotubes and thus suggests a complex
growth mechanism. The growth could involve both base and tip growth (hybrid growth mechanism) taking into account the liquid-particle model [13,14]. According to Nerushev et al [13], who observed a similar phenomenon, the formation of small layers of graphene over a relatively big and flat metal particle, followed by the motion and coalescence of some of these graphene layers, can be the initial stage of this event.

The size and shape of catalyst particles are usually considered to be important growth parameters [13,14,15]. More specifically, in the literature it is generally assumed that the metal particle size determines directly the resulting CNT diameter, independently on the growth mechanism (either tip or base growth modes are considered). However, due to our data this seems to be valid only for relatively small particles. For large metal particles (> 100 nm), the CNT diameter appears to be no longer dependent on the particle size, and more complex mechanism apparently determines the CNT growth. Therefore, the size of resultant catalyst particles can determines the growth mechanism and characteristics of the carbon nanotubes.

4 CONCLUSIONS

In the thermal chemical vapor deposition method, the carbon nanotube growth is very sensitive to the experimental conditions. A specific combination of different growth parameters has to be reached to obtain the desired final material. Moreover, it was shown that catalytic metal islands with diameters bigger than 100 nm tend to form CNTs of considerably smaller diameters with metal present at both ends of the nanotubes suggesting a complex growth mechanism. In other words, the initial size of the metal particles can influence not only the diameter but also the growth mechanism of carbon nanotubes.

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6 REFERENCES