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Full Length Research Paper

Various temperature effects on the growth of carbon nanotubes (CNTs) by thermal chemical vapor deposition (TCVD) method

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The growth behavior of carbon nanotubes synthesized from C_2H_2 at the temperature range of 700 to 900°C and using thermal chemical vapor deposition (TCVD) method has been investigated. Thin films of nickel (Ni) catalyst, were coated on SiO_2 substrates by ion beam sputtering technique. The formation of catalytic nickel nanoparticles was much increased when using NH_3 as the environment gas which implies both the formation and the separation of graphitic layer. Scanning electron microscopy (SEM) and Raman results show that the temperature of growth is the effective parameter on the formation of carbon nanotubes (CNTs).

Key words: Carbon nanotubes, chemical vapor déposition, température.

INTRODUCTION

Carbon nanotubes (CNTs) are quasi one-dimensional nanostructures with extreme mechanical characteristics and tunable electrical properties (Loiseau et al., 2006). It has been shown that CNT exhibits excellent thermal, electrical, chemical and mechanical properties (Collins and Avouris, 2000), and has a wide range of applications (Baughman et al., 2002).The growth of CNTs involves dissociation of hydrocarbon molecules over metal clusters acting as a catalyst. Previous studies have shown that the pyrolysis of hydrocarbons over metals can result in the formation of different forms of carbon, depending on the reaction conditions (Jablonski et al., 1992a, b). Over the past decade, many techniques have been developed for synthesizing CNTs, such as arc discharge (Takikawa et al., 2002), laser ablation (Zhang et al., 2001) and chemical vapour deposition (CVD) ways, CVD is one of the most efficient and versatile techniques. This method has already shown its ability to (Singh et al., 2002). Among carbon nanotubes synthesis grow at low temperature single-, double- or either multi-walled carbon nanotubes with a noticeable selectivity (Murakami et al., 2004; Yamada et al., 2006) and location control (Endo et al., 2005). It has been found that the growth temperature is crucial for selective and controlled growth of CNTs, which is necessary for many applications. A number of research groups reported that the growth of CNTs could be controlled by varying the growth parameters of CVD process (Franklin et al., 2001; Choi et al., 2000; Bower et al., 2000; Sinnott et al., 1999). However, there are not many systematic studies on the temperature-controlled growth of CNTs using TCVD. In this paper, we present a study of the different growth temperature effect on the growth of CNTs by TCVD method. CNT structures were investigated by transmission electronic microscopy and Raman spectroscopy.

EXPERIMENTAL

We selected 10 × 10 mm^2 size p-type Si (100) with a resistivity of 4 to 11 Ω cm. The silicon samples were cleaned for 10 min ultrasonically in acetone and alcohol baths consecutively and were rinsed with distilled water. The samples were thermally oxidized at

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800°C for 60 min. The thickness of silicon oxide (SiO_2) layer was estimated approximately as 8 nm. Ni of 40 nm thicknesses was deposited on SiO_2 substrates as catalyst for the growth of CNTs by ion beam sputtering technique at 400°C. During the sputtering, the ion beam power for Ni target was fixed at 2.2 kV. The TCVD setup in our experiment is an electric furnace composed of a horizontal quartz glass tube with an internal diameter of 75 mm and a length of 800 mm which was operated in atmospheric pressure. Argon (Ar) gas with a flow rate of 200 standard centimeter cubic per minutes (sccm) was supplied into the CVD reactor to prevent the oxidation of catalytic metal while raising the temperature to 400°C. Then, Ar flow was switched off to H_2 as an etchant and diluting gas when the samples are heated to the reduction temperature at 700°C. Samples were pretreated by NH_3 and H_2 gas, with a flow rate of 70 and 130 sccm, respectively to form the catalytic particles in nano meter size for 20 min at 700°C. The CNTs were grown using C_2H_2 gas added to the previous mixture with different temperature. The chamber was cooled slowly to the room temperature under Ar flow rate of 200 sccm after the growth. The purities of the gas employed in the experiment were all higher than 99.5%. For the analysis of nickel nanoparticles formation along the substrate (silicon oxide) surface, atomic force microscopy (AFM) analysis in contact mode was used. The CNTs were examined by SEM (LEO.440i, 15 to 20.KV) to measure the length, diameter, uniformity and density. A Raman spectroscopy using an Nd: Ylf laser (532) was used to identify the structure and the crystallinity of CNTs.

RESULTS AND DISCUSSION

AFM images of the surface topography are of 40 nm amorphous Ni catalyst film, and are presented in Figure 1a and b. As it is clear, the formation of catalyst particles or grains with relatively smooth surface can be observed. For the analysis of the uniformity of catalyst distribution along the substrate (silicon oxide) surface, it is helpful to calculate the roughness value. Figure 1a shows the surface of sample just after the nickel film deposition, before any treatment. It can be seen that the deposition process itself creates relatively rough surface. The average roughness of unpretreated sample is 6.36 Å. Figure 1 b is the AFM image which shows the surface morphology of the Ni film pretreated in NH_3 and H_2 at 700°C with the average roughness of 90.3 Å. Figure 2 shows the SEM image of Ni/Si surface after treatment at 700°C in NH_3 and H_2 for 20 min. It is seen that the Ni film breaks into small islands. It is confirmed that the NH_3 and H_2 pretreatment plays an important role in promoting the formation of uniformly separated Ni nanoparticles. Figures 3 to 5 show the SEM images for the CNTs grown on Ni-deposited Sio_2 substrate at 900, 800 and 700°C, respectively. As it is clear, CNTs are grown at all three temperatures. Besides the silicon substrate, the quartz tube itself is covered with a dense film of CNTs along most of the heated zone of the furnace. Figure 3a and b shows the spaghetti-like' CNTs, grown at 900°C for 30 min with different magnifications. The diameter of carbon nanotubes is approximately 200 nm while the diameter of CNTs grown at 800°C is approximately 60 to 70 nm and the length of CNTs is up to several micrometers. Figure 5 also shows that the diameter of CNTs grown at 700°C is

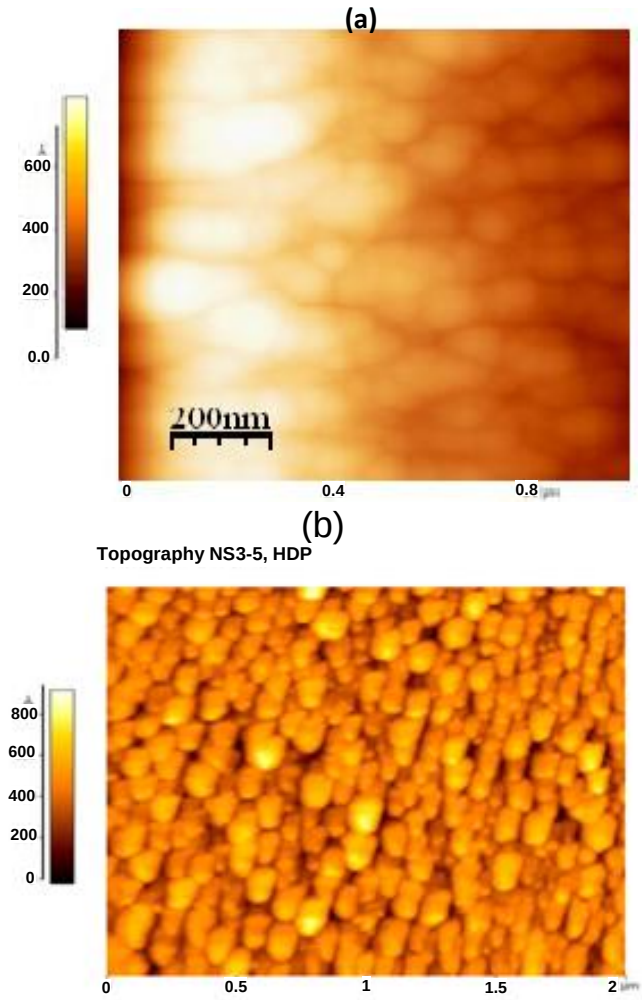

Figure 1. AFM images of Ni thin films (a) without any pretreatment and (b) pretreated at 700°C in NH_3 and H_2 for 20 min.

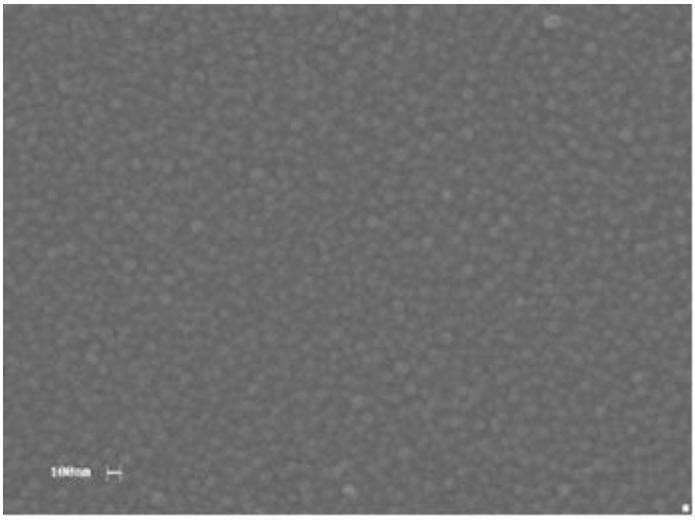

Figure 2. SEM images of Ni thin films pretreated at 700°C in NH_3 and H_2 for 20 min.

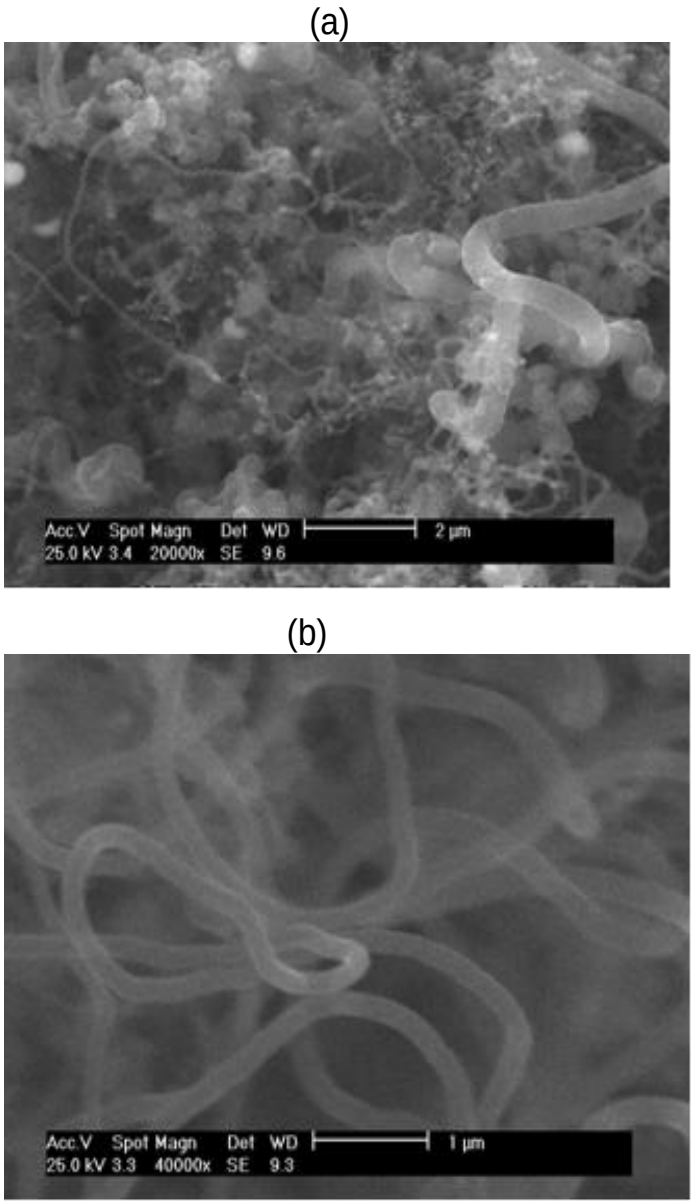

Figure 3. Morphologies of CNTs synthesized at 900°C for 30 min: (a) low magnification and (b) high magnification.

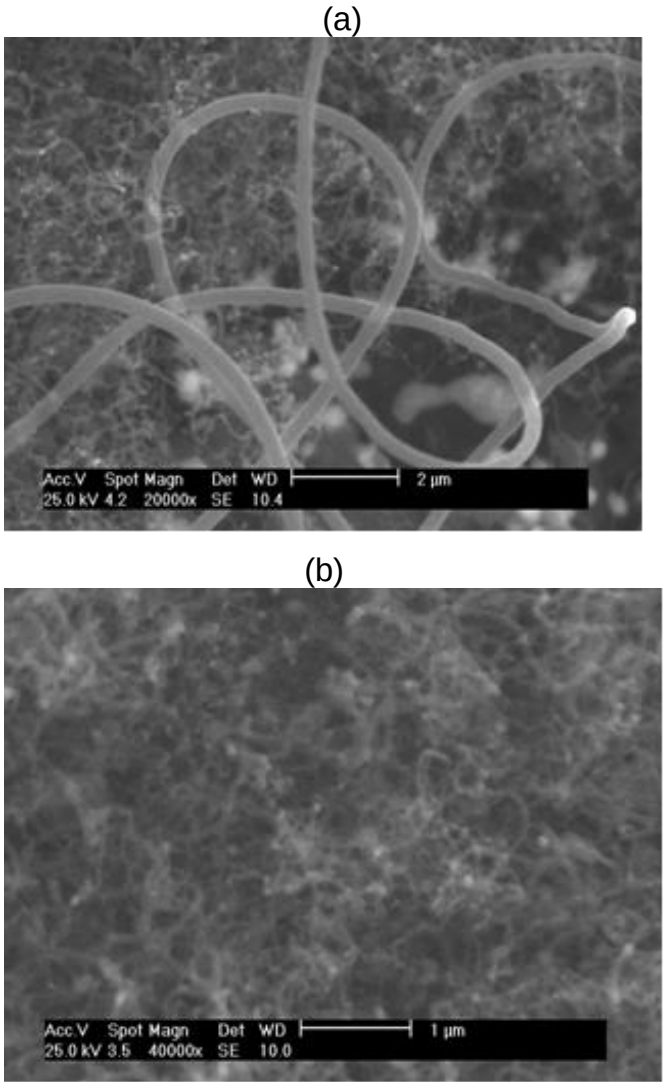

Figure 4. Morphologies of CNTs synthesized at 800°C for 30 min: (a) low magnification and (b) high magnification.

approximately 45 to 55 nm. The result demonstrates that the diameter of CNTs can be controlled by adjusting the growth temperature, and increasing the temperature leads to increasing the diameter of CNTs. To explain this behavior, we suggest that at the higher temperature, the agglomerated Ni particles may be adhered together and formed the particles with higher diameter size. It is believed that the CNTs formation depends strongly on catalyst size (Emmenegger et al., 2003). The first order Raman spectra of the grown CNTs at 900, 800 and 700°C are as shown in Figure 6. All spectra show mainly two Raman bands at ~1335 cm^{-1} (D band) and ~1600 cm^{-1} (G band) (Tuinstra et al., 1970). The rather sharp D and

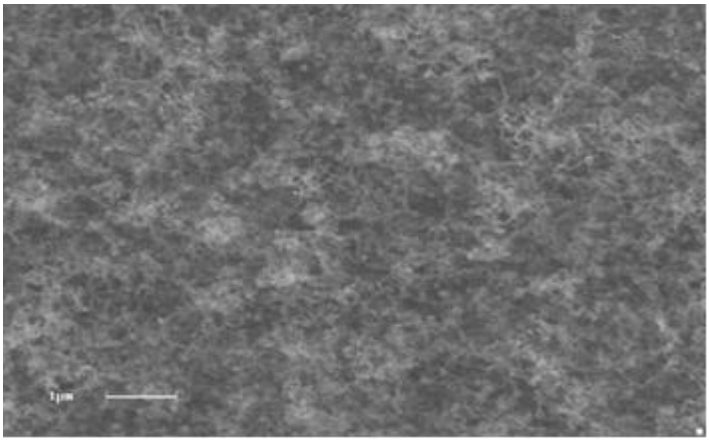

Figure 5. Morphologies of carbon nanotube synthesized at 700°C for 30 min.

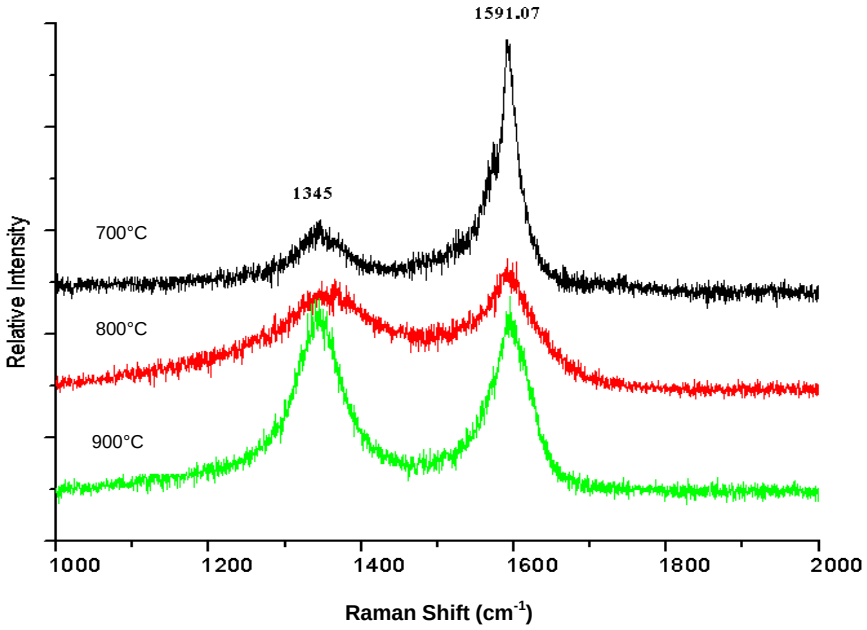

Figure 6. Raman spectra of the CNTs synthesized by TCVD at different temperature.

G features, together with the evident high frequency shoulder of the G peak, indicate the order and crystallinity of the CNTs (Ferrari and Robertson, 2000). Low frequency radial breathing modes are not seen in the CNFs. A comparison between Raman intensity at different temperatures implies that CNTs grown on sample in lower growth of temperature have a higher quality due to higher I_G/I_D.

Conclusion

In our experiment, the growth of carbon nanotubes occurred during different temperatures after an appropriate pretreatment of Ni/Si catalyst in NH_3 and H_2 at 750°C for 20 min. Also, we enhance the growth of carbon nanotube by controlling the temperature of growth. With the temperature decreasing from 900 to 700°C, the diameter of CNTs become smaller and the purity increases.

REFERENCES

Baughman RH, Zakhidov AA, Heer WA (2002). Carbon nanotubes - the route toward applications. Science, 297: 787–792.
Bower C, Zhou OW, Zhu D, Werder J, Jin S (2000). Nucleation and Growth of Carbon Nanotubes by Microwave Plasma Chemical Vapor Deposition. Appl. Phys. Lett., 77: 2767.
Choi YC, Shin YM, Lee YH, Park G-S, Choi WB, Lee NS, Kim JM (2000). Controlling the diameter, growth rate, and density of vertically aligned carbon nanotubes synthesized by microwave plasma-enhanced chemical vapor deposition. Appl. Phys. Lett., 76: 2367
Collins PG, Avouris P (2000). Nanotubes for electronics. Sci. Am., 283 (6): 62–69.
Emmenegger CJM, Bonardb P, Maurona P, Sudana A, Leporac B, Grobetyc A, Züttela L (2003). Schlapbacha, Carbon, 41: 539–547.
Endo MH, Muramatsu H, Hayashi T, Kim YA, Terrones MS (2005). Dresselhaus, Nature, pp. 433-476.
Ferrari w13x AC, Robertson J (2000). Interpretation of Raman spectra of disordered and amorphous carbon. Phys. Rev. B., 61: 14095-14107.
Franklin NR, Li Y, Chen RJ, Javey A, Dai H (2001). Patterned growth of single-walled carbon nanotubes on full 4-inch wafers. Appl. Phys. Lett., 79: 4571.
Jablonski GA, Geurts FW, Sacco ARR (1992a). Biederman, Carbon 30: 87.
Jablonski GA, Geurts FW, Sacco ARR (1992b). Carbon deposition over Fe, Ni, and Co foils from CO-H2-CH4-CO_2-H_2O, CO-CO_2, CH4-H_2, and CO-H_2-H_2O gas mixtures: I. Morphology Carbon, 30: 99.
Loiseau A, Launois P, Petit P, Roche S, Salvetat JP (2006). Understanding Carbon Nanotubes: From Basics to Applications, Lecture Notes in Physics, p. 677, Springer, Berlin.
Murakami Y, Chiashi S, Miyauchi Y, Hu M, Ogura M, Okubo T, **S**. Maruyama (2004). Carbon and oxide nanostructure. Chem. Phys. Lett., 385: 298.
Singh C, Shaffer M, Kinloch I, Windle A (2002). Production of aligned carbon nanotubes by the CVD injection method, Phys. B: Condens. Matter, 323: 339-340.
Sinnott SB, Andrews R, Gian D, Rao AM, Mao Z, Dickey E, Derbyshire C (1999). Model of carbon nanotube growth through chemical vapor deposition, Chem. Phys. Lett., p. 315.
Takikawa H, Ikeda MK, Hirahara K, Hibi Y, Tao Y, Ruiz PAT, Sakakibara S (2002). Itoh, and S. Iijima, Fabrication of single-walled carbon nanotubes and nanohorns by means of a torch arc in open air, Phys. B: Condens. Matter., 323: 277–279.
Tuinstra FJL, Koenig J, Chem P (1970). Raman Spectrum of Graphite. phys., 53: 1126
Yamada T, Namai T, Hata K, Futaba ND, Mizuno K, Fan J, Yudasaka M, Yumura M, Iijima S (2006). Size-selective growth of double-walled carbon nanotube forests from engineered iron catalysts Nature Nanotechol., pp. 1-131.
Zhang M, Yudasaka M, Iijima S (2001). Single-wall carbon nanotubes: A high yield of tubes through laser ablation of a crude-tube target, Chem. Phys. Lett., 336: 196–200.